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AB INITIO CALCULATION OF THE STRUCTURES AND PROPERTIES OF MOLECULES

Clifford E. Dykstra

School of Chemical Sciences,
University of Illinois,
Urbana, IL 61801, U.S.A.

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CONTENTS

Preface

Finding structures and properties of molecules directly by computation may well be the fastest way to get answers to crucial chemical questions, given the awesome speed and capacity of modern computers. However, there are many levels of theory that may be employed in a calculation, and naturally accuracy of the results is subject to the level of theory. A chemical question at hand might not be answered until some level of accuracy is assured. *Ab initio* electronic structure theory provides the quantum mechanical footing and numerous calculational approaches for molecular structure and properties. Predictions of stand-alone quality, that is, predictions that are reliable and not needing laboratory verification, are presumed *possible* if only the quantum mechanics of the molecular species can be dealt with properly. As attempts are made to reach ever closer to an exact solution of the quantum mechanical problem of the electron distribution in molecules, this field has become highly sophisticated and detailed in terms of computer programs and the associated theoretical methods. There is a risk in such sophistication, which is that the area becomes unapproachable to all but the specialist. That is not desirable when the intended benefit of electronic structure technology is in all areas of molecular science.

This volume is intended to provide a guide to the *ab initio* calculation of molecular structure and properties. It should provide the working information for the non-specialist to use and understand electronic structure methods and related computing technology, despite the high level of sophistication of quantum chemical methods. The first three chapters define and outline theoretical concepts, methods, and computational approaches. Descriptive information and definitions of the terminology (i.e., jargon and acronyms) are given first. More detailed and mathematical explanations come afterwards. They are primarily an outline, though, since there are already a number of superb texts that fully develop the quantum mechanical aspects of electronic structure theory. Even without attention to the formulas and expressions, it is anticipated that the first chapters give the background information to use the extensive literature of *ab initio* electronic structure theory.

Chapter Five first provides an overview of the technical issues relating to molecular properties, and then gives a rather detailed but general development. The latter part is mainly intended for those first encountering the methodologies of property determination and intending to pursue further developments. The other chapters are, in part, reviews of calculations in the literature and assessments of factors influencing accuracy. The discussions of calculational results are not comprehensive. The literature on the topics covered is enormous, making a comprehensive review almost impossible. The sampling of calculational results does strive to be representative of the scope of contemporary calculations, though there are very many high quality studies that have not been mentioned. Furthermore, since the focus of the volume is on molecular structure and molecular properties, many areas of application of electronic structure techniques are not considered, such as reactions.

The list of cited papers has been prepared for use as a bibliography. Titles are given for all papers and books. In the text, literature citations are given with a letter and a number, such as [B-5]. The letter is from the last name of the first author, and the number is the sequence number in the bibliography.

My thanks go to several colleagues for providing figures, for reading sections of the manuscript and offering comments, or otherwise contributing to my efforts to complete this volume. They are Dr. Thom. H. Dunning, Jr., Professors R. L. Belford, B. Kirtman, D. J. Malik and D. Secrest. During the course of preparing this volume, several of my students carried out a few calculations that helped fill in holes in tables, etc. For this, I thank J. D. Augspurger, D. E. Bernholdt, and S.-Y. Liu.

C. E. D.

Urbana, Illinois
May, 1988

Chapter One

COMPUTATIONAL AND THEORETICAL TOOLS FOR MOLECULAR STRUCTURE

Questions related to molecular structure are always at the forefront of chemical research because of the important correlation of structure with properties and functions. The synthesis or identification of new molecules with novel structures becomes particularly exciting when there is the prospect for novel physical or chemical properties, as might be suggested from some known correlations. The determination of molecular structure has long been under the domain of spectroscopy, for the most part, but another set of tools has emerged in the last decade. It is the direct application of rigorous quantum mechanical principles by way of large scale computation or the application of calculational methods devised from fundamental chemical and physical concepts.

A starting point for computational, structural tools is the Born-Oppenheimer approximation. It is extremely significant in our concept of molecular structure, because it is only within the context of the Born-Oppenheimer separation of nuclear and electronic motion that a potential energy surface exists. What is the equilibrium structure of a species corresponds to a minimum on such a surface. The approximation is also important in the calculation of molecular structure because it reduces the complete quantum mechanical problem to a problem of electronic structure. It is from electronic wavefunctions and electronic energies at particular geometrical structures that a potential energy surface takes shape.

Spectroscopic tools differ from calculational tools in the nature of the information they provide. For one thing, there are different measures of reliability or accuracy. In contrast with the measurement uncertainty or instrument resolution in an experiment, the reliability of a calculation is determined indirectly through an assessment of subtle factors. Even so, these factors can be understood, they can be anticipated in most calculational studies, and as a result, the reliability of state-of-the-art calculations of molecular structures and properties is outstanding. That type of understanding is a focus of this volume.

Another way in which spectroscopic and calculational tools differ concerns the dynamics of nuclear motion. For instance, equilibrium structural parameters are well-defined points on a potential surface, but are not directly measured. In principle, it is possible to calculate vibrationally averaged molecular bond lengths and angles using potential surface information. These, rather than equilibrium bond lengths and angles, are compared with experimental results. Such calculation, though, requires electronic structure calculations at numerous points that span regions of the potential energy surface, or equivalent information. Since the shape of the surface affects how the molecule vibrates, the electronic structure calculations must be able to accurately determine that shape in addition to providing the location of the equilibrium.

Molecular properties such as electric dipole and quadrupole moments, magnetic susceptibilities, polarizabilities, vibrational frequencies, and electric field gradients are intimately connected with molecular structure. Correlations of some of these properties over a particular series of molecules may provide insight into what governs molecular structure and vice versa. The calculation of such properties is not separate from the calculational determination of molecular structure. Most properties, such as electric multipole moments, are direct functions of the nuclear position coordinates. They depend on the structure of the species just as the electronic energy does, and surfaces of properties arise in exactly the same way as potential energy surfaces. This volume is intended to consider molecular structure, potential energy surfaces and properties from the standpoint of computational and theoretical determinations, while also considering the comparison with experimental measurements and the interface between the spectroscopic and the computational tools.

A few examples of simple molecular problems may offer a glimpse of what theoretical tools can provide in tackling problems of new molecule structures and properties. The unifying thread in these examples is that each species is a potential interstellar molecule. The great clouds of low density molecules that are observed from Earth have a rich chemistry judging by the growing list of molecules known to exist in interstellar space [L-1,S-1]. This is a chemistry with many unknowns but with many possibilities as well. Already, molecules not known in terrestrial laboratories have been seen in space, through their rotational spectra characterization. It is quite possible that many unknown, exotic molecules not yet imagined may be viable species under conditions such as those of the cold, low-density realms of interstellar space. Their properties may be as unique as their chemical structures could be, and some may play a role in condensing clouds or may be precursors of biomolecules. Computational tools have been used in a relatively small way on problems such as this, but their potential is enormous. The examples indicate that high quality calculation can be an efficient means of exploring the possibilities for new molecules, for predicting their structures, and for confirming their existence.

The H_3^+ Ion. Protonation of the hydrogen molecule yields about the simplest polyatomic molecule, and recent high level theoretical and spectroscopic studies make it an excellent example system. Several potential energy surfaces for H_3^+ have been reported, one of the first extensive studies being that of Carney and Porter [C-1:2]. A much more complete treatment of the electronic wavefunctions was carried out a number of years later by Dykstra and Swope [D-1], and this was followed by surface calculations by Burton et al. [B-1], Schinke et al. [S-2], and Meyer, Botschwina and Burton [M-1]. The qualitative structural information obtained in every calculation is simply that the equilibrium structure is that of an equilateral triangle. The sole unique parameter, the H-H bond length, shows good consistency among different calculational levels (TABLE 1.1), though this is not very typical of structural determinations of molecules.

More challenging than the bond length prediction has been the prediction of the vibrational spectra, for this tests the surface accuracy more fully. To make such predictions, the surface must be fitted so that it is known most everywhere, not just at grid points. Then, the quantum mechanical problem of the vibrational motion must be solved. Both of these two steps have been carried out to beautiful precision, with the report by Carney et al. [C-3] providing especially detailed analysis that culminated a number of earlier studies. Very nice vibrational predictions have been obtained by Tennyson and Sutcliffe [T-1] and Burton and coworkers [B-2,M-2] as well, but the values given by Carney best serve to show how accurately this problem can be treated.

Vibrational frequencies obtained theoretically are sometimes "equilibrium frequencies" which are the frequencies of vibration that a molecule would have if its motion displaced it but infinitesimally from the equilibrium. Such frequencies depend on the shape of the potential only in the vicinity of the equilibrium. Transition frequencies, on the other hand, depend on eigenstate determinations that sample higher regions of the potential energy surface. They can be compared directly with experimental

TABLE 1.1

Equilibrium bond lengths calculated for H_3^+.

1.6525 a.u.	Burton et al. [B-1]
1.6500 a.u.	Carney and Porter [C-1]
1.6504 a.u.	Dykstra and Swope [D-1]
1.6504 a.u.	Meyer et al. [M-1]
1.650 a.u.	Salmon and Poshusta [S-3]

measurement. Also, they are sensitive to isotopic substitution other than by a ratio of masses, and so isotopically substituted values are a good accuracy check. Agreement in frequencies for a few isotopes and/or for overtone transitions insures that the potential surface (and the dynamical analysis) is truly accurate. A single transition frequency can be found fortuitously to be the right value because of cancellation of errors. Carney has obtained transition frequencies for all isotopic forms of H_3^+ for fundamental and overtone transitions. The results for which there exist corresponding experimental

TABLE 1.2

Vibrational intervals in cm^{-1} for isotopic H_3^+ from Carney et al [C-3].

	Experimental [a]	*Calculated (Dykstra-Swope surface)*
H_3^+	2521.6	2522
		3180
H_2D^+	2205.9	2207
	2335.4	2336
	2992.5	2994
HD_2^+	1968.1	1969
	2078.4	2080
	2737.0	2739
D_3^+	1835.7	1835
		2303

[a] References [O-1:2], [A-1], [L-2]; also see [C-3].

values are shown in TABLE 1.2. The accuracy of the calculated values is uniform through all isotopic forms. The impressive agreement, to within 2 cm^{-1} of measured frequencies, shows the attainable reliability of potential energy surface calculations. Meyer, Burton and Botschwina [M-1] have obtained equally impressive values.

Protonated Hydrogen Cyanide. The relatively high occurrence of protons and molecular hydrogen in interstellar clouds means there are ample reactants for protonation reactions. A number of the species identified in interstellar space are, in fact, positively-charged, hydrogen-containing molecules. The existence of non-polar molecules, such as N_2, which have no radiofrequency fingerprint is sometimes inferred by detection of polar, protonated forms, e.g. HNN^+. The protonated form of hydrogen cyanide, $HCNH^+$, is an interesting species because through electron attachment and subsequent dissociation, it may be part of the reaction sequence that controls HCN and HNC density in interstellar clouds. In 1980, when $HCNH^+$ was not yet known to exist in space and when there was no laboratory data available, Dardi and Dykstra [D-2] set out to use calculations to "fingerprint" this species, to find its rotational transition frequency. For molecules as small as this one, the percent accuracy sought in the value of the rotational constant requires that there be about equally good accuracy in the values of the bond lengths. (With larger systems, there tends to be less sensitivity to errors in individual bond lengths plus some error cancellation, and so it is possible for the rotational constant to be somewhat more reliable on a percent basis than any one bond length.) Accuracy to the thousandth or even ten-thousandth Angstrom level was sought in the calculations that Dardi carried out.

In 1984, Altman, Crofton and Oka [A-2] reported the first spectroscopic study of $HCNH^+$. Their laboratory data on the vibrational spectrum yielded a $J=0\leftarrow1$ transition frequency of 74.11 GHz which compared with the value of 74.07 GHz calculated by Dardi and Dykstra several years before. The theoretical value included an estimate of the vibrational averaging effect on the rotational constant; that could be done such that the largest possible error in the estimate was likely to affect the transition frequency by only 0.04 GHz or so. A larger refinement of 0.2 GHz was made by anticipating the lingering errors in the calculational determinations of the bond lengths, though these corrections amounted to no more than 0.002 Angstroms. An experimental, substitution structure has already been obtained [A-3] from microwave data, and it shows very nice agreement with the calculated structure that Dardi obtained. There is also good agreement with more recent, high-level ab initio calculations, especially those of Botschwina [B-3], and this is shown by the

TABLE 1.3
$HCNH^+$ bond length predictions in Angstroms.

R_{HC}	R_{CN}	R_{NH}	
1.0779	1.1368	1.0091	Amano and Tanaka [A-3] (expt.)
1.0771	1.1352	1.0129	Dardi and Dykstra [D-2] (adjusted)
1.0751	1.1337	1.0109	Dardi and Dykstra [D-2]
1.0785	1.1346	1.0116	Botschwina [B-3] (adjusted)
1.0795	1.1348	1.0132	Botschwina [B-3]
1.0823	1.1411	1.0153	DeFrees, Loew and McLean [D-3]
1.080	1.144	1.0151	Lee and Schaefer [L-3]

values listed in TABLE 1.3.

Ab initio calculations of vibrational frequencies of $HCNH^+$ have also proved to be quite successful. A recent report on that subject is by Botschwina [B-3]. For the CH stretching frequency, Botschwina's anharmonic frequency is 3203 cm^{-1} which is only 15 cm^{-1} greater than the experimental value [A-2] of 3188 cm^{-1}. For the NH stretching frequency, the calculated [B-3] and measured [A-2:5] frequencies are 3505 and 3483 cm^{-1}, respectively. Correspondingly good agreement was obtained for deuterated forms. For this molecular system, then, the computational tool for molecular structure has proved its worth, and through the theoretical and laboratory efforts to fingerprint the species, it has now joined the list [S-1] of molecules confirmed to exist in interstellar clouds.

Hydroxyacetylene. This is a remarkably uncomplicated molecule, yet until 1986, it had not been synthesized. Ab initio calculations have indicated that hydroxyacetylene may be a viable molecular species, the first calculations being those of Radom, Hehre and Pople [R-1] and of Dykstra [D-4]. Both studies found that hydroxyacetylene would be 35 kcal less stable than the most stable isomer, ketene. The geometry search in the latter of the two studies provided firm evidence that this isomer did correspond to a minimum in a reasonably deep well, and that's the basis for claiming its viability as a molecule. The carbon-carbon bond was predicted to be 1.193 Angstroms, quite in line with a triply bonded system, while the carbon-oxygen bond was found to be 1.322 Angstroms. There have been a number of subsequent, more detailed ab initio studies of hydroxyacetylene [B-4, T-2]. Some have considered the barriers for dissociation or rearrangement and others have refined the structural parameters. Since it is not the most stable H_2C_2O isomer, the conditions of interstellar space make it a candidate for existence there. Terrestrial synthesis has finally been accomplished [V-1] and identification in space can now be optimistically awaited.

Isocyanamide. Vincent carried out the first ab initio study of the cyanamide-isocyanamide rearrangement reaction in 1980 [V-2]. Isocyanamide had never been seen or spectroscopically characterized in the gas phase. The calculations revealed that there would be a hefty 46 kcal barrier for unimolecular rearrangement. At the same time, it was determined that isocyanamide would be much less stable than cyanamide, the energy difference being 53 kcal. However, the large activation barrier for undergoing rearrangement meant that it could be a viable species in the isolated molecule limit, at cold temperatures. Cyanamide was already known to exist in interstellar clouds, and the calculations pointed to the possibility that isocyanamide might be found, too.

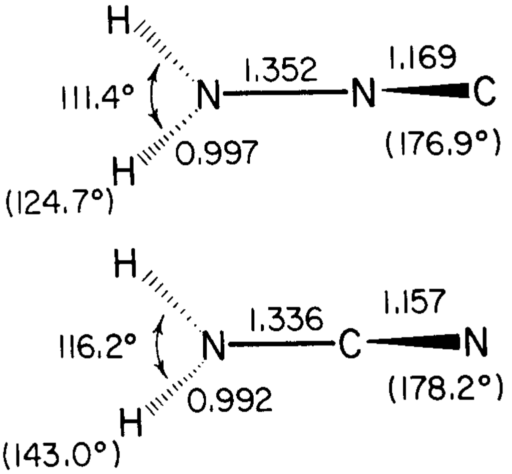


FIGURE 1.1

The calculated structures of isocyanamide and cyanamide reported by Vincent and Dykstra [V-2]. The angles in parentheses are elevation angles, either the angles the HNH planes make with the plane of the drawing, or the out-of-plane angles for the CN or NC terminal groups. Isocyanamide is more pyramidal shaped than cyanamide and it has a larger inversion barrier.

TABLE 1.4
Theoretically determined [V-2] and experimental [S-4:5] rotational constants of isocyanamide (in GHz).

	Calculated	*Experimental*
A	294.45	282.68
(B+C)/2	10.76	10.64
B - C	0.233	0.232

In 1981, Schafer et al. [S-4:5] obtained the rotation-inversion spectrum of isocyanamide that served to finally fingerprint this elusive species. The measured rotational constants compared well with Vincent's calculated values [V-2] as shown in TABLE 1.4. Furthermore, the inversion barrier calculated by Vincent helped to verify that the spectra obtained by Schafer and Winnewisser [S-4] was definitely due to isocyanamide. Clearly the discovery of new molecules can be aided by computational investigation of molecular structure.

Long Carbon Chains in Space. From the first discovery of molecules in interstellar space, it has been fascinating to consider the complexity that molecules in those environments might achieve. Thus, one of the most interesting developments in interstellar molecular spectroscopy in recent years has been the discovery of long carbon chain molecules with remarkably high abundance. These observations were made in the Taurus molecular cloud complex TMC-1. Members of several polyyne series have been detected, including cyanopolyynes, $HC_{2n}CN$, and methyl polyynes, $CH_3C_{2n}H$. The longest of the known carbon chain molecules is $HC_{11}N$ [B-5].

The abundance measurements that have been made for the carbon chain molecules may yield some tantalizing information. Stahler has proposed using the cyanopolyynes as a chemical clock [S-6]. The age of an interstellar cloud would be the time required to grow the longest chain present; a sudden drop in abundance ratios at a certain chain length might benchmark the cloud's age. There is also the possibility that the decreases in abundance with chain length may stop at some point and a plateau would be reached, possibly because of some destruction reaction not managing to completely destroy the longer chains. If this were found to occur, it would mean that large, complicated molecular species exist in space.

Computational molecular structure has played a helpful role in the study of carbon chain species in space through evaluation of an essential property. The abundance of a molecule in an interstellar cloud is based on the quantum mechanical probability for rotational transition and on the emission signal strength measured with a radiotelescope. The value of the molecular dipole moment is required to convert the signal strength into an abundance, referred to as a column density, because the transition probability is proportional to the dipole moment. A number of molecules that have now been seen in space have no measured dipole moment because they have not yet been studied in the laboratory. For instance, there is no laboratory measurement of the dipole moment of $HC_{11}N$, and that would tend to preclude a determination of its abundance. Fortunately, ab initio calculations can be easily employed to get reasonably accurate values of dipole moments of new molecules, and this has been done for three series of polyynes [S-7]. With a small empirical adjustment to account for vibrational averaging and certain neglected effects, the dipole moment of $HC_{11}N$ according to calculations is 5.00 Debye, with an estimated accuracy of 5%. This replaces the best guess of 6.0 Debye and makes for a noticeable increase in the determined abundance of this long species. As this is the most recently studied cyanopolyyne, there may be measurement refinements that could lead to changes in the abundance value later. It is exciting that after the calculated dipole moments are used to get the bet possible determination of abundances, there appears to be a nearly constant ratio of the abundance of one cyanopolyyne to the next one in the series [S-7]. This is illustrated in FIGURE 1.2. Similar ratios are obtained for two other series, though data is less complete for them. The constant abundance ratio suggests that there is a key reaction sequence leading to polyyne growth, and that leads one to expect that there are still larger molecules in these clouds.

The five examples demonstrate that calculation has been a useful tool for problems connected with molecular structure. It has provided vibrational potentials, stabilities and structures of new molecules prior to experimental work, and it has provided rotational constants, dipole moments, and so on. This tool, however, is not always easy to use. Not every calculation, not even if it is strictly ab initio, will automatically give accurate results. Attention must be given to electronic structure factors related to the molecular structural problem at hand, as was done in the calculations of the five examples. How that should be done is a focus of this volume.

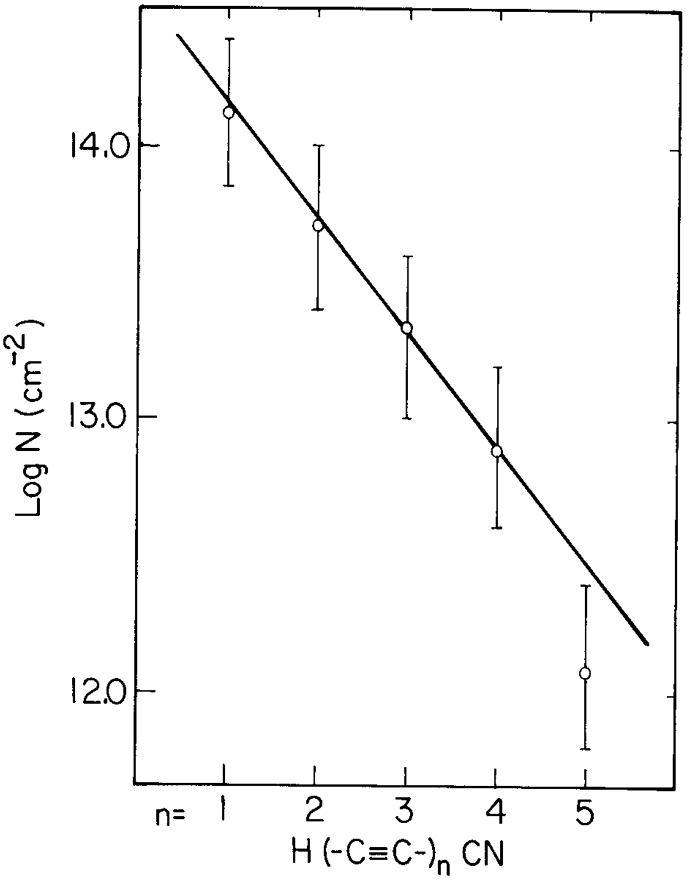


FIGURE 1.2

Interstellar abundances of cyanopolyynes in TMC-1 [S-7]. The logarithms of column densities are plotted against the carbon chain length. The error bars assume a factor of two uncertainty in the column densities. The straight line is a least squares fit, not using the last data point. The slope of this line gives the ratio between abundances of adjacent members of the polyyne series: $N(HC_{2n+1}N) / N(HC_{2n+3}N) = 2.5$.

Chapter Two

POTENTIAL ENERGY AND PROPERTY SURFACES

A surface is a mathematical representation of the dependence of some quantity on the geometrical parameters of a molecular species. This could be the dependence of the electronic energy, components of the energy, or certain properties. Slices or cuts through a complete surface result from fixing or constraining one or more of the parameters. These slices or cuts are themselves surfaces, unless there remains but one free parameter in which case they are simple curves. A *potential energy surface* refers specifically to a representation of the dependence of the total electronic energy plus the total nuclear repulsion energy on geometrical parameters. The use of such a surface implies working within the Born-Oppenheimer approximation. The surface may be a point-by-point representation, where the potential energy is known at many particular choices of the geometrical parameters, or it may be a functional representation.

An equilibrium structure of a molecule is associated with a global minimum on the potential energy surface. Because such a definition is possible only within the Born-Oppenheimer approximation, equilibrium structural parameters are directly obtainable only by theoretical means. The dictates of the quantum mechanical world mean that laboratory measurements of structure are necessarily averages; the measurements must be carried out on moving systems since zero-point vibrational motion prevents the nuclei from being at rest.

Equilibrium values can be deduced or inferred from measured averages, but that amounts to inverting the process of solving for nuclear motion dynamics. This is to say that quantum mechanics must be employed both for the forward mapping of the potential energy surface onto a manifold of internal motion (vibration) states and for the reverse mapping of a spectrum of transition frequencies onto a potential energy surface. The more completely the potential energy surface is known, the more accurately the energy levels can be determined; likewise, the more complete the spectral information, the more accurately the potential surface can be constructed. However, except possibly for the case of H_3^+ and a few other small molecules, the two sides of the problem are rarely so complete that they meet perfectly. In addition, any approximations introduced into the dynamical analysis going in either direction may enlarge the mismatch [D-10]. In the end, one must accept that the use of theoretical tools for very precise structure determinations follows a different course than the use of spectroscopic tools, and the detailed comparisons between the two require careful consideration of the limits of measurement and calculation as well as of the significance of the particular values. Current efforts at understanding the structure of floppy, or easily distorted, molecules and complexes are continually faced with this difficulty when trying to relate theoretical results to experimental results. The solution will undoubtedly be further computation, in the form of higher level analysis of nuclear motion.

Much qualitative information can be obtained from a potential energy surface. FIGURES 2.1 and 2.2 display contours of two hypothetical surfaces that illustrate some of what can be "read" from a surface. Each plot consists of a set of contour lines which connect points of the same potential energy. Two geometrical parameters, r_1 and r_2, specify any particular point on the surface or any particular structure of the hypothetical molecular system. If there were other geometrical parameters, it is assumed that they are fixed. In that case, these plots would represent slices through the complete multi-dimensional surfaces. FIGURE 2.1, with its more closely spaced contours is relatively steep in the vicinity of the minimum, which is designated with "+". In contrast, the surface depicted in FIGURE 2.2 is shallow near its bottom. The labels on the contours indicate that the depths of the two potential wells are about the same; it is their shapes that are different.

The relative flatness of the FIGURE 2.2 surface should mean greater zero-point vibrational excursions than for a comparably massive system experiencing the FIGURE 2.1 surface, assuming that a bound, vibrational state exists and that it is fairly low-lying in either of the wells. On average, the FIGURE 2.2 system is likely to be displaced further from its potential minimum than the FIGURE 2.1 system. This lessens the significance of the potential minimum of the FIGURE 2.2 system compared to the FIGURE 2.1 system. If the vibrational excursions are small, the average structure must be close to the structure corresponding to the potential minimum. But with greater vibrational excursions, the average structure does not represent how the molecule exists as well and the average structure may turn out to be further removed from the equilibrium. For a very floppy molecule, one with a shallow near-equilibrium surface and large amplitude zero-point excursions, the "structure" of the molecule is appropriately identified by just locating the flat region on the

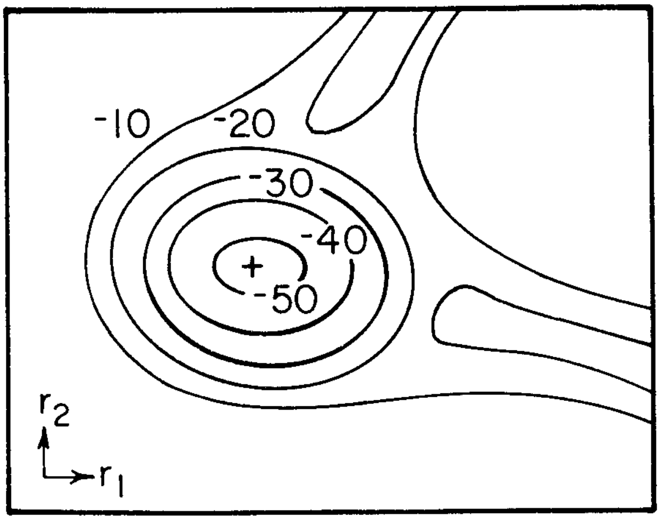


FIGURE 2.1

Idealized two coordinate potential energy surface represented by contours labelled with energies in arbitrary units.

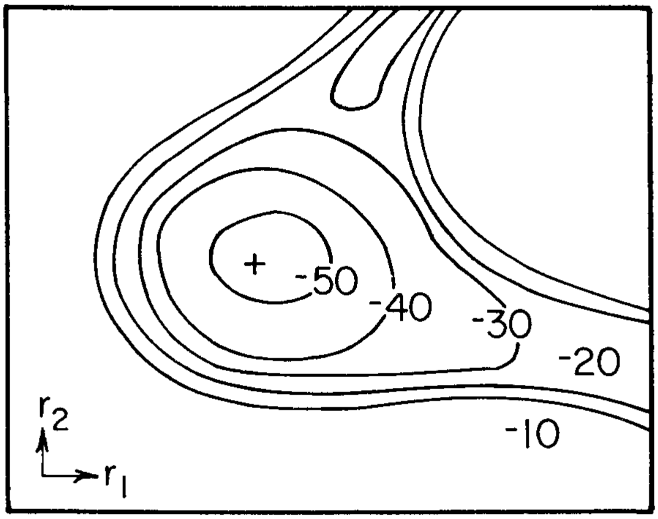


FIGURE 2.2

Idealized potential energy surface contours with a shallower region around the minimum than in FIGURE 2.1. Points nearby the minimum are less differentiated from it, and zero-point vibrational excursions will tend to be greater.

surface. Were a system's behavior classical, a potential minimum would be the point at which everything may be at rest. Identifying such a point would be as meaningful for a steep well as for a shallow one. The qauntum features of the molecular world preclude such static existence, and so structural information tends to be connected with dynamical features, primarily vibrational excursions. This distinction in how one considers "structure" is important because of the complexity of the molecules being studied today. And this distinction is particularly important for molecular species known to be floppy, such as rare gas complexes or flexible biomolecules.

There are computational considerations that relate to the nature of a surface. Finding the true minimum for the surface in FIGURE 2.2 to a specific degree of precision demands greater care than finding the minimum for the surface in FIGURE 2.1. This is because small errors or numerical limitations will be more significant in locating the minimum of a shallower surface.

A potential surface will have certain features of interest other than its minimum. For one, there may be other minima called *local minima*. These are the lowest potential energy points within some fixed, local region. Numerous local minima not too far from the global minimum are often found on the potential surfaces of weakly bound complexes. Another feature of interest is a *saddle point* or transition state structure. This is a point at which the surface is downhill in all but one and only one direction. A three-dimensional representation of a surface in two coordinates would have the shape of a saddle in the region of a saddle point. Another typical feature, a *trough,* is just what the name implies, a region where the surface is uphill in every direction except one where it is slowly changing. A *minimum energy path* is a trough that connects two minima or saddle points.

Shapes of Potential Energy Surfaces. The shape of a potential energy surface about a selected point or structure is numerically characterized by how the energy is changing with respect to the geometrical parameters, in other words by the derivatives of the energy with respect to the parameters. Since a definition of a minimum is a point where the first derivatives are all zero, the shape of a surface in the vicinity of a minimum is characterized by the values of the second derivatives of the energy. This characterization is equivalent to a valid functional representation of the potential energy surface for small displacements from the minimum; for small displacements, the leading terms in a power series expansion of the potential energy in terms of the geometrical parameters would be the terms containing the second derivatives. Higher derivatives provide further characterization, and when used in a power series expansion, they provide a representation of the surface that is valid for larger displacements from the minimum.

In a diatomic molecule, the second derivative of the potential energy with respect to the stretching coordinate evaluated at the minimum is the stretching force constant. Its value, divided by the reduced mass, is the square of the *harmonic vibrational frequency*, and so it is also referred to as the harmonic force constant. The higher derivatives are termed anharmonic force constants.

Calculation of a harmonic frequency is most useful if comparison is with experimentally deduced harmonic frequencies. The experimental determination of an equilibrium vibrational frequency for a diatomic is often based on fitting the transition frequencies to a power series in $(v + 1/2)$ where v is the vibrational quantum number. The value of an equilibrium frequency, or equivalently the harmonic force constant, obtained in this way will show a dependence on how many terms were used in the power series and how many transition frequencies were used for the fit. These two factors relate to how the transition frequencies are theoretically mapped onto the potential curve. The anharmonic force constants will also be dependent on them. TABLE 2.1 illustrates what variations in the constants may result from the way the analysis is performed. For this example, a high quality *ab initio* potential curve was used to numerically calculate a manifold of vibrational states. Differences between the energies of these states were taken as the input data or "experimental" transition frequencies for the analysis. The molecule is hydrogen fluoride and the fundamental and first overtone frequencies agree to within just a few cm^{-1} of spectroscopic values. There is a sharp dependence of the equilibrium frequency on the level of truncation in the power series. With different numbers of transition energies used, the range of variation in the harmonic frequency, for a given level of truncation is small, only around 0.1%. However, for the first anharmonicity constant that range is larger, around 10%. Thus, the harmonic and anharmonic force constants, which are directly obtainable in a theoretical treatment, certainly may reach a point where comparison with experimental values is limited by the completeness of the measured data. In that case, a more meaningful comparison might be made between calculated transition frequencies, if they can be obtained, and the measured transition frequencies rather than a comparison of force constants.

Normal Modes. Normal mode analysis provides a certain useful level of understanding of internal molecular dynamics that is based on just the

TABLE 2.1

Equilibrium frequencies and anharmonicity constants calculated from ab initio transition frequencies for hydrogen fluoride. Values are in cm^{-1}. The constants listed were obtained from a power series fit in terms of $(v + 1/2)$ truncated at the nth power.

	Number of Transitions Used in Fit	*Computed Equilibrium Frequency*	*Computed Anharmonicity Constants:*		
			First	*Second*	*Third*
n = 2:	2	4026.9	-131.2		
n = 3:	3	4140.1	-92.2	1.94	
	4	4144.9	-96.9	2.92	
	5	4157.4	-106.4	4.51	
n = 4:	4	4139.7	-90.1	0.37	0.29
	5	4136.8	-84.7	-2.12	0.61

second derivatives of the energy. The *normal coordinates* that result from this analysis are a transformed set of atomic displacement coordinates. The mathematical process is a non-unitary transformation that comes about by a simultaneous diagonalization of two tensors, one of which depends on the second derivatives of the energy.

The classical normal modes analysis begins with a fixed coordinate system with generalized coordinates $\{x_1, x_2, \ldots, x_{3N}\}$ that describe the positions of the particles, and in this discussion the particles are the nuclei of a molecule. The kinetic energy, T, is quadratic in the velocities of the particles. The velocities, of course, are the first derivatives with respect to time of the position coordinates. The expression for T must be developed for the particular system of coordinates (e.g., Cartesian coordinates, or angle and bond length displacements, etc.). From the expression for T, the first tensor in the normal mode analysis is defined.

$$\mathbf{M}_{ij} = \frac{\partial^2 T}{\partial \dot{x}_i \, \partial \dot{x}_j} \tag{2-1}$$

This tensor may be regarded as a *matrix representation* of T and certain of the procedures for matrix representations in quantum problems will turn out to be the same. The second tensor is defined from the second derivatives of the potential.

$$\mathbf{K}_{ij} = \left.\frac{\partial^2 V}{\partial x_i \partial x_j}\right|_{eq} \tag{2-2}$$

K may be thought of as a matrix representation of the quadratic part of the potential. The derivatives making up this tensor are evaluated at the equilibrium, which is where the first derivatives are zero.

An approximation is made in the normal modes analysis. It is an important and serious approximation that the potential is strictly quadratic, or equivalently, that the displacements are sufficiently small that the power series expansion of the potential may be truncated after the quadratic terms. With the following designation for the vector of position coordinates,

$$x = (x_1, x_2, \ldots, x_{3N}) \tag{2-3}$$

the classical Hamiltonian, H, takes on a simple form.

$$\mathrm{H} = \frac{1}{2}\dot{\vec{x}}^{\mathrm{T}}\,\mathbf{M}\,\dot{\vec{x}} + \frac{1}{2}\vec{x}^{\mathrm{T}}\,\mathbf{K}\,\vec{x} \tag{2-4}$$

If both tensors are diagonal or can be brought into diagonal form, the Hamiltonian will have additive, quadratic terms for each coordinate direction. The system would then be mechanically equivalent to a system of independent harmonic oscillators. The system of coordinates for which **K** and **M** are diagonal constitutes the normal coordinate system for the particular problem. The normal coordinates may be found in terms of the original coordinate system by the simultaneous diagonalization of the two tensors, a process which leads to a linear but non-unitary transformation.

Simultaneous diagonalization is accomplished in three steps. First, one matrix is diagonalized and for the normal modes problem, it is the **M** matrix. Notice, that if the original coordinates were Cartesian coordinates, **M** would start out being diagonal. The second step is the non-unitary transformation that will make **M** equal to **1**, the unit or identity matrix. The transformation matrix for this step is a diagonal matrix whose elements are the inverse square roots of the eigenvalues of **M**. This step introduces a mass-dependence into the coordinates. These first two transformation must be applied to the **K** matrix so that it remains in the same coordinate system as the **M** matrix. The third step is the diagonalization of this transformed **K** matrix by way of a linear, unitary transformation. Applying this final transformation to the **M** matrix leaves it diagonal (and still **1**), and so both matrices have been diagonalized. The potential tensor, **K**, is a matrix of force constants. In a normal coordinate system, where **K** is diagonal, there can be no off-diagonal force constants. In the Wilson FG matrix approach to normal modes [W-2], the two tensors are made rectangular to exclude rotation and translation. The F matrix is the potential tensor and the inverse of the G matrix is the mass or kinetic energy tensor.

A *normal mode* corresponds to harmonic motion along a normal coordinate, which is some linear combination of atomic displacement coordinates, the specific nature of which results from the simultaneous diagonalization procedure. The normal modes are the simplest vibrational motion of the system. Motion in any one mode has all nuclei moving with exactly the same frequency and the same phase. All particles reach their points of maximum displacement at the same instant, and all pass through their equilibrium position at the same instant. Any other vibrational motion can be described as a linear combination, or superposition, of normal mode vibrations. Consequently, normal mode wavefunctions can be used as a basis set for more complete vibrational analysis.

Normal mode analysis is directly employed in quantum mechanical systems through the usual correspondence of classical variables with quantum mechanical operators. The classical Hamiltonian in Eqn. (2-4) becomes a quantum mechanical Hamiltonian operator in the same way that the classical Hamiltonian of a one-dimensional harmonic oscillator can be converted into a quantum mechanical operator. The key feature of the normal mode analysis is that with **K** and **M** being diagonal, the quantum mechanical Hamiltonian yields a Schrodinger equation which is separable in each of the normal coordinates. Thus, within the normal modes approximation, the quantum mechanical (normal mode) oscillators are independent and the wavefunction for a molecular system is a simple product of harmonic oscillator functions over the modes. The small amplitude approximation, though, means that the wavefunction describing the system is based on an approximate potential. It has been found that a harmonic frequency will approximate a true transition frequency to within 10% in many cases, and this offers an idea of the size of error that may be associated with the normal modes analysis for molecular vibrations. One specific example is HCN, where calculated results for the stretching vibrations place the harmonic frequency for one mode just 1% above the measured transition frequency, and for the other mode, the agreement is 3% [D-11]. For floppy molecules, normal mode analysis is less likely to be suitable because of the relatively large amplitude excursions that occur even in the ground state.

Surface Features. A saddle point or transition state is a special surface feature, and as already mentioned it is any point at which the surface is downhill for both forward and backward motion along one coordinate only and uphill for both forward and backward motion along all other internal coordinates. In terms of energy derivatives, saddle points have the property that one and only one force constant is negative (downhill). Since harmonic frequencies are proportional to the square root of the force constant, another way of saying this is that there is an imaginary frequency for one vibrational mode at a saddle point. This property can be used to establish a particular structure as being a saddle point or transition state. One can prove that equilibrium and saddle points are unique and that their locations are independent of how the coordinate system is specified.

The path of steepest descent connecting a saddle point with the nearest surface minimum is a minimum energy path. The minimum energy path is often used to define a reaction coordinate, that coordinate being one whose direction is always along the minimum energy path. This makes that path rather significant in transition state analysis or quantum dynamical studies that use the surface. An unfortunate complication is that the minimum energy path's location is not invariant to all coordinate transformations, even though the end points (minimum and saddle points) are. What has been recognized as a convenient choice [F-2,M-9:10,T-4] for a coordinate system to describe the minimum energy path is a mass-weighted set of coordinates, such as done implicitly in the normal modes analysis. Mass-weighting takes a diagonal mass tensor or into a constant tensor which is then invariant to any subsequent unitary coordinate transformation. Truhlar [T-5] describes these as "isoinertial" coordinates. The mass-weighting transformation doesn't have to introduce units of mass into the coordinates, though. Each coordinate can be re-scaled, if desired, to some unit mass choice. This amounts to a relative mass-weighting.

An illustration of how the coordinate system affects the appearance of the potential energy surface is shown for a very simple system, the weakly bound complex of the hydrogen molecule and hydrogen fluoride. FIGURE 2.3 shows the coordinate system and FIGURE 2.4 shows potential surface contours obtained by Bernholdt et al. [B-6]. These contours are from slices along the two in-plane orientational angles of the complex. According to the *ab initio* calculations done on this system, the equilibrium structure is T-shaped, with the HF's hydrogen pointing into H_2. There is saddle point on the potential surface which corresponds to the system being linear with the

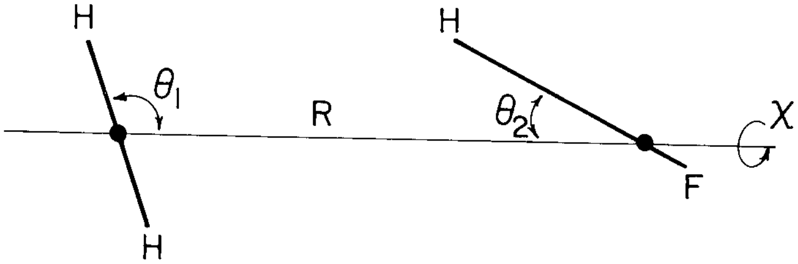


FIGURE 2.3

Internal coordinates for the hydrogen fluoride-hydrogen complex.

fluorine end of HF pointing toward the hydrogen molecule. The potential surface in FIGURE 2.4 is periodic because it is in terms of angular coordinates. The minimum energy path goes form one minimum, through a saddle point and then back down to another minimum that is equivalent to the first.

Another useful choice for the angular coordinates in terms of the coordinates in FIGURE 2.3 is:

$$\theta'_1 = \theta - 90^\circ \tag{2-5a}$$

$$\theta'_2 = \theta_2 + \theta_1 - 90^\circ \tag{2-5b}$$

Though quite simple, this coordinate transformation changes the appearance of the potential, as shown in FIGURE 2.5. The minimum energy path appears to be straighter in this coordinate frame, but is really no different. FIGURE 2.6 is another illustration of this potential surface. It shows the relative compression of one axis from mass-weighting.

Electronic structure calculations can map out a potential energy surface as a set of points on the surface. This may be done with a regular grid or with an irregular spacing, perhaps to have a greater density of points in regions where the surface is changing the most. In many problems, a complete potential surface, that is, a set of many points spanning all regions of the surface, isn't needed. If an activation barrier is sought, it may only be of interest to locate the transition state and the equilibrium structure. Even that information requires a series of calculations, however, and efficient means of locating the stationary points can be quite advantageous.

There are a number of ways one can go about searching for stationary points and for finding minimum energy paths [B-17:18,K-2,M-11,P-6:7,S-11:13], several of which employ energy gradient values. One optimal

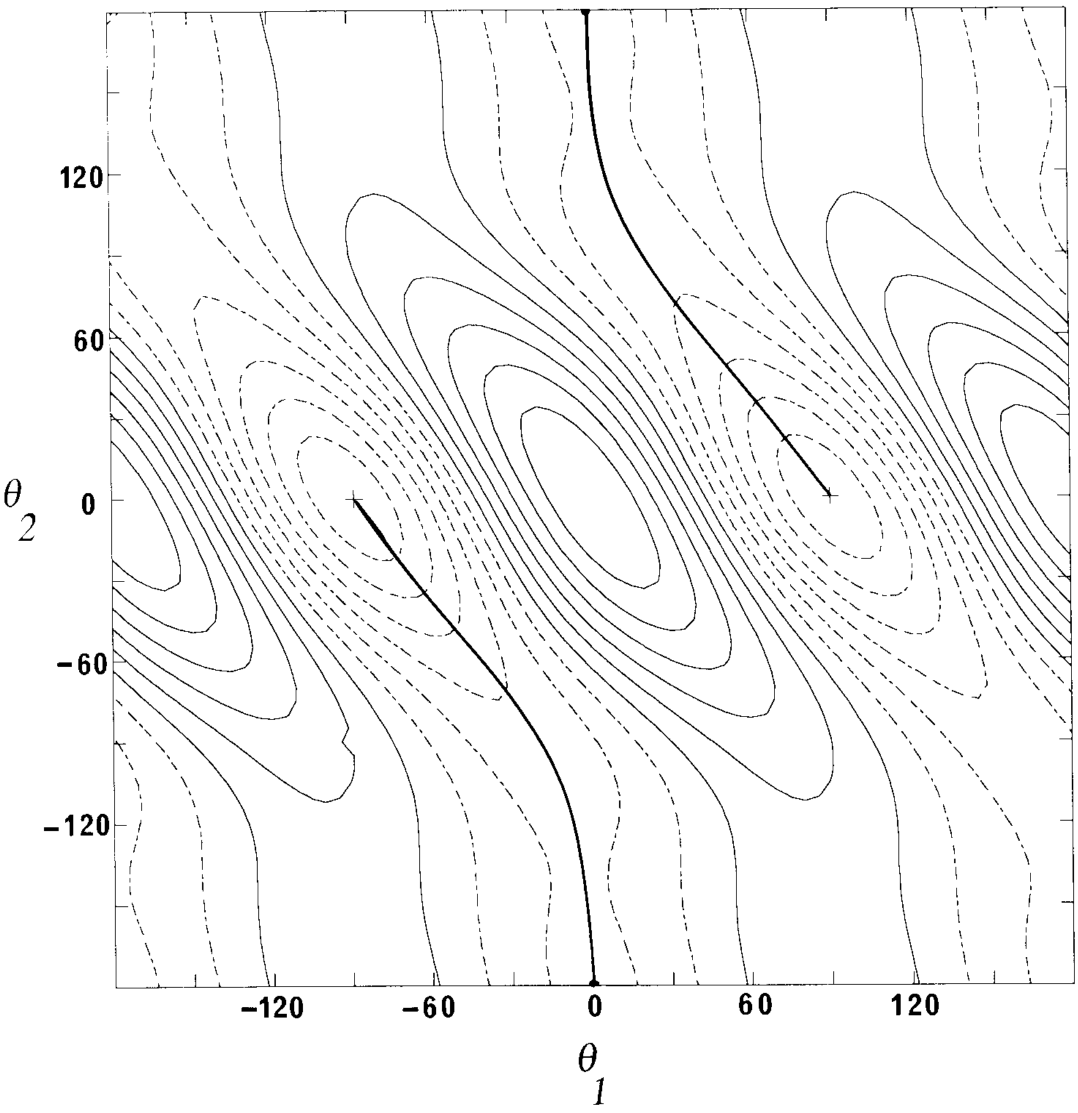


FIGURE 2.4

Contour plot of a potential energy surface for the H_2-HF complex. Contour lines are in 50 cm^{-1} steps relative to the separated limit energy. Dashed lines are contours where the structure is more stable than at the separated limit, while solid lines correspond to repulsive regions of the surface. The orientational angles are those shown in FIGURE 2.3, and so the vertical axis is the HF orientational angle while the horizontal axis is the H_2 angle. The symmetry of the system dictates a 180^o periodicity along the horizontal axis, and a 360^o periodicity vertically. "+" designates the minimum and a solid line that connects at the top and bottom of the plot if the minimum energy path from the T-shaped equilibrium to the linear transition state and then to the equivalent minimum on the other side.

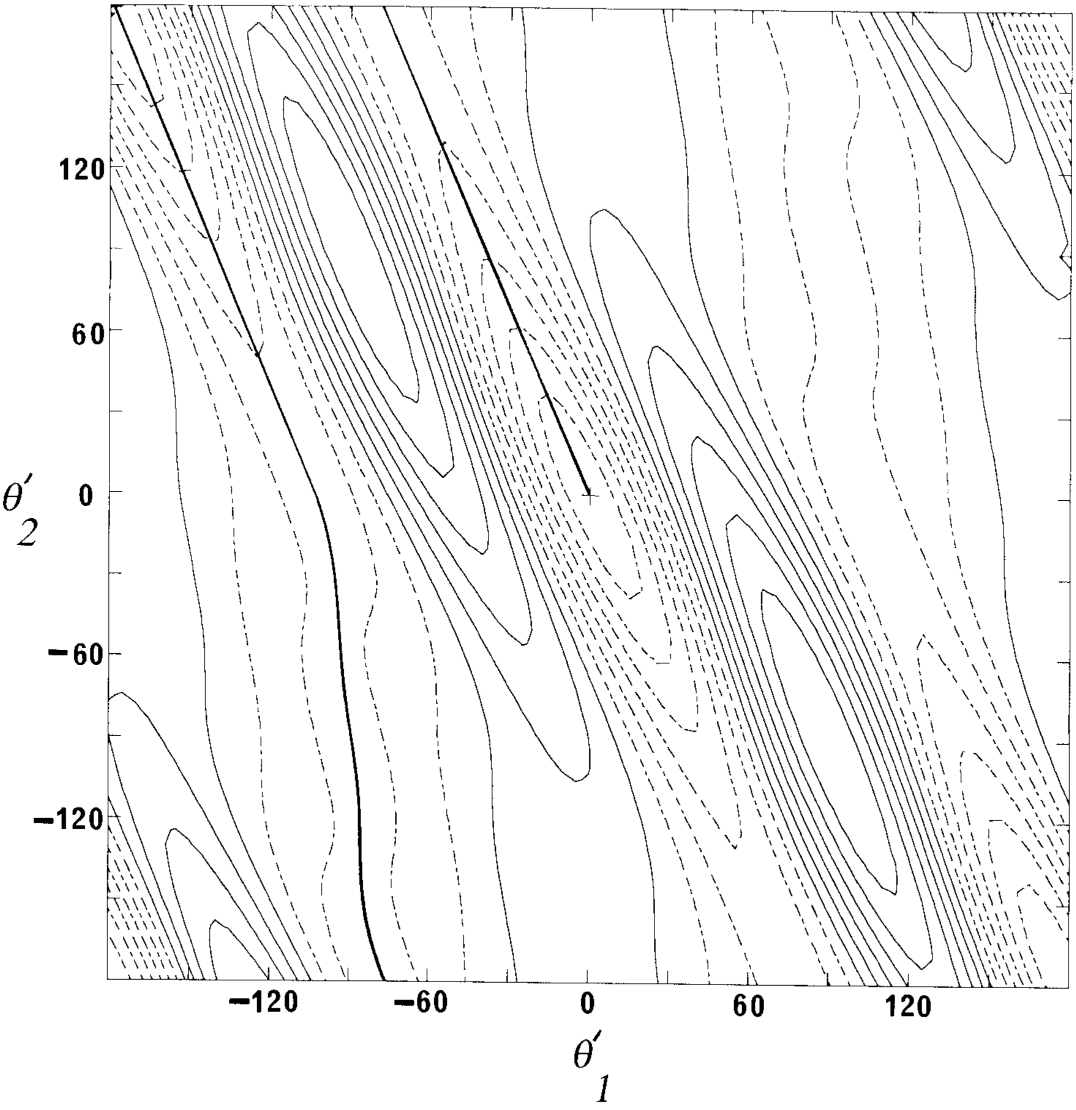


FIGURE 2.5

A contour plot of the potential energy surface of the H_2-HF complex with the transformed orientational angular coordinates. The saddle point for interconversion is now at the upper left corner and only one of the equivalent minima is shown. It is in the middle of the figure. The minimum energy path appears to be somewhat straightened out relative to the path in FIGURE 2.4. The main reason for this is that this linear coordinate transformation has stretched the flat transition state regions while squeezing the hills and valleys. Coordinate transformations that are not linear may have even more drastic effects on the appearance of the surface contours.

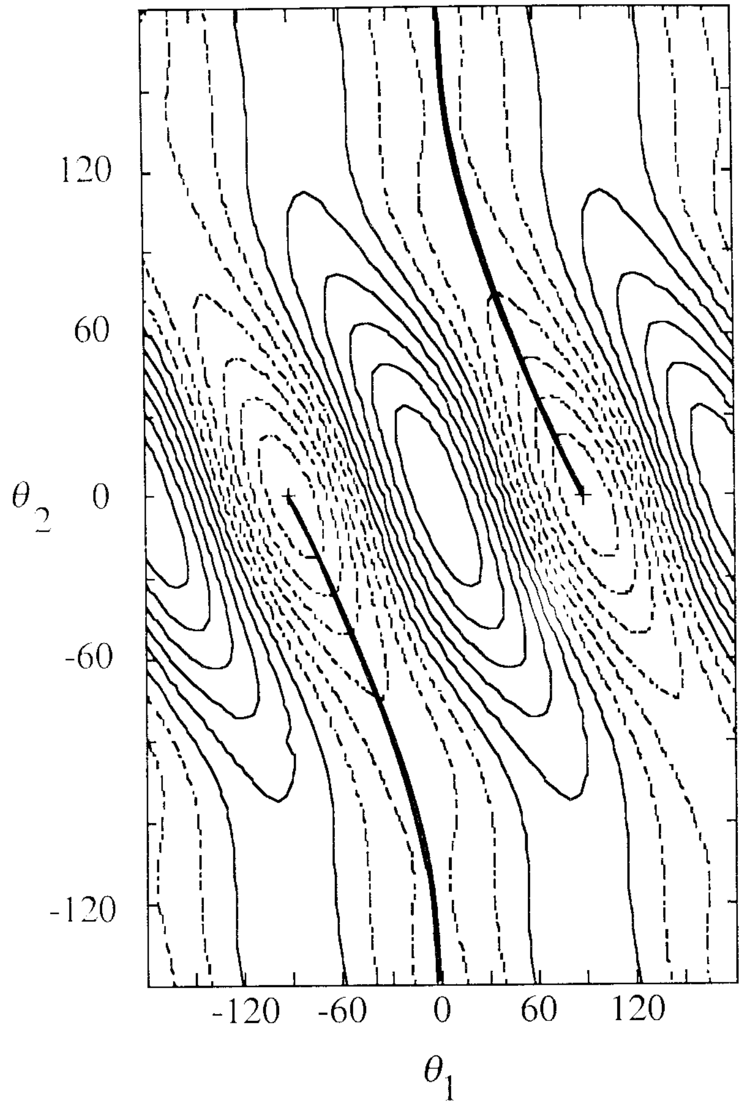


FIGURE 2.6

The isoinertial coordinate contour plot of the potential energy surface of the H_2-HF complex. The horizontal axis has been rescaled relative to FIGURE 2.4 by the square root of the ratio of the H_2 moment of inertia to the HF moment of inertia. This compresses the horizontal axis and leads to a rectangular plot. The apparent curvature of the minimum energy path is not as noticeable. Isotopic substitution would change the rescaling due to transformation to the isoinertial coordinates and so this type of surface representation is specific to one isotopomer.

procedure has been developed recently by Comeau, Zellmer and Shavitt [C-8] and outlining it serves to explain how stationary may be found. Atomic displacement coordinates are used with certain atoms to constrain the search to be overall internal displacements; rotation and translation are excluded. Symmetry constraints may be invoked as needed by fixing other atomic coordinates. A least squares fit to a simple polynomial is carried out for points in some selected region of the surface. The data points for the fit are meant to include not only the energies but also the energy gradients. Low order polynomials are limited in their ability to faithfully represent potential surfaces, and so the polynomial fit is useful only in a small region. The stationary points of the polynomial function are found straightforwardly. A new set of points is then calculated in a narrowed vicinity of one of these stationary points and an improved determination of a minimum energy structure or a transition state structure results from the next polynomial fit. Starting at a particular stationary point and taking small steps tangent to the gradient at each point, in a mass-weighted coordinate system, the reaction path can be mapped out with this procedure. Banerjee et al. [B-17] have used rational functions in a local region in a somewhat similar way.

Bell and Creighton [B-18] have presented one of the most effective techniques for locating transition states and have given a very thorough comparison with other procedures. Williams and Maggiora [W-3] have highlighted the difficulties in following coordinates to find transition states. Searching a potential surface is an important task in studying molecular structure by theoretical means, and considerable algorithmic finesse is desirable. Certainly, there are already powerful and sophisticated methods for searching potential energy surfaces.

One place where new theoretical developments should prove quite valuable is in the dynamical analysis of vibrational motion and also of the rotational coupling to vibration. General techniques for studying internal motion of polyatomics will have widespread application because electronic structure theory can provide potential surfaces of high accuracy.

For diatomic molecules, the vibrational analysis can be done numerically (exactly) with considerable ease using what is usually referred to as the Numerov-Cooley method [C-9:10]. This method is not immediately extendable to the many degrees of freedom of a polyatomic molecule unfortunately, and other procedures are needed, and several there are recent promising developments. The discrete variable representation (DVR) method of Light and coworkers [L-7] approximates a numerical solution of a few-dimensional problem in a manner that has some resemblance to Gaussian quadratures. Light's distributed Gaussian bases (DGB) approach [H-4] is a basis set expansion that was found to be more suitable than DVR for nonseparable potentials and thus for polyatomic vibrations. A self-consistent field treatment of vibrational wavefunctions that leads to an averaged separation of vibrational degrees of freedom was developed by Bowman

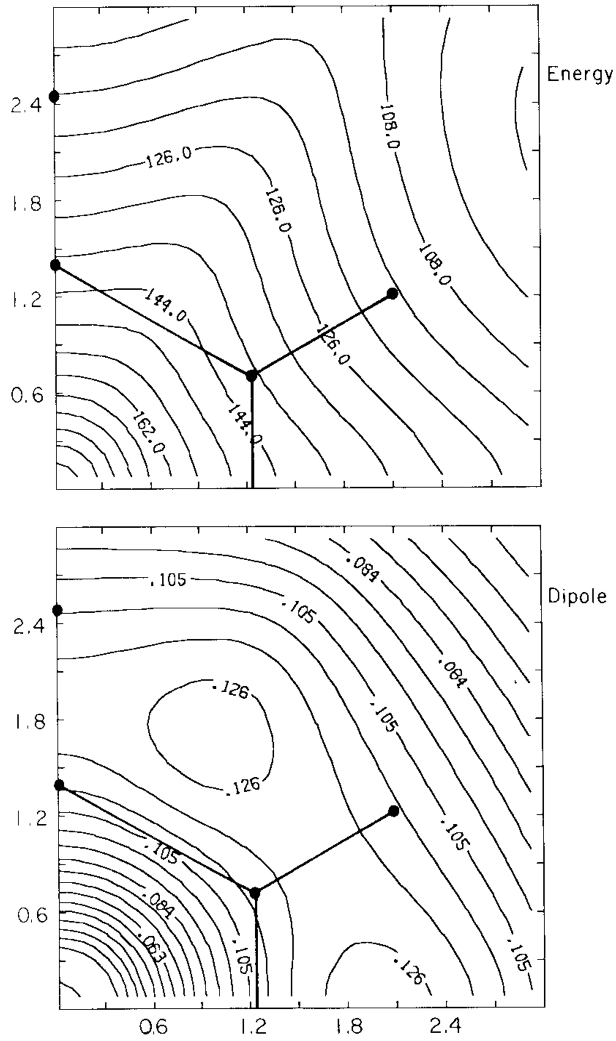


FIGURE 2.7

A potential energy surface (top) and a property surface (bottom) for the complex of Ar with benzene. The argon atom is above the plane of the benzene at a position given relative to the center of the benzene ring by the coordinates of the horizontal and vertical axes. The positions of two carbon and two hydrogen atoms are shown as dots. The stabilization energy in cm^{-1} is shown for the contours in the top figure. The dipole moment of the complex in Debyes is shown for the contours in the bottom figure.

[B-11]. It has been used with considerable success on many problems. A full-blown, non-approximate solution of the vibrational-rotational problem has been formally developed by Estes and Secrest [E-1] and implemented and applied to triatomic molecules. Along with other methods that have been reported or are being developed, these dynamical theories are likely to provide the key link between electronic structure calculations and molecular spectroscopy.

Property Surfaces. Though one may think of a polar, diatomic molecule as possessing a specific dipole moment, the dipole of that molecule is actually changing during the course of its vibrational motion. At each separation distance, the dipole moment will be different. The only specific dipole moment value to rightfully associate with the molecule is the vibrational average. Properties such as the dipole moment are normally dependent on structural parameters, and property surfaces can be constructed just as well as potential energy surfaces. One example is given in FIGURE 2.7. Identifying the lowest energy regions on a potential energy surface and then finding the corresponding regions on a property surface is one way to anticipate what the measured property value will be. Sometimes properties can be found that demonstrate a noticeable electronic reorganization, and if there are sharp changes in the potential surface in the same region, then a correlation might exist between the property and the structure.

Chapter Three

ELECTRONIC STRUCTURE METHODS FOR POTENTIAL ENERGY SURFACES

The names and acronyms of electronic structure methods reported in the literature are numerous, but the types of methods being employed are by no means disparate. A reference point for understanding methods is the self-consistent field (SCF) approximation. It is an important approximation that is the basis for *any* molecular orbital picture of electronic structure. Physically, the approximation is a neglect of instantaneous electron-electron repulsions. Within SCF, each electron interacts with the on-average charge distribution arising from each of the other electrons. This means the electrons see each other as distributions rather than as distinct particles. A derivable result of invoking this approximation is that the two-body electron-electron repulsion term in the molecular Hamiltonian can be replaced by an effective one-body potential term, which includes a non-local part because the electrons are indistinguishable and their wavefunctions must be antisymmetric with respect to particle exchange. The SCF effective potential corresponds to the on-average field of the total electron charge distribution, something which is dependent on the wavefunction. Thus, solving the SCF Schrodinger equation is done self-consistently. Since the operator itself is dependent on the wavefunction, an adjustment in one orbital may lead to an adjustment in the form of another orbital.

An important consequence of the SCF approximation is the simplification in the form of the electronic wavefunction. Because the SCF Hamiltonian has no explicit two-body terms, a separability of sorts arises and the wavefunction may be written as a product (antisymmetrized) of functions of individual electron position vectors. These one-electron functions are the orbitals. This (antisymmetrized) product form of a wavefunction is obtainable from the solution of a set of integro-differential equations called the Hartree-Fock equations. Such a wavefunction is variational. The energy can be shown to be a minimum within the constraint that the wavefunction have this simple product, or one-determinantal form (i.e., consisting of one Slater determinant). The Hartree-Fock equations are sometimes solved numerically, but as Roothaan showed [R-2:3], they can be put into matrix form by expansion into a basis of atomic orbital functions. Each molecular orbital being sought is considered to be a linear combination of all specified atomic orbitals of the species, and the task is to find the expansion coefficients. Again, this is accomplished variationally.

The Hartree-Fock-Roothaan (HFR) theory is very convenient computationally, and it is very much the foundation for contemporary methodologies. HFR solutions differ from solutions of the HF integro-differential equations, though, in that the basic set of atomic functions is necessarily finite and there is some degree of truncation error. Current usage of terminology is that "SCF" identifies any wavefunction found from invoking the SCF approximation, regardless of basis truncation or certain other subtleties. An "HF" wavefunction most often means something more specific, a numerical solution of the HF equations. The Hartree-Fock limit is the point at which a basis set expansion of the SCF wavefunction is considered or shown to be negligibly close to the HF wavefunction. True HF-limit calculations are rare, but very meaningful "near HF-limit" calculations are often found.

Electron Correlation. SCF has remarkable value in molecular electronic structure, but it is not complete in its description. Electrons are particles and they do interact as particles. Because of electrical repulsion, a true wavefunction must yield a diminished probability of finding one electron in the vicinity of another at any one instant, not just on-average. The SCF picture is reasonable to the extent that most of the time electrons are well separated in spaced and their on-average interaction is what is most important. The instantaneous part of the interaction that SCF neglects is referred to as *electron correlation*. It should be pointed out that there is a correlation of motions among electrons even at the SCF level since the electrons are not independent of one another. However, that is not instantaneous correlation, and so in the special terminology of electronic structure, correlation is meant to be the distinction between invoking the SCF approximation and not doing so. Correlation energies and correlation effects, then, are measured against corresponding SCF results.

The mathematical freedom required to account for electron correlation can come about through configuration mixing, which is simply allowing the wavefunction to be a linear combination of electron configurations. A configuration is any spin-adapted linear combination of Slater determinants, and so it is equivalent to view the mixing in terms of either configurations or determinants. In the case of a closed-shell SCF configuration, which means no partially occupied spatial orbitals, no other configuration can be constructed from those orbitals. Thus, other configurations must be constructed in part from orbitals that are not used in the SCF wavefunction. These are referred to as *virtual* or *external orbitals*. By mixing configurations, fractional population of orbitals becomes allowed. As the example in TABLE 3.1 shows, correlation typically diminishes slightly the populations of orbitals that are fully occupied in an SCF wavefunction and produces only small populations in the virtual orbitals.

TABLE 3.1

An example of orbital occupation numbers. Occupation numbers are listed in order of size for a correlated wavefunction of hydrogen fluoride. The table does not list the virtual orbitals with the smallest populations, so the sum of the populations is slightly less than ten, the number of electrons.

Orbital	*SCF Wavefunction Occupation*	*Correlated Wavefunction Occupation*
1	2.0	2.0
2	2.0	1.98796
3	2.0	1.97184
4	2.0	1.97904
5	2.0	1.97904
6	0.0	0.01463
7	0.0	0.01463
8	0.0	0.01285
9	0.0	0.01058
10	0.0	0.00514
11	0.0	0.00426
12	0.0	0.00313
13	0.0	0.00313
14	0.0	0.00303

The means for determining the linear combinations of electron configurations that give a good accounting of electron correlation are several. Perhaps the most direct way is to let the linear expansion coefficients of the configurations be variational parameters. This approach is specifically identified as *configuration interaction* (CI). Another way of mixing together configurations is to define the difference between the true molecular Hamiltonian and the SCF Hamiltonian as a perturbation. With the set of all configurations constructed form SCF determined orbitals taken to be a zeroeth order set of state functions, perturbation theory to some desired order can be used to find the mixing of these states. Moeller and Plesset, in a very early paper, considered the perturbative order to which the SCF energy is correct [M-4], and it has become common to identify certain perturbational calculations as "MPn" (n=2,3,4,5,...); "n" is the order of perturbation. There is no level "MP1" because what Moeller and Plesset showed was that the first order correction to the SCF energy is zero, or that the SCF energy is correct through first order. Perturbative configuration mixing also goes under the more obvious label MBPT (many-body perturbation theory) for exactly the same thing, and RSPT (Rayleigh-Schrodinger perturbation theory) for a different zeroeth order specification [see for example, B-7].

Configurations are referred to in classes that give the number of differing spin-orbitals from some reference, usually the SCF configuration. There are configurations which differ by a single spin-orbital, single substitutions, and there are double substitutions, triple substitutions and so on. Single capital letters are often used to designate that a given level of substituted configurations has been built into a correlated wavefunction. For example, "CISDTQ" is a label for a variational expansion with all singly, doubly, triply and quadruply substituted configurations. A general rule is that accuracy improves as the level of substitution increases, and this is simply expected because of the enlargement of the N-electron (configuration) basis that goes with upping the substitution level. The limiting point where all N-electron substitutions are included is termed a *full-CI*. It can be shown that all variational parameters have been optimized in a CI calculation with all substitutions, and so a full-CI result is exact within the finiteness of the basis of atomic functions originally chosen for the system.

The number of configurations that might be included in a correlated wavefunction can be enormous. If there are K occupied orbitals in the SCF description of a given molecular species, and if there are L virtual orbitals to construct configurations, the number of singly substituted configurations is K times L. The number of double substituted configurations is about $(KL)^2/2$. In most calculations of reasonable quality, L is at least as large as K, and so the number of substitutions grows as K^2 raised to the power of the substitution number. Clearly the number of configurations can get to be very numerous even for small molecules.

There are important differences between the type of configurations in terms of what they describe and how they interact. The single substitutions have a zero matrix element with the SCF wavefunction according to Brillouin's theorem [M-3]. A "CIS" calculation, were it to be performed, could only yield the SCF result for this reason. Doubly substituted configurations may have a non-zero Hamiltonian matrix element with the SCF configuration, and can be mixed by way of CI or perturbative treatments. Triply substituted configurations have a zero Hamiltonian matrix element with the reference because the Hamiltonian has only one and two-body operators. Triply substituted configurations mix only because of their interaction with the doubly or singly substituted configurations. In perturbative terms, the doubly substituted configurations and only the doubly substituted configurations enter the correlated wavefunction at first order. Consequently, correlation effects arising from triple, quadruple and further substitutions tend to be small. They are often referred to as *higher order effects.*

Another means for bringing about configuration mixing is the *coupled cluster* (CC) approach [B-7:8,C-4:5,H-1,P-1]. Large scale calculations employing this approach are still fairly new, but the successes of it are noteworthy. The coupled cluster approach generates the correlated wavefunction by application of an exponential substitution operator to a reference configuration, typically the SCF configuration. CI can be expressed in the same way, except that then the substitution operator is linear, not exponential. For instance, a particular CID wavefunction could be considered as arising from application of a multi-term operator to the reference such that each term makes one of the double substitutions and then scales it by its proper expansion coefficient. Coupled cluster theory uses the exponential of that multi-term operator. This exponential, of course, is just another operator, and for convenience it is usually written as a power series in terms of the original operator. The first term of the series is 1.0, the second term is the double substitution operator itself, and the third term is that operator squared (divided by two). What that third piece of the expansion does when applied to the reference configuration is make all double substitutions of all double substitutions. In other words it generates quadruple substitutions. The fourth term in the power series generates hextuple substitutions, and so forth. In this way, higher order effects are built into the wavefunction, yet the number of adjustable parameters is just the number in the substitution operator. Thus, "CID" and "CCD" (coupled cluster with double substitutions) have the same number of adjustable parameters, one coefficient for each doubly substituted configuration. However, the CCD wavefunction has many more configurations, and those additional configurations have expansion coefficients that are products of the expansion coefficients of the doubly substituted configurations.

There are several names in use for coupled cluster treatments and for approximate versions. The coupled electron paid approximation (CEPA) is really several approximations introduced by Meyer [M-5:6], Kutzelnigg [K-1] and Ahlrichs [A-6]. The coupling of electron pairs is accomplished relative to a CID treatment by replacing the correlation energy with some combination of pair correlation energies, or in the case of CEPA-0, with zero. These approximations are the simplest to implement, but have certain formal shortcomings. For instance, CEPA-1, CEPA-2 and CEPA-3 do not possess the orbital invariance that CCD does. Even so, CEPA has yielded some very impressive results, especially when higher order correlation effects have been important. CPMET (coupled pair many electron theory) is another label for CCD that was used in Cizek's pioneering work with these types of wavefunctions [C-4:5]. Linear coupled cluster methods are approximations that ignore Hamiltonian matrix elements that are quadratic in expansion coefficients. LCCD (linear CCD) is the same as LCPMET and the same as CEPA-0. Hurley [H-1] refers to CCD as the coupled pair approximation (CPA) and has several forms that are equivalent to LCCD plus the CEPA's.

A recent approximation to coupled cluster treatment is the ACCD (approximate CCD) method [B-9,C-7,J-1] which has also been labelled ACP-D45 or just ACP. ACCD has all the formal features of CCD and keeps most of the complete calculation of Hamiltonian matrix element terms. However, two sets of terms tend to be opposed in their effects, and taken together these are neglected with rather little effect. There is some beneficial cancellation, and it has been suggested that the part which does not fully cancel is the part that would cancel when quadruple substitutions are included into the cluster operator [P-2]. In other words, ACCD is at the least a good approximation to CCD and at the best, a usable approximation to an even more complete treatment, CCDQ.

Several computational approaches to CCD have evolved from perturbational methods [B-7,P-1]. Nakatsuji [N-1:2] has cast the cluster expansion into a very workable form referred to as SAC for symmetry-adapted cluster theory. A direct, matrix-oriented form that solves for the wavefunction in terms of the atomic basis functions was developed in 1980 [C-12]. In all, it is fair to say that the computational cost of CCD is quite like that of the less complete CID wavefunction. That makes sense since both wavefunctions employ the same number and type of adjustable parameters. It is likely that optimally formulated extensions to CCSDT, CCSDTQ, ... will show computational costs comparable to CISDT, CISDTQ, ... respectively. However, it is nowhere near so important to extend CC approaches as CI approaches because higher order effects are immediately incorporated into CC wavefunctions.

An estimator for higher order correlation effects was introduced by Davidson [D-6:7,L-5] and is often referred to as "Davidson's correction." The concept for this estimator can be approached in several ways, and one of those uses the notions of coupled cluster expansions. In a CCD wavefunction, the importance or weighting of the quadruple substitutions is essentially a quadratic function of the importance of the double substitutions. The correlation energy gained from the inclusion of the quadruple substitutions will have a corresponding dependence on the double substitutions. In a normalized CID wavefunction, with C_0 being the expansion coefficient of the reference or SCF configuration, the sum of the squares of the other expansion coefficients is $(1 - C_0^2)$. This simple factor has an averaged quadratic dependence on the expansion coefficients or weighting of the doubly substituted configurations, and in the Davidson correction, this factor scales the correlation energy to estimate the quadruple substitution contributions to the energy.

$$E_Q^{corr} \approx (1 - C_0^2)\, E_D^{corr} \qquad (3\text{-}1)$$

This formula is obviously very simple and serves to give an idea of the higher order correlation effects without carrying out a CI that includes higher order substitutions. There have been examinations and modifications of this original formula [D-7,S-9] and the connection with CCD has been spelled out in some depth [D-8].

When chemical bonds are breaking or forming, the SCF approximation can lead to a poor description in certain cases, yet this is not because of electron correlation effects in the sense that they have been discussed so far. The hydrogen molecule's wavefunction serves as a good, and often used illustration. When stretched nearly to dissociation, a poor description of the wavefunction results from requiring the two electrons to occupy the same spatial orbital. This is because as complete separation of the atoms occurs, the symmetric combination of the two 1s atomic orbitals becomes energetically equivalent to the antisymmetric combination. In other words, there are two molecular orbital descriptions that must have equal weighting (probability density) at dissociation. An SCF wavefunction is constrained to be but one configuration and can not do the job. Merely letting the wavefunction span the mathematical space of two configurations, though, can provide a vast improvement in the description of the dissociated system. The energy will be lowered significantly by mixing in the second configuration. We may call that energy lowering a correlation effect, but it is clearer to distinguish that as a *non-dynamical* correlation effect [S-8]. Non-dynamical correlation is found when a one-configuration representation of the wavefunction is unsuited, when there are configurations degenerate or nearly degenerate with the reference configuration, or when mixing a small number of configurations yields a dominant description that a single configuration would not. Dynamical correlation is whatever correlation remains to be accounted for. On an energetic basis, dynamical correlation might be distinguished from non-dynamical correlation. There will be a much more sizable energy lowering from the mixing of a given configuration when its inclusion in the wavefunction is important for non-dynamical correlation than if it were important for dynamical correlation. The distinction between these two types of correlation effects has no sharp cut-off. It is a practical more than a mathematically precise distinction. Configuration mixing that accounts for non-dynamical correlation can also be said to be giving some accounting of dynamical correlation.

Except for full-CI, wavefunctions are always truncated in the extent of configuration mixing. A CISD wavefunction, for instance, includes a subset of the configurations in a CISDQ wavefunction, which includes but a subset of a CISDTQ configuration list, and so on. In some instances, configuration lists are truncated so that only part of the substitutions of a given level (S, D, T, ...) are included. The degree of configurational truncation always lurks as a threat to accuracy. Fortunately, much transferable experience is available to understand limitations on accuracy. Underlying this experience is a common and obvious notion that how well a truncated wavefunction dominates the true wavefunction -- were it known -- has much to do with how well the truncated level of treatment can accurately predict structures and properties. In this sense, the SCF wavefunction is the most truncated of any, but it is still capable of meaningful predictions if it gives a strongly dominant description. Dominance might be measured by how close to 1.0 its expansion coefficient is in an extensive CI wavefunction. For the hydrogen molecule, the SCF configuration strongly dominates even in the most detailed calculation of the complete wavefunction in the vicinity of the equilibrium bond length. A two configuration description, taking the two configurations as a single function, dominates not only in the vicinity of the equilibrium but also all the way to dissociation. Thus, if non-dynamical correlation effects are properly incorporated, a not too extensive wavefunction may serve well in calculating molecular structures and properties.

For qualitatively differentiating a species as being chemically bound or being unbound, treatments that include only the non-dynamical correlation effects are consistently correct. That is, either a single SCF configuration or a small set of configurations consistently succeeds in determining the existence of chemical bonds. What may be the only exception known to date is a very special case, the tetrahedral cluster of four magnesium atoms [C-6,B-10,P-3]. SCF level calculations indicated that this cluster was unbound, having no potential minimum, or was at most a van der Waals complex with a very shallow minimum. Correlation effects of the 3s magnesium electrons grow sharply as the atoms are brought into proximity [C-6], and a potential minimum at least 10 kcal deep develops. This appears to be a dynamical correlation effect. Many configurations contribute and the SCF configuration dominates in the correlated wavefunction uniformly well throughout all regions. Recognizing this as a very special case highlights the soundness of the general orbital foundation for molecular electronic structure and the current understanding of configurational mixing.

CI is most often carried out subsequent to an SCF calculation. SCF determines the orbitals that make up the configurations in the CI expansion. The energy of a CI wavefunction which includes complete levels of substitution (S, D, T, ...) can be shown to be invariant to unitary orbital transformations that are entirely within shells. This is as it should be. Going from symmetry adapted orbitals in the SCF wavefunction of the water molecule to local hydrogen-oxygen bond orbitals, a simple unitary transformation, shouldn't change the correlation energy. However, a transformation that mixed one of those doubly occupied orbitals with an external or virtual orbital could change the correlation energy. This suggests that orbitals could be adjusted to improve (i.e., lower) the energy of a configuration expansion, and the general name for this process is MCSCF, *multi-configuration* SCF.

MCSCF methods are extremely powerful and efficient in problems with non-dynamical correlation. Typically, the configuration list can be chosen to include several, or tens, or hundreds of configurations and then the simultaneous optimization of the configuration expansion coefficients and the orbitals yields wavefunctions which would be strongly dominant descriptions within even the exact molecular wavefunctions. This means that CI calculations performed subsequently with a still larger configuration list, such as all double substitutions from the multi-configurational reference list, often leave scant correlation effects unaccounted. Methods have been developed that achieve quadratic convergence in solving for MCSCF wavefunctions [L-4,W-1,Y-1] and this has significantly elevated the applications impact of these approaches.

One particular type of MCSCF wavefunction is designated CASSCF for *complete active space* SCF [R-4:5]. This is similar to Ruedenberg's earlier idea of a fully optimized reaction space (FORS) [R-6:8]. The active space consists of all orbital that are neither fully occupied nor empty in every configuration of the MC list. The MC list becomes "complete" by including all possible configurations in the active space. This replaces the sometimes troublesome task of selecting dominant configurations for an MCSCF calculation with a more chemically oriented task of selecting the active space orbitals. One disadvantage is the strong dependence of the number of configurations on the number of electrons. That can make for longer configuration lists than with other MCSCF approaches.

An extensively applied and highly successful treatment which can be classified as an MCSCF method is the generalized valence bond (GVB) method [G-1:3,H-3]. Formally, GVB wavefunctions use non-orthogonal orbitals to describe a bonding pair of electrons and in so doing can more uniformly describe changes in the bonding, antibonding and non-bonding of electrons than can SCF. The difficulties of spin recoupling in the course of chemical reactions are properly treated with GVB. For computational purposes, the GVB wavefunction can be recast into orthogonal orbital form, and then the correspondence to MCSCF is direct. Dunning has carried out calculations on the nitrogen molecule [D-5] that give a comparison of multi-configurational methods. The calculated dissociation energies were 5.08 eV at the SCF level, 7.21 eV at the GVB level, 8.76 eV with CASSCF and 8.96 eV with a CI expansion from the GVB reference, while the measured value is 9.905 eV. The GVB bonding orbitals of N_2 are given in FIGURE 3.1. These are non-orthogonal orbitals optimized for the multi-configurational GVB

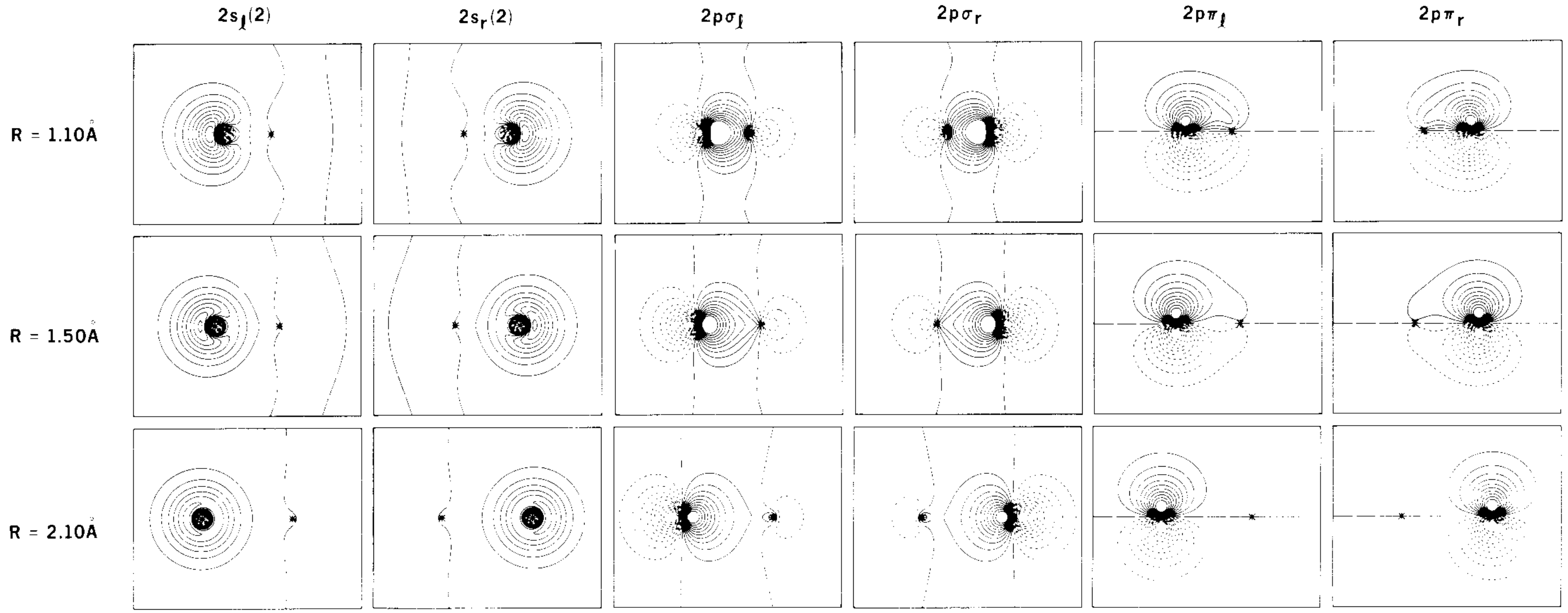


FIGURE 3.1

Contour plots of Dunning et al. [D-17] of the valence bond forms of the perfect-pairing GVB orbitals of N_2 at three separation distances. These non-orthogonal orbitals are found in pairs, left (*l*) and right (*r*). As dissociation proceeds, the orbitals go smoothly into the form of the proper atomic orbitals. The contours are in steps of 0.05 a.u. from -0.5 a.u. to +0.5 a.u.

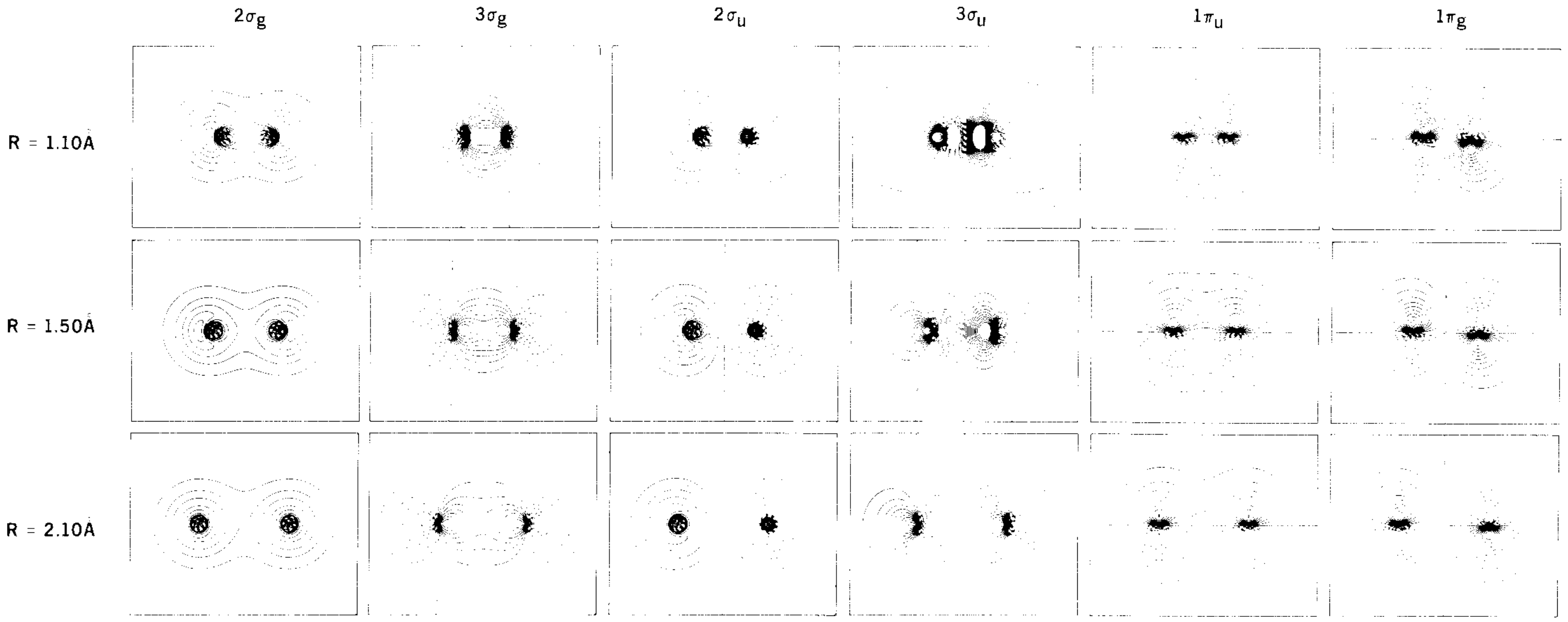


FIGURE 3.2

Contour plots of Dunning et al. [D-17] of the natural orbital forms of the perfect-pairing GVB orbitals of N_2 at three separation distances. The contours are at the same values as those in FIGURE 3.1.

wavefunction. A symmetry-adapted form of these same orbitals is shown in FIGURE 3.2.

The use of non-orthogonal orbitals shows up in a number of methods besides GVB. In a formal sense, there's nothing special about orbitals that are not orthogonal since they can always be orthogonalized by suitable transformation. However, relaxing the orthogonality constraint can be exploited to bring in additional correlation effects when the configuration list is truncated. PNO-CI [M-5:6,A-6] (pair or pseudo natural orbital CI) employed non-orthogonal orbitals to get the most correlation effect out of a subset of the doubly substituted configurations. In other words, a much shorter configuration list than that of a CID wavefunction could do just as well. Meyer's PNO-CI study of methane [M-6] remains as a landmark investigation in electronic structure having obtained results which have not been materially challenged by newer studies in the succeeding decade and a half.

Brueckner orbitals are not widely employed, but they have special virtues and are worth mentioning. The prescription for these orbitals is that they are chosen so that the singly substituted configurations in a CI or CC wavefunction have identically zero expansion coefficients. In the two-configuration MCSCF or the GVB description of the hydrogen molecule this automatically results. In a like manner, Brueckner orbitals may be useful in describing bond breaking and bond forming and have been employed for this purpose [J-2:3]. In this volume, calculations with an appended "/B" mean Brueckner orbitals were calculated and were used for the reference configuration.

Calculational methods identified in the literature of electronic structure calculations go by many different names. Some names identify wavefunction types, and so are very useful labels. Others identify algorithms used to obtain the wavefunctions or sometimes particular implementations of methods. TABLE 3.2 collects many of the commonly used names that primarily identify wavefunction type. Calculations going by other names can often be placed under one of these designations by searching for some mention of the form of the wavefunction.

Lithium hydride is a simple molecule for electronic structure theory because it has so few electrons. It is just about the simplest example where pair correlation and higher order correlation effects can be present. FIGURE 3.3 gives a simple illustration of the effect of electron correlation on the LiH

TABLE 3.2

A partial list of commonly used abbreviations or acronyms of names of electronic structure wavefunctions and methods.

Single Configuration Wavefunctions / Optimized Orbitals	
HF	Hartree-Fock
HFR	Hartree-Fock Roothaan
SCF	Self-consistent field
Multi-configuration Wavefunctions / Optimized Orbitals	
CASSCF	Complete active space SCF
FORS	Fully optimized reaction space
GVB	Generalized valence bond
MCSCF	Multi-configuration SCF
TCSCF	Two configuration SCF
Variational Configuration Expansions	
CI	Configuration interaction
	CI: with double substitutions
	CIDS or CISD: with single and double substitutions
	CISDT: with single, double and triple substitutions
MR-CI	Multi-reference CI; substitutions made with respect to a specified set of configurations
Perturbative Configuration Expansions	
MBPT	Many body perturbation theory
MPn	Moeller-Plesset theory to n-th order (equivalent to MBPT)
RSPT	Rayleigh-Schrodinger perturbation theory
Coupled Cluster Expansions	
CCD	Double substitution coupled cluster expansion
	ACCD: specific approximate form of CCD
	CCDS: with single substitutions
	LCCD: linearized form
CEPA	Coupled electron pair approximation
CPA	Coupled pair approximation
CPMET	Coupled pair many-electron theory
	ACP : specific approximate forms
	LCPMET: linearized form

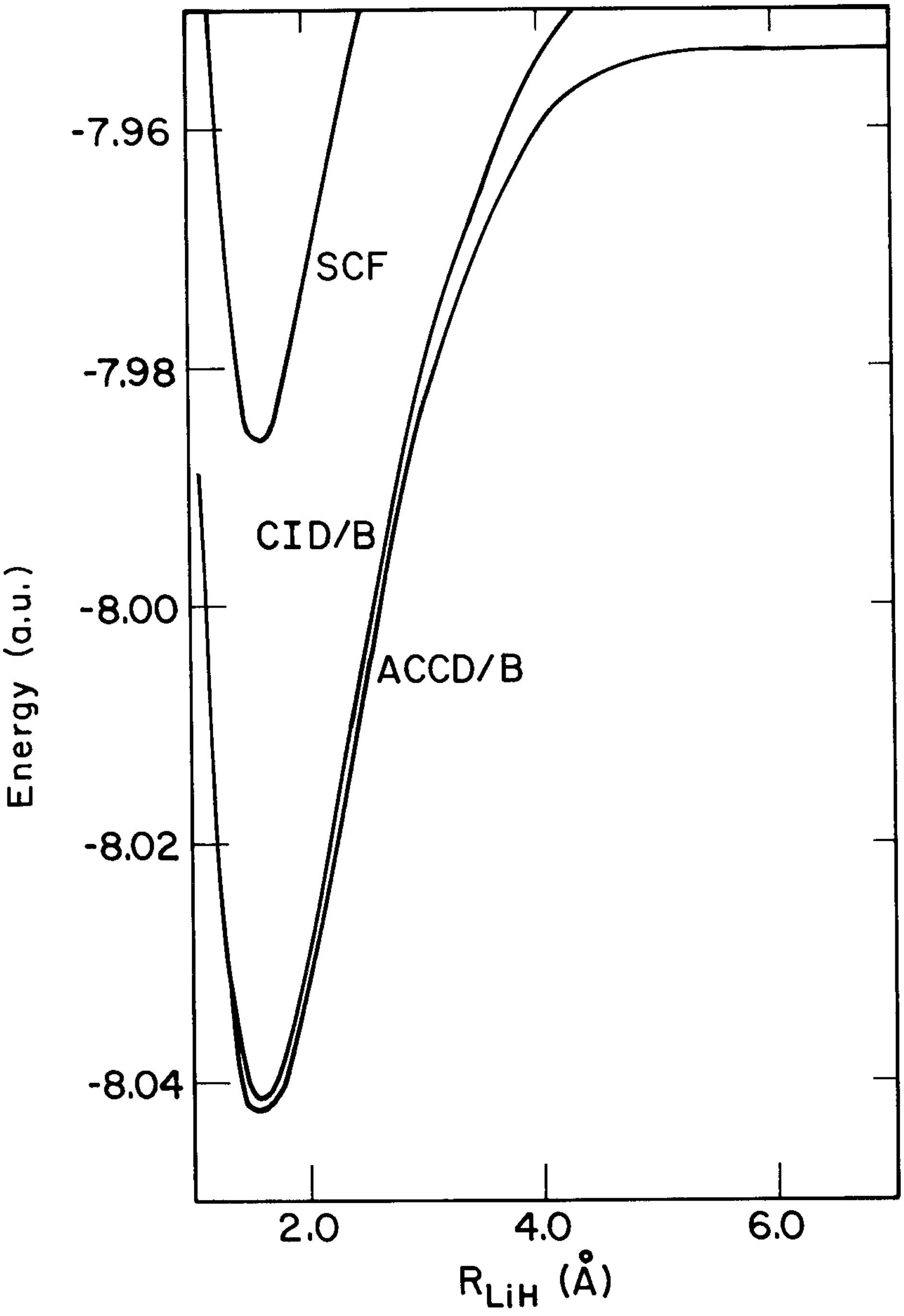


FIGURE 3.3

Lithium hydride potential energy curves [T-3] at the SCF, CID/B and ACCD/B levels. The basis was a (11s 3p 2d/5s 3p 2d) contraction on lithium and a (8s 3p 1d/5s 3p 1d) contraction on hydrogen. The dissociation energy from the ACCD calculation is within 830 cm^{-1}, or a few percent, of the known value [S-14].

potential energy curve. The coupled cluster curve, in this case, provides a better description than the curve obtained with the particular CI treatment. Around the equilibrium, though, the treatments give very similar results.

While correlation lowers the energy at every point on the LiH curve by 0.05 a.u. or more, the SCF level treatment still yields meaningful information about the molecule, especially concerning equilibrium properties. This is suggested by the more detailed view of FIGURE 3.4 where the SCF and ACCD/B curves have been drawn on an energy scale that is relative to the potential minima. The equilibrium bond lengths, the R values at the minima, appear to be about the same and the shape of the two curves show very good agreement. The difference is characteristic of correlation effects, in one sense, which is that correlation tends to fatten out stretching potentials. This in turn leads to lower vibrational frequencies as the LiH results in TABLE 3.3 indicate. Lithium hydride is somewhat of an extreme case in because of its simplicity. It is often used a test case because in many ways the correlation effects of the four electrons are not sizable. In molecules with more electrons, the correlation effects tend to be greater and much more noticeable. The differences between the equilibrium structures obtained with and without correlation effects may be greater. The vibrational frequencies for larger molecules are usually more affected by electron correlation than is the case with lithium hydride.

Basis Sets. FIGURE 3.5 offers one more look at lithium hydride's potential curve. Here, the ACCD potential is compared with three high quality curves taken from the literature. It may be seen that there are differences in the curves even though each incorporates electron correlation rather fully. What causes much of the differences seen in the curves results from another key consideration in electronic structure calculations, basis set effects. As mentioned at the beginning of this chapter, molecular orbitals are most often obtained as a linear combination of some specified set of basis functions. How that set of basis functions is selected is very important in how meaningful the final results of a calculation are. Without a proper basis set, incorporating correlation effects is really putting the cart before the horse.

For convenience in calculation of two-electron integrals, commonly used basis sets employ Gaussian functions. A Gaussian basis function is one which as a radial dependence of the form $e^{-\alpha r^2}$ where r is the distance from the function's center, usually an atom's position in the molecule. The exponent, α, may be different from atom to atom or function to function.

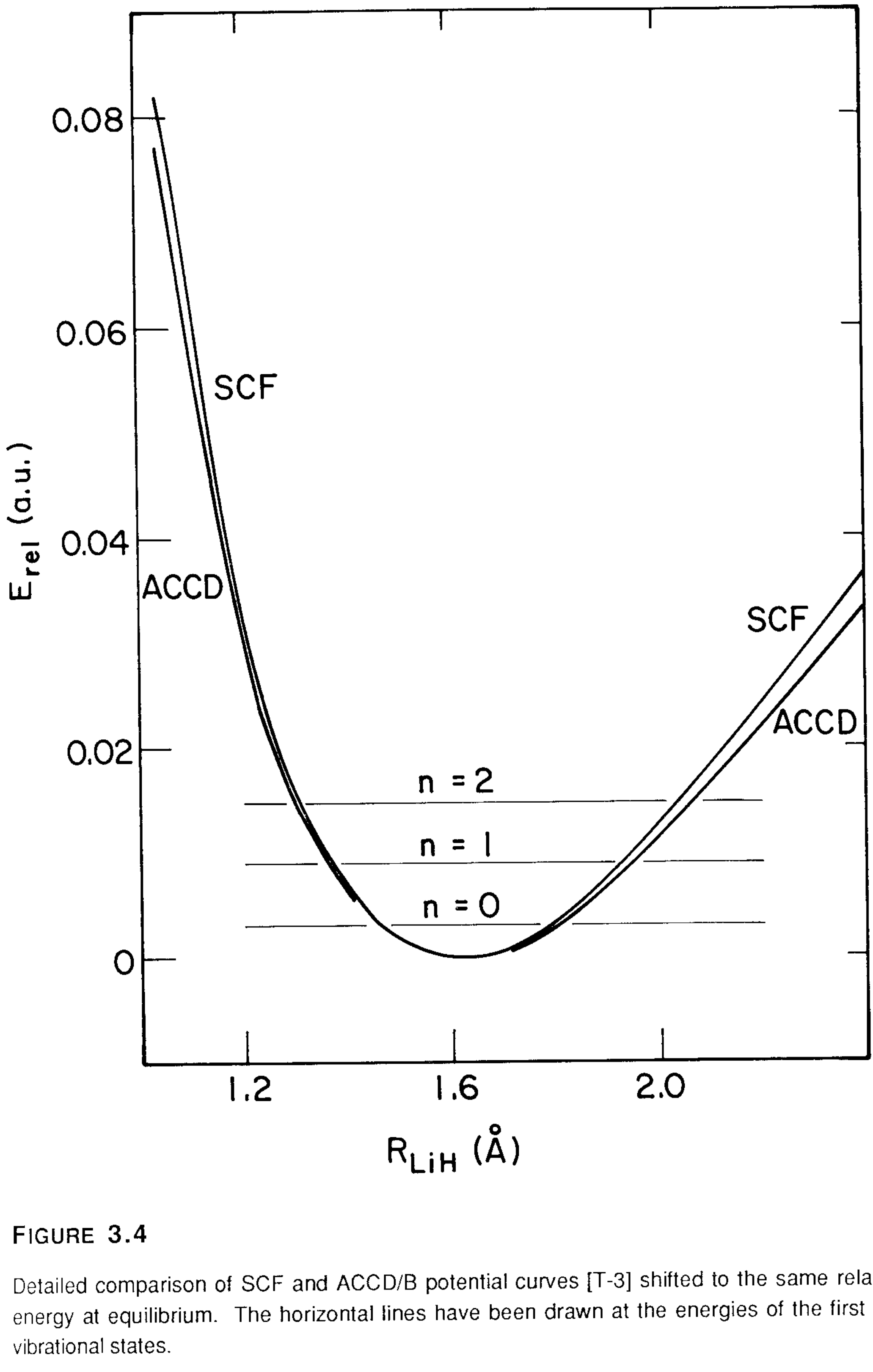


FIGURE 3.4

Detailed comparison of SCF and ACCD/B potential curves [T-3] shifted to the same relative energy at equilibrium. The horizontal lines have been drawn at the energies of the first two vibrational states.

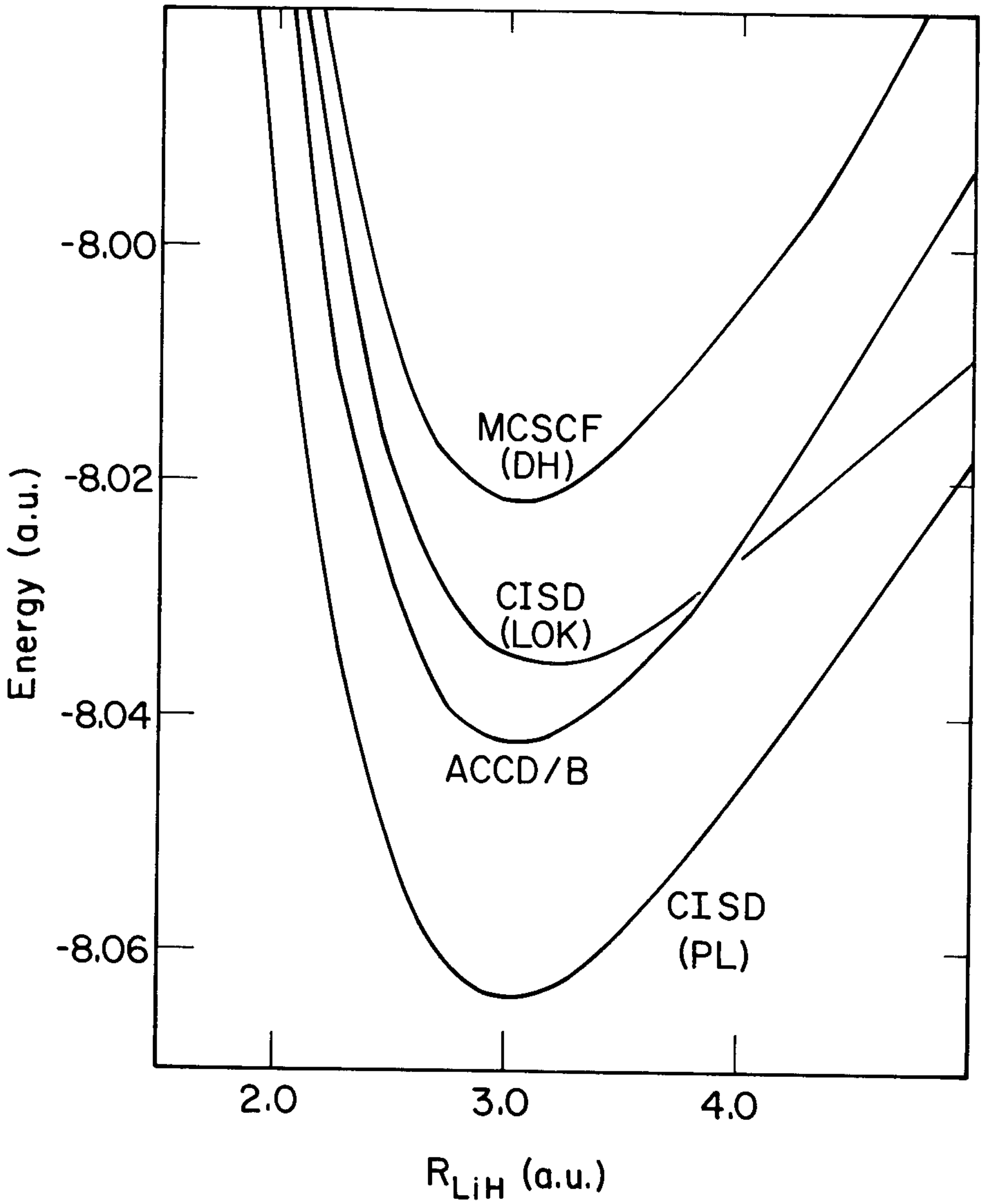


FIGURE 3.5

Comparison of several different ab initio potential energy curves of lithium hydride. The MCSCF (**DH**) curve is that of Docken and Hinze [D-9] who used a Slater basis of 21 σ, 7 π and 4 δ functions. The CISD (**LOK**) curve is that of Liu et al. [L-6] who used a Slater atomic basis, (6s4p2d1f) on lithium and (6s3p2d1f) on hydrogen. The same correlation treatment was employed by Partridge and Langhoff [P-4] (**PL**) with a Slater basis of 22 σ, 12 π and 7 δ functions.

TABLE 3.3

Calculated lithium hydride vibrational state energies [L-11] and properties at the SCF and ACCD (correlated) levels of treatment. A number of Gaussian basis sets were used and convergence of the results with respect to basis set size is apparent. The results for the small sets are quite dependent on the particular choice of the Gaussian exponent values, and these specific values have been reported [L-11]. ACCD results are given for each basis set; SCF results, as indicated, are available for certain of the sets. With the largest basis set calculations, the bond length from the correlated calculations agrees with the spectroscopically inferred value by better than a thousandth of an Angstrom. Vibrational transition frequencies are accurate to 4 cm^{-1}. At the SCF level the vibrational frequencies are consistently over estimated so the error is an order of magnitude greater.

ACCD Energy (a.u.)	*Equilibrium Bond Length (Angstroms)*	*Transition Frequencies (cm^{-1})*			*v=0 State Dipole (Debyes)*
		$0\rightarrow 1$	*$1\rightarrow 2$*	*$2\rightarrow 3$*	
18-FUNCTION BASIS Li (5s2p) and H (4s1p)					
-8.033710	1.5944	1358.0	1314.7	1270.9	5.924
SCF:	1.6037	1401.9	1364.1		
24-FUNCTION BASIS Li (5s2p1d) and H (4s1p)					
-8.036337	1.5888	1365.9	1321.8	1277.6	5.911
36-FUNCTION BASIS Li (5s3p2d) and H (4s2p)					
-8.043490	1.5975	1358.3	1312.4	1266.4	5.949
SCF:	1.6079	1387.5	1348.5		
43-FUNCTION BASIS Li (9s3p2d) and H (7s2p)					
-8.044755	1.5974	1358.1	1312.4	1266.8	5.924
SCF:	1.6071	1389.5	1350.7		
64-FUNCTION BASIS Li (9s6p2d) and H (7s4p1d)					
-8.065068	1.5961	1362.5	1318.4	1274.7	5.943
EXPERIMENTAL VALUES					
[O-3]	1.5957				
[C-14]		1359.8	1314.9	1270.9	
[W-4]					5.882

Angular dependence in the basis set is brought about my multiplying the Gaussian radial functions by Cartesian polynomials, $x^l y^m z^n$, to form Cartesian Gaussians, or by multiplying them by spherical harmonics. In this way, one can specify s, p, d, f . . . type atomic functions. A Cartesian s-function is one for which l+m+n=0. A p-function has l+m+n=1, and so on. The Gaussians do not have a dependence on the principal atomic quantum numbers. There are only s basis functions, not 1s, 2s, 3s, ... The nodal character of the atomic functions develops automatically in a calculation by way of (plus and minus) linear combinations of Gaussians with different exponents, or different extensiveness.

Atomic basis sets of Gaussian functions are normally contracted. That is, instead of individual Gaussian functions, the actual basis functions are linear combinations of Gaussians. The quality of basis set, depends on several features:

- the total number of contracted basis functions
- the number of uncontracted or primitive functions used to construct the contracted set
- the choice of the exponents, the α's
- the choice of the contraction coefficients
- the different types (s,p,d, . . .) of functions included in the basis

The differences between Slater or hydrogenic functions and Gaussian functions is two-fold. The Gaussian functions have a sharper fall-off with increasing r, the radial distance from the atomic center, and the Gaussians have a zero-valued first derivative at the origin. The 1s hydrogen atom orbital obtained analytically from the Schrodinger equation, however, has a finite first derivative or slope at the origin. This means that in general, a Gaussian basis may need to include many "tight" primitives, with large exponents, in order to approach an exact description of the electron density close to the nuclei. Slaters will be more suited. Also, the Gaussian basis may need to include many "diffuse" primitives, with very small exponents, to approach an exact description of the density in the outer regions of a molecule. In spite of this, Gaussians have been found to work quite nicely in electronic structure calculations. These differences mean that special care in Gaussian basis set selection is required when the properties of interest depend strongly on the electron distribution at the outer regions of the molecule or in the vicinity of atomic nuclei.

TABLE 3.4 lists the optimized exponents of s-type Gaussian function basis sets of different sizes for the hydrogen atom. These were obtained by Huzinaga in 1965 [H-2] along with optimum exponents for other elements. The values in TABLE 3.4 show that as the number of primitive Gaussians used to describe the hydrogen atom increases, the range of exponents grows in both directions, larger and smaller. The exponent values spread out to span the range.

Since both the quality of the primitive set of functions and the contraction scheme are important, a notational form is commonly followed for reporting the essential features of the contraction. It is to specify the number of primitive functions of each *l*-type and then the number of contracted functions of each *l*-type. This is done for each atom in a given molecular problem. If the first two Huzinaga functions in the four-function set in TABLE 3.4 were contracted together, this hydrogen atom basis could be designated (4s/3s), meaning four primitive s functions contracted into three.

A *minimum basis* is one that has one contracted function for each occupied core or valence orbital in the atom. A minimum basis for helium is just a single 1s function. For carbon, or nitrogen, or oxygen, a minimum basis would be two s-functions and three p-functions, because of the three-fold degeneracy of p-functions (p_x, p_y, p_z). With Slater basis sets, a set of zeta-values (exponents) defines a minimum basis. For this historical reason, basis sets with multiples (two or three) of the minimum basis set functions are referred to as *double zeta* (DZ) or *triple zeta* (TZ). A double zeta basis for a carbon atom would have to include four s-functions and six p-functions.

Many calculations are carried out with basis sets that are double zeta (or better) in the valence region but only minimal in the core. These can still be referred to as being of double zeta quality. The argument behind their use is that the core electrons are little affected by chemical bonding and so giving them the same flexibility to adjust as the valence electrons isn't essential. One case of basis sets of this sort conveniently incorporates contraction information into the basis set designation. These are the bases developed by Pople and coworkers at Carnegie-Mellon [D-12]. They are split valence sets, being only single-zeta in the core. A basis designated "4-31G" has four primitives contracted into one function for the n=1 atomic shell, i.e., the 1s orbital. After the hyphen comes the valence shell contraction and "31" means three functions contracted into one, plus one uncontracted function, for the n=2 atomic shell.

TABLE 3.4

Optimum exponents for s-type Gaussian basis sets of the hydrogen atom according to Huzinaga [H-2].

	Exponent	*Orbital Coefficient*
2-function set (E = -0.424413 a.u.)		
	1.133248	0.27441
	0.201527	0.82123
3-function set (E = -0.496979 a.u.)		
	4.50038	0.07048
	0.681277	0.40789
	0.151374	0.64767
4-function set (E = -0.499277 a.u.)		
	13.3615	0.01906
	2.01330	0.13424
	0.453757	0.47449
	0.123317	0.50907
5-function set (E = -0.499809 a.u.)		
	33.6444	0.00612
	5.05796	0.04575
	1.14680	0.20572
	0.321144	0.50822
	0.101309	0.37602
6-function set (E = -0.499940 a.u.)		
	68.1600	0.00255
	10.2465	0.01938
	2.34648	0.09280
	0.673320	0.29430
	0.224660	0.49221
	0.082217	0.24260
7-function set (E = -0.499976 a.u.)		
	148.2732	0.00097
	22.17427	0.00753
	4.970178	0.03939
	1.370498	0.15161
	0.436661	0.38487
	0.155858	0.44842
	0.060738	0.11220

Polarization functions are those which are of an *l*-type at least one greater than the highest *l*-type of the valence set. These basis functions are responsible for describing the polarization of an isolated atom in a uniform electric field. The hydrogen atom's polarization functions are p-functions. The oxygen atom's polarization functions are d-functions.

TABLE 3.5 is a guide to certain often encountered basis set designations. As greater accuracy is sought in ab initio calculations, larger and larger basis sets are used. Such sets often don't have standard designations and are, or at least should be, explained in full wherever the calculational results are reported.

A final notational custom that is often encountered is in the specification of a calculated energy or relative energy, obtained at a certain optimized geometrical structure. The basis set and wavefunction type for the energy evaluation are listed first (e.g., TZP/MP3) and the basis set and wavefunction type at which the structure was optimized are listed second. Thus (TZP/MP3 // 4-31G/SCF) means the structure was determined at the SCF level with a 4-31G basis, and then at that structure the energy was evaluated with third order perturbation theory treatment of electron correlation using a TZP basis set.

Basis sets have been carefully constructed for describing the important features of the valence electron distribution. It is well understood how to construct the variationally best (or nearly best) basis of a chosen size and type. What has become much better understood recently is the best basis set choices for molecular properties, including vibrational parameters. The question of basis set effects will come up again, in a more detailed sense, in certain of the chapters that follow.

Procedures for Finding Basic Electronic Wavefunctions. Outlined so far have been the types of wavefunctions that are employed for electronic wavefunctions and the types of basis functions used to represent the wavefunctions. The procedures for finding the wavefunctions and electronic energies involve a number of key computational steps. To understand what those steps are, we must look at the procedures themselves in detail.

Atomic or molecular orbitals are one-electron functions. An orbital ϕ_i is always meant to be a function of some particular electron's spatial coordinates, $\mathbf{r}_i = (x_i, y_i, z_i)$. Even within the self-consistent field approximation,

TABLE 3.5

Summary of basis set types and designations. Names used for a number of commonly used basis sets are listed. For each basis set, the number of primitive Gaussian functions and the number of contracted functions for the atoms hydrogen and carbon are given as: (primitive functions/contracted functions.)

MINIMUM BASIS SETS		
STO-3G		
	Hydrogen (3s/1s)	Carbon(6s3p/2s1p)
DOUBLE ZETA VALENCE SETS		
DZ (Dunning/Huzinaga)		
	Hydrogen (4s2s)	Carbon (9s5p/4s2p)
3-21G		
	Hydrogen (3s2s)	Carbon (6s3p/3s2p)
4-31G		
	Hydrogen (4s2s)	Carbon (8s4p/3s2p)
6-31G		
	Hydrogen (4s2s)	Carbon (10s4p/3s2p)
With polarization functions:		
DZP		
	Hydrogen (4s1p/2s1p)	Carbon (9s5p1d/9s5p1d)
4-31G* or 4-31G(d)		
	Hydrogen (4s2s)	Carbon (8s4p1d/3s2p1d)
4-31G** or 4-31G(d,p)		
	Hydrogen (4s1p/2s1p)	Carbon (8s4p1d/3s2p1d)
TRIPLE ZETA VALENCE SETS		
TZ (Dunning/Huzinaga)		
	Hydrogen (6s/3s)	Carbon (10s6p/6s4p)
6-311G		
	Hydrogen (5s/3s)	Carbon (11s5p/4s3p)

With polarization functions: TZP, 6-311G** or 6-311G(d,p)

With double polarization functions: TZ2P a wavefunction corresponding to the orbital picture of atomic and molecular electronic structure can not be just a simple product of functions, such as,

$$\psi = \prod_i u_i(\mathbf{r}_i) \tag{3-2}$$

where u_i is a spin-orbital, or product of a spatial orbital and an α or β spin function. Such a wavefunction does not obey the Pauli principle: It is not antisymmetric (or symmetric) with respect to interchange of particle coordinates. The simple product wavefunction implies that electron 1 is distinguishable from electron 2, which it is not. Product wavefunctions were a choice as an approximate wavefunction in the early days of quantum chemistry, but the Pauli principle's requirement of antisymmetry of the wavefunction upon exchange or permutation of electrons is quite important. This can be accomplished with an operator which will project an antisymmetrized wavefunction out of the simple product wavefunction of Eqn. (3-2). Consider the effect of an operator that permutes the electrons i and j.

$$\begin{aligned}\hat{p}_{ij}\,\psi(\mathbf{r}_1,\ldots,\mathbf{r}_i,\mathbf{r}_j,\ldots) &= \psi(\mathbf{r}_1,\ldots,\mathbf{r}_j,\mathbf{r}_i,\ldots)\\ &= -\psi(\mathbf{r}_1,\ldots,\mathbf{r}_i,\mathbf{r}_j,\ldots)\end{aligned} \tag{3-3}$$

A product of n successive permutations of two electrons, denoted by P_n, will lead to a sign change of $(-1)^n$. To completely satisfy the Pauli principle, the wavefunction must be antisymmetric with respect to any $\hat{p}_{ij}$ and any product up to P_{N-1} where N is the number of electrons.

Consider a specific case of four electrons and take Φ_o as a simple product wavefunction.

$$\Phi_o = u_1(\mathbf{r}_1)\,u_2(\mathbf{r}_2)\,u_3(\mathbf{r}_3)\,u_4(\mathbf{r}_4) \tag{3-4}$$

Define Φ_1 to be $\hat{p}_{ij}\Phi_o$. Then, the function $(\Phi_o - \Phi_1)$ is antisymmetric with respect to this one permutation operator. Clearly, the operator $(1 - \hat{p}_{ij})$ projects a wavefunction which is antisymmetric with respect to the interchange of the i and j electrons. A completely antisymmetric wavefunction can be generated by successive applications of projection operators for each pair of electrons. This will yield N! individual products, the same as obtained by expanding a determinant whose elements are the orbital functions.

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(\mathbf{r}_1) & u_2(\mathbf{r}_1) & u_3(\mathbf{r}_1) & u_4(\mathbf{r}_1) \\ u_1(\mathbf{r}_2) & u_2(\mathbf{r}_2) & u_3(\mathbf{r}_2) & u_4(\mathbf{r}_2) \\ u_1(\mathbf{r}_3) & u_2(\mathbf{r}_3) & u_3(\mathbf{r}_3) & u_4(\mathbf{r}_3) \\ u_1(\mathbf{r}_4) & u_2(\mathbf{r}_4) & u_3(\mathbf{r}_4) & u_4(\mathbf{r}_4) \end{vmatrix} \qquad (3\text{-}5)$$

Ψ is, of course, a Slater determinant; the factor in front normalizes the function if each of the N orbitals are orthonormal functions. It is useful to realize that a Slater determinant can be formally generated by an operator applied to a simple product function, such as that of Eqn. (3-2), and that this anti-symmetrizing operator is a product involving electron pair permutation operators along with the $\sqrt{N!}$ factor. For notational ease, the product function or the leading diagonal of the determinant is often written alone, sometimes with "det" in front to mean the Slater determinant. Also, since the wavefunction is taken to properly obey the Pauli principle, the electrons are indistinguishable, and so the $\mathbf{r}_i$ coordinates are also dropped from the notation. Thus, the most compact notation would refer to the function in Eqn. (3-5) as $\Psi = |u_1 u_2 u_3 u_4|$. The normalization factor is implied.

Product wavefunctions result when the differential Schrodinger equation is separable. Within the paradigm of molecular and atomic orbitals, chemical intuition may suggest using an orbital product (or antisymmetrized orbital product) wavefunction, so the direction to follow is to find an approximation to the true Hamiltonian such that the resulting differential Schrodinger equation *is* separable. First, the Hamiltonian for a many-electron system is:

$$\hat{H} = -\sum_i^N \left(\frac{\nabla_i^2}{2} + \sum_\alpha^L \frac{Z_\alpha}{r_{i\alpha}} \right) + \frac{1}{2} \sum_{i,j\neq i} \frac{1}{r_{ij}} + V^{nuc} \qquad (3\text{-}6)$$

The summation over i (and j) is a summation over the N electrons in the system and the summation over α is a summation over the L nuclei; $r_{i\alpha}$ is an electron-nuclear distance. This Hamiltonian, specifically the "electronic Hamiltonian," is derived from the complete Hamiltonian after imposing the Born-Oppenheimer approximation in the case of molecules, or treating the nucleus as infinitely heavy in the case of atoms. For either atoms or molecules, then, the nuclei are taken to be fixed in space. The Born-Oppenheimer approximation means treating the Hamiltonian as having a parametric dependence on the nuclear positions, which may be designated, $H^{(R)}$. The choice of the nuclear spatial coordinates determines the Hamiltonian, and the electronic wavefunction must be determined for each particular choice of nuclear positions. The term V^{nuc} is just a simple constant equal to the electrostatic repulsion of the nuclear (point) charges.

The Hamiltonian in Eqn. (3-6) has been written in atomic units (a.u.). The atomic unit of energy is the *hartree* (1 a.u. = 27.21 eV = 219480 cm^{-1}, etc.) and the atomic unit of length is the *bohr* (1 a.u. = 0.529167 Angstroms). The charge of an electron in atomic units is exactly one, and Planck's constant is exactly one, as well.

An operator which collects all the pieces of Eqn. (3-6) that involve one particular electron's coordinates is the following.

$$\hat{F}_i = -\frac{\nabla_i^2}{2} - \sum_{\alpha}^{L} \frac{Z_\alpha}{r_{i\alpha}} + \sum_{j \neq i} \frac{1}{r_{ij}} \tag{3-7}$$

Though this operator represents an effective Hamiltonian for one electron, summing $\hat{F}_i$ for all electrons does not produce the Hamiltonian of the whole system. Such a sum overcounts the electron-electron repulsions. It is the electron-electron repulsions that prevent direct separability of the Schrodinger equation into equations for each electron. The self-consistent field approximation replaces the electron-electron repulsion operator in Eqn. (3-7) with an operator that represents the average field of all the other electrons and makes possible a separation of variables. Care must be taken to prevent overcounting the electron-electron repulsions in this average field approach as well.

To understand the nature of the approximate electron repulsion operator, we imagine that the orbitals, $\{\phi_1, \phi_2, \cdots\}$ (in this sense, spin-spatial products) of all the electrons except for the i^{th} electron are fixed. The i^{th} electron, then, is going to experience or move in the field of all the other electrons, though not in the physically correct "instantaneous" field where the other electrons readjust their motions due to their instantaneous interaction with electron i. It will experience the field corresponding to the charge distribution of the other electrons smeared out in space in their orbitals.

Mathematically this approximation is the replacement of the electron-electron repulsion operators by the operator which shall be designated $\hat{g}_i^{\phi}$. The superscript on this operator serves to remind one that the operator depends on the orbital functions, because this operator must give the interaction of the i^{th} electron with all the other electrons, fixed in their particular orbitals. The Fock operator, which is the effective one-electron operator in the self-consistent field approximation is,

$$\hat{F}_i^{\phi} = -\frac{\nabla_i^2}{2} - \sum_{\alpha}^{L} \frac{Z_\alpha}{r_{i\alpha}} + \hat{g}_i^{\phi} \qquad (3\text{-}8)$$

Like the operator in Eqn. (3-7), a sum of the Fock operators for all the electrons will not yield the molecular Hamiltonian because there will be an overcounting of interactions. That remains to be considered.

The subtlety of the $\hat{g}_i^{\phi}$ operators is the difficult point in a conceptual understanding of SCF. Viewing its effect from a matrix element standpoint may be helpful. Matrix elements involving $\hat{g}_i^{\phi}$ and many of the operators used in electronic structure involve *two-electron integrals*. They correspond to a double integral over the coordinates of two electrons in specific orbitals. A notational convenience is to identify a two-electron integral value with the indices of the corresponding orbitals:

$$(ij \mid kl) = \int d\tau_{r_1}\, \phi_i^*(\mathbf{r}_1) \left[\int d\tau_{r_2}\, \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_l(\mathbf{r}_2) \right] \phi_j(\mathbf{r}_1) \qquad (3\text{-}9)$$

r_{12} is the distance between electron 1 and electron 2 which depends on the position coordinates of the integration, $\mathbf{r}_1$ and $\mathbf{r}_2$. In the notation used here, i and j refer to orbital functions of the same electron coordinates, while k and l refer to the other electron coordinates. In other sources, the integral given above would be designated (ik|lj) to be consistent with the order of the orbitals in the integral. Whichever scheme is followed, it must be used consistently, because the order is important in the meaning of the integral. Since the interpretation of $\phi\phi^*$ is a probability or density function, the charge distribution function associated with the occupation of one orbital by one electron is given by the one-particle function, $\phi_i\phi_i^* = \rho_i$. The classical electrostatic interaction of two such charge densities is an integral over the geometrical space of the two distributions.

$$\iint d\tau_{r_1}\, d\tau_{r_2}\; \rho(\mathbf{r}_1)\, \rho(\mathbf{r}_2) \tag{3-10}$$

Comparing Eqns. (3-9) and (3-10) shows that the two-electron integral (ii|jj) may be associated with the simple Coulombic interaction between an electron in orbital i and an electron in orbital j. The fact that we have and need other integrals other than where the first two indices and the last two indices are the same is a consequence of quantum features. These other types of integrals do not have a simple physical basis. One special type of integral, (ij|ij), is usually referred to as an *exchange integral*, while an (ii|jj) integral is referred to as a *Coulomb integral*. It is interesting to realize that in the energy expressions for simple product wavefunctions that have not been antisymmetrized, only Coulomb integrals appear. These wavefunctions turn out to be not only conceptually pleasant, but also, they are unfortunately rather classical in their energetics.

As a tool for understanding the manipulations of two-electron integrals, Coulomb and exchange matrix operators, designated **J** and **K**, respectively, will be used. These operators are defined in terms of orbital matrix elements:

$$\left\langle \phi_k \mid \mathbf{J}^{ii} \mid \phi_l \right\rangle = (ii \mid kl) = [\mathbf{J}^{ii}]_{kl} \tag{3-11}$$

$$\left\langle \phi_k \mid \mathbf{K}^{ii} \mid \phi_l \right\rangle = (ik \mid il) = [\mathbf{K}^{ii}]_{kl} \tag{3-12}$$

One-electron integrals may be represented in a similar way through the following definition.

$$\left\langle \phi_k \mid \hat{h}_1 \mid \phi_l \right\rangle = \int d\tau_{r_1}\, \phi_k^*(\mathbf{r}_1) \left(-\frac{\nabla_1^2}{2} - \sum_{\alpha}^{L} \frac{Z_\alpha}{r_{1\alpha}} \right) \phi_l(\mathbf{r}_1) \tag{3-13}$$

$$= \mathbf{I}_{kl}$$

With these definitions, the expectation value of the Fock operators and the expectation value of the Hamiltonian can be written in a concise form. Before doing this in a general way, let us consider a specific example, the orbital wavefunction of the ground state of the helium atom.

The orbital wavefunction corresponding to a $1s^2$ electron occupancy is

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} \tag{3-14}$$

The expectation value of the energy of the helium wavefunction may be written in terms of the **I**, **J** and **K** integrals by expanding the Slater determinant in Eqn. (3-14) and then carrying out the integration over spin and spatial coordinates with each of the operators in the Hamiltonian. For instance,

$$\left\langle \Psi \,|\, \hat{h}_1 \,|\, \Psi \right\rangle = \frac{1}{2} \left\{ \begin{array}{l} \left\langle 1s\alpha(1)\, 1s\beta(2) \,|\, \hat{h}_1 \,|\, 1s\alpha(1)\, 1s\beta(2) \right\rangle \\ + \left\langle 1s\alpha(2)\, 1s\beta(1) \,|\, \hat{h}_1 \,|\, 1s\alpha(2)\, 1s\beta(1) \right\rangle \\ - \left\langle 1s\alpha(1)\, 1s\beta(2) \,|\, \hat{h}_1 \,|\, 1s\alpha(2)\, 1s\beta(1) \right\rangle \\ - \left\langle 1s\alpha(2)\, 1s\beta(1) \,|\, \hat{h}_1 \,|\, 1s\alpha(1)\, 1s\beta(2) \right\rangle \end{array} \right\}$$

$$= \frac{1}{2} \left\{ \begin{array}{l} \left\langle 1s(1) \,|\, \hat{h}_1 \,|\, 1s(1) \right\rangle \left\langle \alpha(1) \,|\, \alpha(1) \right\rangle \left\langle 1s(2) \,|\, 1s(2) \right\rangle \left\langle \beta(2) \,|\, \beta(2) \right\rangle \\ + \ldots \\ - \left\langle 1s(2) \,|\, 1s(2) \right\rangle \left\langle \alpha(2) \,|\, \beta(2) \right\rangle \left\langle 1s(1) \,|\, \hat{h}_1 \,|\, 1s(1) \right\rangle \left\langle \beta(1) \,|\, \alpha(1) \right\rangle \end{array} \right\}$$

$$= \frac{1}{2} \left\{ \mathbf{I}_{1s1s} + \mathbf{I}_{1s1s} \right\} = \mathbf{I}_{1s1s} \tag{3-15}$$

The third line of Eqn. (3-15) results from the orthonormality of the spin functions, α and β (i.e., $\left\langle \alpha \,|\, \beta \right\rangle = 0$).

In general, expectation values and matrix elements between Slater determinant wavefunctions are obtained by separation into products of integrals over the different spin and spatial coordinates as done above. With N! individual products contained in a Slater determinant, it can be a tiresome chore to evaluate a matrix element because of the $(N!)^2$ possible terms. Fortunately, this has been worked out in a general way, and compact formulas, called the *Slater-Condon rules*, give the desired expressions for any pair of Slater determinants. To itemize the Slater-Condon rules, we assume that there is a set of orthonormal spin-orbitals $\{ u_i \}$. Four determinants will be sufficient to represent all types of matrix elements, and these are the following.

$$\begin{aligned} \Phi^{(0)} &= \left| u_1 u_2 \cdots u_R \cdots u_S \cdots u_T \cdots \right| \\ \Phi^{(1)} &= \left| u_1 u_2 \cdots u_{\tilde{R}} \cdots u_S \cdots u_T \cdots \right| \\ \Phi^{(2)} &= \left| u_1 u_2 \cdots u_{\tilde{R}} \cdots u_{\tilde{S}} \cdots u_T \cdots \right| \\ \Phi^{(3)} &= \left| u_1 u_2 \cdots u_{\tilde{R}} \cdots u_{\tilde{S}} \cdots u_{\tilde{T}} \cdots \right| \end{aligned} \tag{3-16}$$

The spin-orbital $u_{\tilde{R}}$ is a spin-orbital different from u_R or any other spin-orbital in the determinant, and likewise for u_S and u_T and their substitutions. Thus, the second determinant is related to the first determinant by a single substitution of spin-orbitals; the third is related by a double substitution of spin-orbitals, and the fourth is related by a triple substitution. The Slater-Condon rules in terms of these determinants are the following.

$$\begin{aligned} \left\langle \Phi^{(0)} | H | \Phi^{(0)} \right\rangle &= \sum_R \mathbf{I}_{RR} + \frac{1}{2} \sum_{R,S} \left[(RR|SS)_{spin} - (RS|RS)_{spin} \right] \\ \left\langle \Phi^{(1)} | H | \Phi^{(0)} \right\rangle &= \mathbf{I}_{R\tilde{R}\text{-}spin} + \sum_{S \neq R} \left[(\tilde{R}R|SS)_{spin} - (\tilde{R}S|RS)_{spin} \right] \\ \left\langle \Phi^{(2)} | H | \Phi^{(0)} \right\rangle &= (\tilde{R}R|\tilde{S}S)_{spin} - (\tilde{R}S|\tilde{S}R)_{spin} \\ \left\langle \Phi^{(3)} | H | \Phi^{(0)} \right\rangle &= 0 \end{aligned} \tag{3-17}$$

The *spin* subscripts label those values of spatial integrals that must be multiplied by the appropriate result of spin integration with the corresponding spin-orbitals. The sums are over all occupied spin-orbitals. The last rule simply reflects the fact that since the Hamiltonian contains additive pieces that involve only one or only two electrons, then the matrix element between determinants that differ by more than two orbital substitutions is identically zero.

At this point, the discussion is specialized for *closed shell* wavefunctions, which are those single Slater determinants where every spatial orbital is occupied by both an α spin electron and a β spin electron. Given this, the spin integration factors in Eqn. (3-17) can be worked out in general. The expectation value for the energy of a closed shell wavefunction is found to be,

$$E = \sum_{R}^{N_{\text{occupied}}} 2\,\mathbf{I}_{RR} + \sum_{R,S} \left[2(RR|SS) - (RS|RS) \right] + V^{nuc} \qquad (3\text{-}18)$$

This expression may be rewritten in terms of the Coulomb and exchange matrix operators from Eqns. (3-11) and (3-12).

$$E = \sum_{R} 2\mathbf{I}_{RR} + \sum_{S} \left\langle \phi_R \middle| 2\mathbf{J}^{SS} - \mathbf{K}^{SS} \middle| \phi_R \right\rangle + V^{nuc} \qquad (3\text{-}19)$$

The field operator, g_i^{φ}, in its matrix form can be deduced by comparing Eqn. (3-19) with the Hamiltonian and comparing Eqns. (3-8) and (3-7). The result is that the matrix representation of this operator is

$$\sum_{S} \left(2\mathbf{J}^{SS} - \mathbf{K}^{SS} \right) \qquad (3\text{-}20)$$

The matrix representation of the Fock operator happens to be simply this term plus **I**, the one-electron operator in matrix form.

The Fock operator is used to find the optimum orbitals. The many particle differential Schrodinger equation from the exact Hamiltonian is replaced by a set of single particle differential equations where $\hat{F}_i^{o}$ in Eqn. (3-8) is the effective Hamiltonian for the ith particle. These equations are coupled because the Fock operators are dependent on their own eigenfunctions, and so their solution must come about self-consistently. A subtle aspect is that the Fock operators for the individual electrons can be made to look exactly the same, and this has already been done for the matrix form. What makes the i electron's Fock operator different from the j electron's

Fock operator is that there is no interaction with the i electron in the former and no interaction with the j electron in the latter, while there is an interaction with the j electron in the former and an interaction with the i electron in the latter. It is just a matter of an electron not experiencing its own field. However, the combination of Coulomb and exchange operators in Eqn. (3-20) eliminates this problem yet represents the effect of the field of *all* N electrons at once. The following manipulation shows why.

$$\left\langle \phi_R \,|\, 2\mathbf{J}^{RR} - \mathbf{K}^{RR} \,|\, \phi_R \right\rangle = 2(RR\,|\,RR) - (RR\,|\,RR) \qquad (3\text{-}21)$$
$$= (RR\,|\,RR)$$

The (RR|RR) integral is the term which arises from the interaction of one electron in the R orbital with the other electron in that same orbital, but the self-term has dropped out. This is clearly true for all the electrons, and so the sum of Coulomb and exchange operators represents the two-electron interaction operator for each electron.

The Hartree-Fock-Roothaan procedure, the basis set form of the Hartree-Fock integro-differential equations, begins with writing the molecular orbitals as a linear combination of functions from some chosen basis set.

$$\phi_i = \sum_\alpha c_{i\alpha}\chi_\alpha \quad \text{or} \quad \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \cdots \end{bmatrix} = \mathbf{C} \begin{bmatrix} \chi_1 \\ \chi_2 \\ \chi_3 \\ \cdots \end{bmatrix} \qquad (3\text{-}22)$$

The application of variation theory to the task of finding the coefficients in the matrix **C** leads to the condition that the Fock operator matrix must be diagonal in the basis of energy-optimum orbitals.

Diagonalization of a matrix is usually corresponds to solving an eigenvalue problem. In this case, though we seek a diagonal Fock matrix, the Fock operator is *basis-dependent* operator. If a matrix of coefficients, **C**, may be found by diagonalizing a Fock operator, but those new orbitals represented by **C** prescribe an entirely new Fock operator. The only obvious thing to do then is construct the matrix representation of the new Fock operator and diagonalize it. One continues until "self-consistency" is achieved which means that the last iteration's representation of the Fock operator is diagonal. Computational implementation of SCF implies an iterative approach which at its conclusion, does correspond to electrons moving in "average" fields of the other electrons.

The energy of the wavefunction comes from the expectation value expression using one and two-electron integrals over the self-consistent orbitals. The energy is not evaluated from the eigenvalues of the Fock matrix because of the problem of double-counting electron-electron interactions. Those eigenvalues are the *orbital energies* of the system.

The sequence of steps in an ab initio calculation of an SCF wavefunction with a basis set expansion begins with the evaluation of all one and two-electron integrals over those functions. This basis is transformed into an orthonormal basis by a diagonalization of the matrix of overlap integrals and then normalization of each transformed function. This provides the first set of orbitals for which the Fock operator matrix is constructed. The sequence of diagonalization and reconstruction of the Fock matrix is then initiated and continued until some convergence limit is achieved.

The construction of the Fock matrix is an important computational step because it involves all N^4 two-electron integrals to assemble the N^2 elements of the matrix. Diagonalization tends to be somewhat less important, often one-third of the calculational effort. It scales in computing cost as N^3. Since the details of the construction process are not presented here, it should be pointed out that the Fock matrix is most efficiently constructed from the original set of two-electron integrals over the basis functions. It is not necessary to explicitly obtain individual two-electron integrals over the different orbital sets generated in the iterative process.

Finding Correlated Wavefunctions. To find molecular orbitals or SCF wavefunctions, the basis is a set of *one-electron functions.* To find correlated wavefunctions, the basis is a set of *N-electron functions*, either Slater determinants or electron configurations. In the N-electron basis, the matrix representation of the Hamiltonian may be constructed using the Slater-Condon rules. The elements in this matrix may be used to carry out a perturbation theory analysis or a variational treatment, which implies diagonalization of the matrix. This matrix representation of the Hamiltonian is usually referred to as the *CI matrix.*

A basis of electron configurations constructed from Slater determinants may be viewed as arising from a unitary transformation of an N-electron Slater determinant basis, assuming all the Slater determinants used to construct all the configurations were included. However, the Slater determinant basis is larger than necessary. Certain of the independent linear combinations of determinants correspond to functions with different spin and symmetry. Since the Hamiltonian is a totally symmetric, and for now, a spinless operator, then configurations of differing spin/symmetry must have a zero valued Hamiltonian matrix element between them [T-6]. This means, that the CI matrix in terms of configurations may be blocked according to spin and symmetry properties. If certain spin/symmetry states are not of interest, then the use of configurations instead of Slater determinants for the N-electron basis is much more compact.

The task of constructing a Hamiltonian CI matrix or finding the same information without explicit construction of a matrix can be a massive computational undertaking. For this reason considerable effort over at least two decades has been devoted to improving how this task is performed. The spectacular results of these efforts have been incredible computational speed and efficiency and a much expanded problem size capability. If one could compare computational approaches among different problems in the physical sciences, it would likely turn out that contemporary electronic structure methods for electron correlation are among the most sophisticated.

There have been several key ideas that have led to this high level of sophistication. First is the *direct* approach which refers to an iterative treatment where individual Hamiltonian matrix elements (or equivalent quantities) are used to update or correct the wavefunction as they are computed. This avoids explicit construction of the CI matrix and it eliminates redundancy in the logic operations connected with identifying elements when they are computed and again when they are used to determine the configuration expansion coefficients. *Direct-CI* methods were first introduced in the mid 1970's [H-16,R-11:12,S-32] and immediately increased the capability for large-scale configuration expansions. Other key ideas are concerned with the process of computing the Hamiltonian matrix elements. The self-consistent electron pairs (SCEP) method that Meyer developed [M-7] organized the logic at the level of electron pairs rather than at the level of electron configurations, there being far fewer pairs than configurations. SCEP is a *matrix-oriented* approach because the electron pair organization neatly arranges intermediate quantities in matrices of dimension K, the number of basis functions. Meyer's development anticipated the vector processing capability of modern supercomputers because the operations were almost entirely matrix operations. The graphical unitary group approach (GUGA) that Shavitt worked out [S-29], following on the unitary group work of Paldus [P-19], is an elegant and highly efficient means of applying the Slater-Condon rules for direct-CI. It organizes, or really generates, the configuration list in a precise manner that greatly minimizes the redundancies that show up in the evaluation of matrix elements. GUGA has been extended and widely used, and it now stands as a mature piece of electronic structure technology. Along the way, there has been beneficial confluence with matrix-oriented techniques [M-8,J-8]; the literature on these issues has become quite extensive and beyond the scope of this volume.

As discussed earlier, coupled cluster (CC) methods provide the most extensive incorporation of electron correlation effects of contemporary methods. The literature is quite extensive, and a complete explanation is well beyond this discussion. However, the connection between CC methods and the more traditional CI picture is straightforward, and in fact, CC methods can take advantage of all the ideas mentioned in the preceding paragraph. It is useful to introduce an operator $\hat{t}$ that acts on a configuration to generate a new configuration of the same spin and symmetry but with some number of orbitals replaced by other orbitals that were unoccupied. A specific substitution operator will have subscripts identifying the orbitals that get replaced and superscripts that identify the orbitals that take their place. Thus, $\hat{t}_{ij}^{ab}\,\Phi_{SCF}$ means the doubly substituted configuration where the one *electron hole* has taken the place of one electron each in the i orbital and the j orbital of the SCF configuration, and one electron each is now found in the a and b orbitals. In a CID wavefunction, the correlating configurations would be all such double substitutions and each would have an expansion coefficient or amplitude, a_{ij}^{ab}.

$$\Psi_{CID} = \Phi_{SCF} + \sum_{a>b}\sum_{i>j} a_{ij}^{ab}\,\hat{t}_{ij}^{ab}\,\Phi_{SCF} \qquad (3\text{-}23)$$

(Intermediate normalization, where the expansion coefficient of the SCF reference configuration is kept at 1.0, is implicit in Eqn. (3-23).) This expression of the form of a CID wavefunction suggests a definition of a collective double substitution operator, $\hat{T}_2$, where the subscript identifies the level of substitution (1=single, 2=double, . . .).

$$\hat{T}_2 = \sum_{a>b} \sum_{i>j} a_{ij}^{ab} \hat{t}_{ij}^{ab} \qquad (3\text{-}24)$$

The coupled cluster approach is to use such a substitution operator exponentially.

The exponential substitution operator of CC can be expanded in a power series.

$$e^{\hat{T}} \Phi = \left(1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + \ldots \right) \Phi \qquad (3\text{-}25)$$

If $\hat{T}$ is truncated to be just $\hat{T}_2$, the resulting CCD wavefunction would differ from the CID wavefunction in Eqn. (3-23) because of the non-linear terms. The number of expansion coefficients or amplitudes that must be found, though, are the same for CID and CCD. The difference is that CCD includes higher order correlation effects.

The Density Matrix. The density function and its matrix representation are useful in finding and understanding atomic and molecular properties. A density function, ρ, which is the square of the wavefunction, $\psi\psi^*$, is a function of the coordinates of all N electrons. If the wavefunction is a linear expansion in a basis of Slater determinants, Φ_i,

$$\psi = \sum_{i}^{N} c_i \Phi_i \qquad (3\text{-}26)$$

then the density function may be represented in the basis of determinants.

$$\begin{aligned} \rho &= \left(\sum_i c_i \Phi_i \right) \left(\sum_i c_j^* \Phi_j^* \right) \\ &= \sum_{ij} c_i c_j^* \Phi_i \Phi_j^* \qquad (3\text{-}27) \\ &= \sum_{ij} \mathbf{D}_{ij} \Phi_i \Phi_j^* \end{aligned}$$

D is the matrix representation of the N-electron density function in the basis of determinants. Reduced density functions are obtained by integrating the N-electron density over the coordinates of some number of the electrons.

The one-electron density, $\rho^{(1)}$, is obtained by integrating over the coordinates of all but one electron, and is done using the Slater-Condon rules. Integration of the right-hand-side of Eqn. (3-27) will result in a contribution from each pair of determinants, i and j. This contribution to the density is given by

$$\rho_{ij}^{(1)} = \sum_{\alpha,\beta} \phi_\alpha \phi_\beta^* \left[\mathbf{d}_{ij}^{(1)} \right]_{\alpha\beta} \tag{3-28}$$

where $\mathbf{d}_{ij}^{(1)}$ is the *transition density* matrix for the i and j labelled Slater determinants in the basis of molecular spin-orbitals $\{\phi\}$. If the determinants differ by more than one spin orbital, this density matrix is zero. If not, then the following applies.

$$\left[\mathbf{d}_{ij}^{(1)} \right]_{\alpha\beta} = \delta_{\alpha\beta}\,\delta_{ij} + \delta_{\alpha\kappa}\,\delta_{\beta\lambda}\,(1 - \delta_{ij}) \tag{3-29}$$

κ and λ label the two spin-orbitals which may be different in the two Slater determinants.

Since the molecular orbitals are expansions over basis functions (atomic orbitals), the density function $\phi_\alpha\ \phi_\beta^*$ may be represented by a matrix that refers to the atomic orbital set.

$$\begin{aligned} \phi_\alpha \phi_\beta^* &= \left(\sum_r C_{\alpha r} \chi_r \right) \left(\sum_s C_{\beta s}^* \chi_s^* \right) \\ &= \sum_{r,s} [\, \Delta_{\alpha\beta} \,]_{rs}\ \chi_r \chi_s^* \end{aligned} \tag{3-30}$$

With these definitions, the one-electron density function can be expressed in terms of the elements of the three matrix representations, **D**, **d** and Δ, and the products of the basis functions, $\chi_r\,\chi_s$.

The one-electron density for an SCF wavefunction may be regarded as a special case of the above analysis. It is an "expansion" over only one configuration, and so **D** has only one element and the value of that element is 1.0. There is only one **d** matrix and from Eqn. (3-29), it can be seen that it will be a diagonal matrix, with 1.0 for each occupied spin-orbital and zero for each unoccupied spin orbital. Thus, the one-electron density function for an SCF or single-determinant is,

$$\rho^{(1)} = \sum_{\alpha}^{\text{occupied}} [\mathbf{d}]_{\alpha\alpha} \sum_{r,s} [\, \Delta_{\alpha\alpha}]_{rs}\, \chi_r \chi_s^* \tag{3-31}$$

If this expression is applied to a closed shell determinant, and if integration is carried out over the spin coordinates, then a very simple expression for the spin-less one-electron density may be written.

$$\tilde{\rho}^{(1)} = 2 \sum_{r,s} \mathbf{R}_{rs} \chi_r \chi_s^* \tag{3-32}$$

where

$$\mathbf{R}_{rs} = \sum_{\alpha}^{\text{occupied}} C_{\alpha r} C_{\beta s}^* \tag{3-33}$$

Chapter Four

CALCULATION OF MOLECULAR STRUCTURE

The proving grounds for ideas concerning how electronic factors contribute to determining molecular structure and molecular properties are the small and medium sized molecules. Small means different things in the many areas of molecular science, and here it means molecules whose structures can be examined to fine detail with spectroscopic methods. Two kinds of understanding serve to connect electronic factors with molecular structure. The first kind is qualitative and is what one normally considers as the chemical concepts of valence bonds, hybrid orbitals, and so on. The second kind of connective understanding is more quantitative and might be labelled as quantum molecular engineering. This is the understanding of how basis set choices and electron correlation affect the theoretical predictions and how levels of treatment should be selected for a particular problem. That is the focus of this chapter, though the qualitative concepts are inextricably tied-in.

Core and Valence Basis Sets. The smallest, common type of atom-centered basis is the minimum basis set. In one sense, this can seem to be adequate since it would be possible to construct a minimum basis set, by way of extensive contraction, so as to give a near Hartree-Fock limit description of an isolated atom. In another sense, though, such a seemingly high-quality basis, along with any other MBS, has a limited amount of flexibility to describe the changes in the electronic wavefunction were the atom made a constituent of a molecule. For elements in the right column of the periodic table, an MBS affords no capability whatsoever to describe weak or strong interaction. The MBS fixes the energy of any rare gas atom since all the orbitals are occupied and since the energy is invariant to any mixing of fully occupied orbitals.

Empty or virtual orbitals will be found in the minimum basis sets only of elements not in the the right-most column of the periodic table. These virtual orbitals are few in number yet must provide all the intra-atomic flexibility for describing the formation of covalent bonding orbitals and anti-bonding orbitals. Because of this limited functional flexibility, minimum basis set calculations often show manifestations of *basis set superposition error* (BSSE). BSSE refers to vacant orbitals on one atomic center being used to make up for a basis set deficiency on a neighboring atom. The vacant orbitals on one atom serve as off-center basis functions for the neighbor atom, and they tend to be populated if the atom-centered set of functions can not provide like flexibility. Typical consequences of BSSE with minimum basis sets are bond lengths that are too short and bond strengths that are too strong. Both result because two atoms may be "attracted" to each other's vacant functions beyond the real chemical attraction. Worse still is that the nature of BSSE effects may vary. The trends can not be relied on. Because a deficiency may come into play in a number of ways, it tends to be that the smaller the basis the broader the error range.

Boys and Bernardi [B-12] established a very useful idea for dealing with the problems that arise through BSSE. They suggested the idea of a *counterpoise correction* to the normally computed energy. In studying the AB diatomic system, the energy would be computed first in the usual way. Then the energy would be computed leaving out the electrons of B and leaving out the B nucleus. The difference between this energy and the energy of A alone, with no nearby functions, is taken to be the "attraction" of A for the functions of B. A like calculation on B with the functions of A present just as they would be in the AB molecule, but no A nucleus or electrons, is taken as the "attraction" of B for the functions on A. Subtracting these two estimates of the artificial attraction from the directly computed bond strength was suggested as a more realistic value for the bond strength.

Many variations of the counterpoise correction scheme have been reported. One reason why there should be many is that the counterpoise correction is only a estimate. It is a most reasonable estimate usually, and it works nicely in certain circumstances. However, it provides neither an upper nor lower bound of the extent of BSSE. Thus, it is much better used as a litmus test for detecting basis set deficiency rather than for improving the reliability of a calculational result. Relatively large basis set superposition effects may be anticipated for minimum basis sets versus larger sets, and this is especially true if the basis has few primitives or in some way isn't well-suited for isolated atoms.

Enlargement of the basis set from minimum to double zeta is really quite significant in terms of the flexibility for electronic readjustment. There being twice as many basis functions in the double zeta set as in the minimum set, at least half the orbitals must be vacant. Most often, use of a double zeta basis improves bond length predictions. This is entirely the consequence of the improved flexibility in the basis, the flexibility being used to make bonding and anti-bonding orbitals of better shape and size. TABLE 4.1 gives a comparison of certain structural predictions made with minimum and double zeta basis sets. With minimum basis sets, bond lengths are usually reliable to 0.05 Angstroms, though better for bonds to hydrogen atoms, whereas with double zeta bases, the reliability for molecules composed of first row elements is generally better than 0.02 Angstroms.

The number of basis functions and the number of primitive Gaussian functions used to make up the basis functions both affect quality of the results. For core orbitals, heavy contraction of the primitive functions is quite appropriate. Atomic core functions are affected indirectly, and then only slightly, by chemical bonding. Functional flexibility is not as necessary as for valence orbitals. However, the field of the core electrons has a significant impact on the wavefunctions for the valence electrons, and so the core should be well-described in the isolated atom limit. This suggests contracting a large number of primitive functions together into just a few core functions. For example, in Dunning's double-zeta contractions [D-13:14] of Huzinaga's optimized primitive sets [H-2], the nine s-type Gaussians for carbon, nitrogen, oxygen and fluorine are contracted into four s-type basis functions by making a linear combination of the six with the largest exponents and leaving the remaining three uncontracted. The six-function contraction is essentially a 1s atomic orbital.

Since flexibility is needed in the valence region more than in the core region of an atomic basis set, some computational economy is achieved by using split valence basis sets. The core set of functions is strictly minimum, but the valence functions are double or triple zeta. The 4-31G basis sets for first row atoms are of this type, and bond lengths predictions with these bases are included with the values in TABLE 4.1.

The usual means for constructing basis sets is to find optimum uncontracted functions, i.e., Gaussian exponents, for an isolated atom and then choose a contraction scheme. In terms of the quality of the final predictions, there is some "coupling" between the choice of primitives (exponents) and the contraction. With increasing experience, basis sets are being made more concise without serious effect on results. In place of 4-31G bases, 3-21G bases are now widely employed. The 3-21G sets have less primitives which results in a small computational savings, and they have been shown to give structural predictions comparable to 4-31G sets [B-13].

TABLE 4.1

Structural predictions at the SCF level with STO-3G minimum basis sets, 4-31G, DZ and TZ basis sets. Bond lengths, R, are in Angstroms and bond angles are in degrees. STO-3G and 4-31G results are those of Lathan [L-8:9] and Ditchfield [D-12] and coworkers.

Molecular and Parameter		*STO-3G*	*4-31G*	*DZ*	*TZ*	*Expt.*
H_2			0.730			0.742
CH_4		1.083	1.081	1.087	1.085	1.085
NH_3	R(NH)	1.033	0.991	0.995		1.012
	∠(HNH)	104.2	115.8	116.3		106.7
H_2O	R(OH)	0.990	0.951	0.951	0.951	0.957
	∠(HOH)			112.3	112.0	105.2
HF				0.920	0.920	0.917
HCN	R(CN)	1.153	1.140	1.151	1.137	1.154
	R(HC)	1.070	1.051	1.055	1.054	1.063
CO		1.148	1.128	1.138	1.124	1.128
N_2		1.134	1.0085	1.100	1.083	1.094
F_2		1.315		1.399	1.384	1.418
HCCH	R(CC)	1.168	1.190	1.201		1.203
	R(HC)	1.065	1.051	1.054		1.061
H_2CCH_2	R(CC)	1.306	1.316			1.330
	R(CH)	1.082	1.073			1.076
	∠(HCH)	115.4	116.0			116.6
H_2CO	R(CO)	1.217	1.206	1.217		1.213
	R(HC)	1.101	1.081	1.083		1.101
	∠(HCH)	114.5	116.4	116.9		116.5
CH_3F	R(CF)	1.371				1.332
	R(CH)	1.097	1.076			
	∠(HCH)	108.3	110.7			109.9

As may be apparent from the various basis set possibilities that have been mentioned, not all DZ sets, or all of any other type, are precisely equivalent in performance. TABLE 4.1 includes results with different DZ-quality basis sets. The structural predictions do show some differences. However, the sizes of those differences are small and that makes it appropriate to regard the zeta-multiple as the overall or predominant factor in basis quality.

Enlarging a basis set to triple zeta makes further changes in structural predictions and certain examples are included in the results in TABLE 4.1. However, in general these results show that triple zeta bases do not necessarily improve reliability relative to the double zeta sets, at least for light atom species. The triple zeta flexibility relative to double zeta has only little to do with structural parameters for the most part.

When working at the SCF level, it is possible for basis set enlargement to worsen the accuracy of the structural predictions. To understand this, consider the approach to the Hartree-Fock limit. Given the complete basis set flexibility at the Hartree-Fock limit, the SCF approximation will be unchecked in its intrinsic exaggeration of the electron density in most bonding regions of a molecule. This is because of the neglect of instantaneous electron-electron repulsions at the SCF level. The exaggeration of electron-electron density will tend to pull the positively charged nuclei closer together, just as the electrons are denser in the regions between nuclei. That is a straightforward electrostatic effect. Thus, at the Hartree-Fock limit, bond lengths are expected to be too short, perhaps by several hundreths of an Angstrom, and this is often the case. Triple-zeta basis sets turn out to be approaching the Hartree-Fock limit relative to double zeta sets just enough so that this underestimation of bond lengths is sometimes found. The reliability, on average, may actually be worse with basis sets beyond double zeta as long as electron correlation effects are neglected.

Polarization Functions. The addition of polarization functions to a basis usually makes a noticeable difference in calculated structures. The polarization functions may contribute only slightly to the optimum form of the valence molecular orbitals, but that contribution is important in terms of orientational flexibility. In usual qualitative terms, an sp^2 hybrid can be made to point at slightly different angles by fractionally becoming an spd hybrid. In quantitative terms, atomic polarization functions on first row elements will affect bond angles by two to three degrees, typically, with up to five degrees not unlikely.

FIGURE 4.1 is a density difference plot [P-5] of N_2H_2 that illustrates the effect of polarization functions. The electron density of the molecule was computed from the SCF wavefunction with a double zeta basis and then with a polarized double zeta basis. The density amplitudes were subtracted and the plot in FIGURE 4.1 is of the contours of the difference. The changes are very small relative to the total density, but the curving path of the "hills" and "valleys" of this contour plot suggests how polarization functions can have an orientational effect on the bonding structure. The most obvious feature of FIGURE 4.1 is that the hills, the regions where electron density is built up because of the inclusion of polarization functions, are between bonds. The polarization functions are contributing to the exaggeration of the electron density in the bonding regions, and this is sharply noticed in the bond length contractions in going from DZ to DZP basis sets, as shown by the values in TABLE 4.2.

Basis sets may be augmented or extended as desired. Some choices are reasonable steps at improvement, and some are not. Polarization functions augmenting a minimum basis set, for instance, may be criticized because the polarization functions' role may end up being partly to correct an MBS valence deficiency. A lowering of the total electronic energy upon some particular basis set augmentation may not always serve as justification for that augmentation. When the goal is to obtain molecular properties that are influenced by the electron density in the fringe regions of a molecule, the proper basis augmentation (i.e., diffuse functions) is likely to have little effect on the total energy or the structural parameters. Generally, a basis set may be expanded, built up, or augmented by systematic consideration of the spatial regions around each atom that require the greatest flexibility in the basis in order to yield an accurate representation of the electron distribution. There is no reason to view basis sets as arbitrary or random, and little point to analyze their "randomness." All in all, many well-tested basis sets exist and these can be used with great confidence. Further elaboration of these points and other useful information about basis set selection has been given recently in a review by Davidson and Feller [D-20].

Electron correlation. Electron correlation plays an important role in making very critical predictions of molecular structure. Correlation effects undo exaggerations in the electron density due to the SCF approximation. In

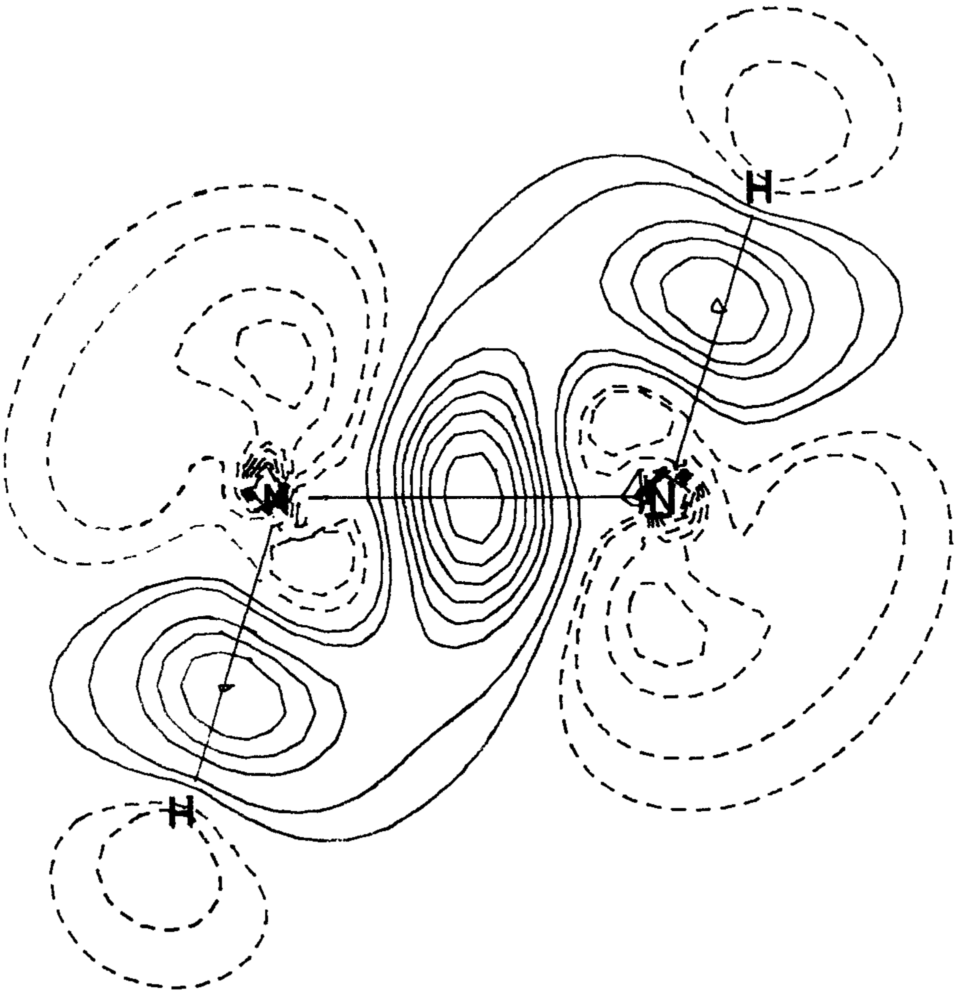


FIGURE 4.1

Density difference contour plot showing the effect of polarization functions on the electron distribution. The molecule is trans-diimide and the plot is from the calculations of Parsons and Dykstra [P-5]. The solid lines are contours in the regions where the computed electron density at the SCF level is increased upon enlarging the basis set from DZ to DZP. The dashed lines are the negative contours. With the DZP basis, density is clearly seen to increase in the bonding regions. The extent of this increase is small, on the order of a tenth of an electron when integrated over the volume. This increase in density in the bonding regions helps account for the fact that the NN bond length is shorter at the DZP/SCF level than at the DZ/SCF level (see TABLE 4.2). The increased amount of negative charge holds the positive nuclei closer. This plot also shows diminished density along lines that roughly bisect the N-N-H angles. The fractional d-hybridization that becomes possible with polarization functions twists or reorients density around the atoms and this is manifested in the values of the calculated bond angles.

TABLE 4.2

Calculated structural parameters of N_2H_2 and C_2H_2. All calculations were at the SCF level. Bond lengths are in Angstroms and bond angles are in degrees.

R(NN/CC)	*R(NH/CH)*	*Angle(NNH/CCH)*	*Basis Set*
AMINONITRENE			
1.27	1.04	118	STO-3G [B-14:15]
1.260	1.004	116	DZ [P-5]
1.249	1.002	116	TZ [P-5]
1.224	1.012	116	DZP [P-5]
1.215	1.011	116	TZP [P-5]
TRANS-DIIMIDE			
1.277	1.127	104	MBS [S-10]
1.242	1.015	111	DZ [P-5]
1.234	1.013	110	TZ [P-5]
1.222	1.016	108	DZP [P-5]
1.215	1.013	108	TZP [P-5]
1.252	1.028	107	expt. [C-11]
CIS-DIIMIDE			
1.242	1.023	116	DZ [P-5]
1.234	1.023	116	TZ [P-5]
1.221	1.019	113	DZP [P-5]
1.215	1.017	113	TZP [P-5]
ACETYLENE			
1.201	1.054		DZ [D-15]
1.191	1.060		DZP [D-15]
1.203	1.060		expt. [H-7]
VINYLIDENE			
1.314	1.076	121	DZ [D-15]
1.300	1.079	120	DZP [D-15]

many cases, electron correlation will diminish the density in bonding regions. This tends to put the equilibrium separation of the atoms at a greater distance which means that correlation lengthens bonds. With trans-diimide continuing as the primary example system, FIGURE 4.2 reveals the correlation effect on the density. This plot is of the contours of the difference in electron density between a DZP correlated wavefunction and a DZP/SCF wavefunction. There is a clear, but small decrease in the density between each pair of

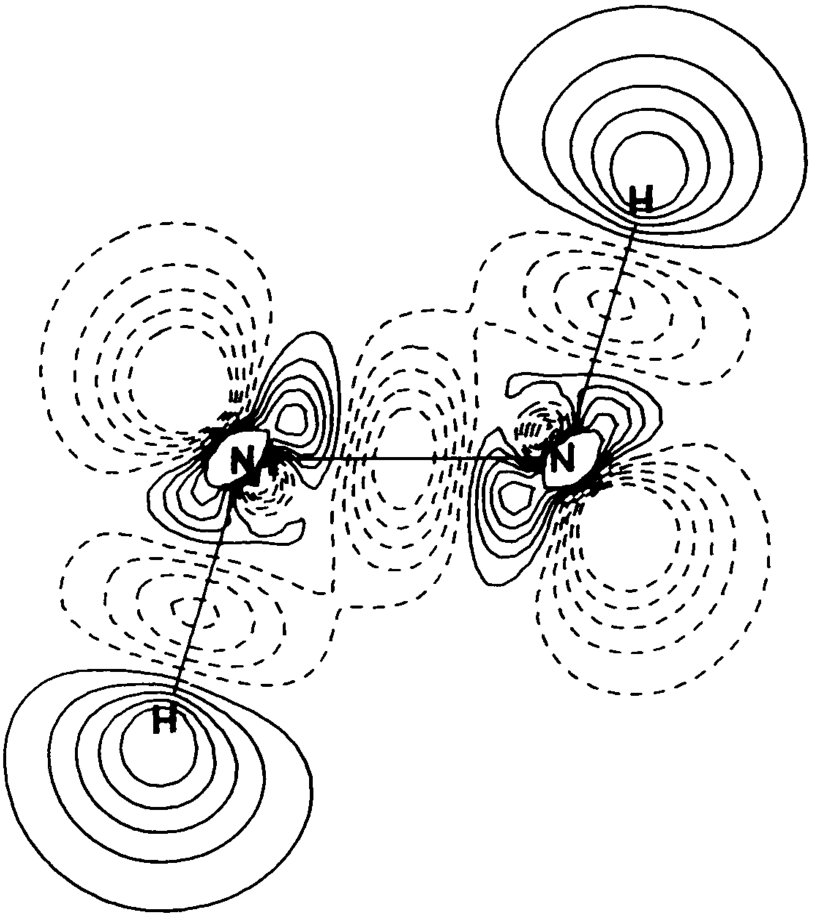


FIGURE 4.2

Density difference plot showing the effect of electron correlation on the one-electron density [P-5] of trans-diimide. The one-electron density function at the SCF level was subtracted from the one-electron density function at the CISD level. The solid lines are contours of increased density due to correlation, while the dashed lines are the corresponding contours of diminished density.

atoms. FIGURE 4.3 shows the manifestation of this type of change on the computed equilibrium bond lengths. Correlation may also affect predictions of bond angles, typically by a degree or so, though for such small differences, general trends are difficult to establish.

The computationally simplest electron correlation treatment is second order MBPT or as it is also known, MP2. TABLE 4.3 gives the predicted bond lengths for a number of small molecules at this and other correlated levels. In some systems, MP2 may overshoot the correlation effect and give structural predictions much less reliable than more complete levels of treatment. It may be less reliable than SCF in certain situations. Of the molecules listed in TABLE 4.3, MP2 does give a good accounting of the change in a bond length prediction caused by correlation, though there is a definite overshoot in comparison with CISD results. CISD level results are more similar to third

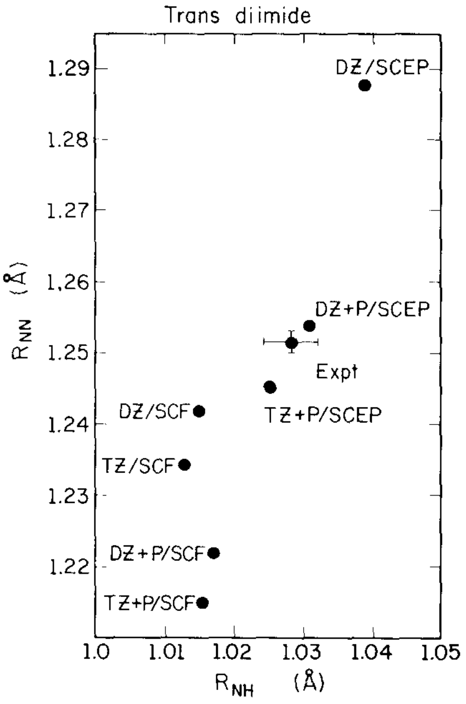


FIGURE 4.3

Optimized equilibrium bond lengths of trans-diimide [P-5]. SCEP, self-consistent electron pairs [M-7:8,D-16] is a CISD level treatment.

order MBPT or MP3 results. With DZP or like-quality basis sets, the accuracy of these levels of treatment is such that bond lengths of molecules composed of first row atoms are almost always determined to better than 0.02 Angstroms.

As more correlation effects are incorporated through expansion of the list of correlating configurations, further bond lengthening may result. Calculational results in TABLE 4.3 contrast the bond lengthening from including pair correlations at the CISD level and further bond lengthening from including higher order correlations at a coupled cluster level. The differences are rather small, but they are important refinements if bond lengths need to be known to better than 0.01 Angstroms. It should be recalled that the coupled cluster treatment goes beyond CISD by bringing in unlinked substitutions of higher order. In this sense, CCD or ACCD predictions should be very similar to CISDQ predictions.

In a rough sense, correlation and polarization basis function effects are opposite for bond length predictions. FIGURES 4.1 and 4.2 have qualitatively opposite contour profiles, especially along the bond axes. Thus, while a DZP/CISD structure determination may be extremely good, it is not surprising that a DZ/SCF prediction is almost as good. The accuracy of the DZ/SCF result is a consequence of simultaneously neglecting two features which tend to play opposing roles in bond length predictions. In practice, this means that there are organized ways of improving the accuracy of a prediction through improving the level of calculation. Going to the Hartree-Fock limit without any correlation effects tends to give unsatisfactory results, and likewise, extensive treatment of electron correlation with tiny basis sets is most often unsatisfactory. A balanced improvement in basis set size and electron correlation effects is the best way to obtain the highest accuracy. DZ/SCF is perhaps the first point of optimum balance, and the results in TABLE 4.1 offer good reason to accept this. Polarizing the basis should be balanced with including the dominant or direct correlation effects, such as included at a CISD level. A step beyond that, such as TZ2P bases and some incorporation of higher order correlation effects, will yield even better accuracy in general, and the lingering calculational influences on structure determinations tend to be down to the thousandth Angstrom level.

There are certainly chemical problems that require structural predictions to a thousandth of an Angstrom, and even better. The understanding of how to get just about to that point is clear. Large, well-chosen basis sets are the first ingredient in the calculation. The second should be a most exhaustive treatment of electron correlation. So far, coupled cluster treatments have provided the widest range of results of that kind. The accuracy of these results suggests that coupled cluster technology can provide the extensive treatment of electron correlation needed to make structural predictions that are consistently accurate to about a thousandth of

TABLE 4.3

The changes in equilibrium bond lengths (in Angstroms) and in bond angles (in degrees) due to electron correlation are given for several small molecules. Correlation typically increases bond length predictions and this is seen for the cases shown here. To identify the correlation effects arising from higher level treatment, the changes from some comparison lower level should be subtracted. Bond lengths, R, are in Angstroms and bond angles are in degrees.

Molecule, Basis Set, and Parameter			*Correlation Effect (Change in Value Relative to SCF)*		
			MP2	*CISD*	*CCSD /ACCDS*
H_2	TZ2P			0.0082	
HF	DZ		0.0311		
	DZP		0.0155	0.0127	
	QZ3P [L-18]			0.0197	0.0226
CH_4	DZ		0.0180		
CO	DZ		0.0518		
	DZP		0.0400	0.0239	
	[7s5p3d] [L-18]				
N_2	DZ		0.0826		
	DZP		0.0904	0.0515	
F_2	DZ		0.1085		
	[7s3p2d] [L-18]				0.0889
cis-HFC=CFH		R_{CF}	0.026		
	DZP [G-11]	R_{CC}	0.026		
		R_{CH}	0.010		
		$\angle^{o}_{FCC}$	-0.3		
		$\angle^{o}_{HCC}$	-0.1		

an Angstrom. More quantitative information needs to be learned about subtle basis set effects in the exhaustive correlation treatments. More studies of molecular structure are needed at the very high levels.

Structures of Weak Complexes. Species that are held together with at least one weak bond, one that is not a true chemical bond, are challenging systems both for calculational investigation and for spectroscopic determination of structures. On both fronts there has been tremendous progress in the last several years. There are numerous complexes whose structures have been quantitatively established form experimental results, and there are quite a number of high-level calculations reported that compare nicely with experimental results. There are also a few interesting cases where experiment and theory are disparate in their pictures of the complexes. Those cases will probably prove quite important in advancing our understanding of the electronic structure and dynamics of weak complexes.

Typically, what is obtained in a calculational study of a weakly bound complex starts with structural information, the usual bond lengths and angles. However, as discussed in Chapter Two, the physical significance of the intermolecular equilibrium structural parameters is not what it is for a rigid molecule. The weak complex is a floppy creature, and what calculations do best to elucidate is the region of shallowness on the potential energy surface around the equilibrium. The equilibrium is a not-too-sharply distinguished point in the region. Since vibrational excursions can lead a floppy system through a large region of coordinate space, the comparison of a calculated equilibrium structure with a spectroscopically determined structure can be a difficult comparison to make. It is probably better to regard the complex's "structure" as being characterized by a vicinity in coordinate space about the equilibrium and by the flatness of the surface there. Even so, specific values for structural parameters are still of interest.

Though species can be found that continuously span the energetic range of bond strengths, it is helpful for discussion to distinguish with an energetic cut-off "weak" and also "very weak" complexes. A common notion is that a "weak" bond is one whose strength is up to about ten kcal/mol. A bond strength of not more than two kcal/mol will be referred to here as very weak. Often the very weak complexes involve non-polar, closed shell atoms or molecules and certain interactions in stronger complexes are absent.

There are many electronic factors that may contribute to a weak or very weak bond. Unraveling these effects calls for close scrutiny of the calculational treatment because there may be a very close balance between them [C-13], and that balance might be shifted by normally minor deficiencies in the calculation. From a rapidly growing body of *ab initio* calculations on weakly bonded systems, several things can be recognized. First, there now exists a collection of system specific structural data and properties for many complexes form many levels of theoretical treatment. This is of potential use both in the spectroscopic investigation of the complexes and in theoretical work on the dynamics of those systems. It also provides the "engineering" information on how to carry out calculations on weakly bound systems to a meaningful degree of accuracy. Finally, there has emerged certain general ideas about how hydrogen bonds and other types of weak bonds are related to the electronic properties of the bonding partners. This is really the heart of the theoretical pursuit of these systems.

A general trend for weak and very weak complexes is that the weak bonds tend to shorten with increasing incorporation of electron correlation effects, the reverse of the typical situation for chemical bonds. As correlation effects are taken into account, weak bonds often get stronger as well as shorter. Contributing to the bond strengths are *dispersion* forces, which are attractive and which only arise with the incorporation of intermolecular electron correlation. For He_2, one of the weakest systems known, there is no attraction, no minimum in the potential energy curve, until correlation effects are included to account for dispersion.

Basis set improvement does not seem to show a consistent trend in the determinations of weak bond lengths. Some improvement, such as that required to allow charge distributions to polarize in the presence of a bonding partner may yield a much improved description, and one that corresponds to a stronger and possibly shorter bond. However, basis set improvement can also lead to a lengthening and weakening in the calculated strength of a weak bond, especially if the improvement undoes basis set superposition error. In such a case the basis set enlargement would be improving the description of the bonding partners' valence electronic structure and contributing only in this indirect way to describing the weak bond.

Calculational results in TABLE 4.4 obtained by Benzel [B-16] for the complexes NN-HF and OC-HF illustrate certain of the effects of basis set selection and correlation. The calculated equilibrium bond lengths for the hydrogen bonds are given, and at the SCF level, basis set enlargement leads to a lengthening mostly. A slight shortening of the bond length is found when the valence set contraction of the 2p-functions is relaxed form three basis functions to four (TZ to TZ' in TABLE 4.4). Correlation effects tend to shorten the bonds. From the last calculation in the table, TZP/ACCD, one sees that the basis set effects are about the same at this correlated level as at the SCF level. For NN-HF, the hydrogen bond is predicted to be 0.105 Angstroms longer at the TZP/SCF level than at the DZP/SCF level, while it is predicted to be 0.111 Angstroms longer at the TZP/ACCD level than at the DZP/ACCD level. This suggests a sort of additivity of correlation effects and the basis enlargement effects of going from DZ to TZ. To some degree, that holds in other systems. However, this additivity may be misleading, for it does not imply that correlation effects are always well determined with the smaller of those bases. For instance, the dissociation energy in cm^{-1} of NN-HF is 737 at the DZP/SCF level, 540 at the TZP/SCF level, 1188 at the DZP/ACCD level and 795 at the TZP/ACCD level. That is, the step up from a DZ to a TZ valence basis reduces the binding energy about 200 cm^{-1} at the SCF level, but 400 cm^{-1} at the correlated ACCD level. In other words, the relative correlation effect from the DZ to TZ basis improvement is about 200 cm^{-1}, a sizable amount relative to the total bond strength.

TABLE 4.4

Calculated equilibrium hydrogen bond lengths for NN-HF and OC-HF [B-16]. Values are in Angstroms and are measured from fluorine to the nearest center on the bonding partner.

R (NN-HF)	*R* (OC-HF)	*Calculation Level*
2.951	3.122	DZ/SCF
3.981	3.169	DZP/SCF
3.186	3.211	TZP/SCF
3.182	3.209	TZ'P/SCF
2.964	3.074	DZP/CISD
2.958	3.076	DZP/ACCD
3.069	3.098	TZP/ACCD

As an aside, one may note that for NN-HF the DZP/SCF binding energy and the TZP/ACCD binding energy were rather close. For OC-HF, this is again the case. The binding energy at the DZP/SCF level is 1031 cm^{-1} and at the TZP/ACCD level it is 1066 cm^{-1} [B-16]. It does seem that there is a cancellation of effects at the DZP/SCF level that makes it a better preliminary examination level than TZP/SCF or DZP/CI. The cancellation, however, is that of significant BSSE, which increases attractiveness, and the neglect of electron correlation, which otherwise would do that job.

The counterpoise correction scheme for BSSE of Boys and Bernardi [B-12], discussed earlier in this chapter, is important as a concept in understanding how structures of weak complexes may be accurately calculated. A variation of it that seems most helpful in the study of weakly bound complexes, where BSSE is potentially a big hazard, has been presented by Loushin et al. [L-12:13]. This form of counterpoise correction is especially concerned with the mutual polarization of complexed partners, and so, it has been designated "pcc" (*polarization counterpoise correction*). It is apparent from many calculations of weak and hydrogen bonded complexes that a primary electronic structure change upon complexation is simply the mutual polarization of the charge distributions of the interacting species. In the standard cc method, the concern is only whether the available basis functions of species B in the A-B complex may augment those being used to describe the valence electronic structure of A, and vice versa. In a hydrogen bonded complex, such as NN-HF, the separation distance is large by chemical bonding standards, and so this is not likely to be very noticeable. In fact, Schwenke and Truhlar [S-19] showed that standard cc fails to evaluate how really big the BSSE is. They used $(HF)_2$ as their model system, and this was also used in the study by Loushin et al.* A reason why standard cc underestimates the extent of BSSE is that in the A-B complex, the functions of B may be serving to describe *polarized* A, and vice versa, but the cc evaluation takes no account of this polarization. As discussed in Chapter Seven, different functions and generally more flexible basis sets are required to describe the electronic wavefunction of a polarized molecule than to describe the unperturbed electronic structure.

The pcc idea is to simulate the polarization effect of a bonding partner through a ghost field and/or field gradient and then to test the "attraction" for the bonding partner's basis functions. In carrying out such calculations, the energy of monomer A in the presence of a ghost field of B is computed with and without the functions of B being near. The difference in energy is the artificial attraction of polarized A for the functions of B. This must be done the other way, too, so as to obtain the artificial attraction of polarized B for the functions on A. Loushin et al. showed that this pcc approach gives a larger value for BSSE than does standard cc and it may show better convergence to large basis set limits. Values selected form those results are given in TABLE 4.5. The size of the basis sets ranged from 11 functions with the 431G basis to 63 functions with the triply polarized basis designated Ext.'3P. Except for the "Ext." sets, the valence bases were either standard GAUSSIAN80 sets [D-12], or Dunning contractions [D-13:14] of Huzinaga primitive sets [H-2]. The valence part of the Ext.2P set is a basis due to Van Duijneveldt and that reported by Rebentrost and Lester [R-10], while the Ext.'3P set is based on that of Werner and Rosmus [W-7].

BSSE that shows up in the energy of a weak complex is also likely to be manifested in the prediction of the equilibrium lengths of weak bonds. If BSSE artificially strengthens a weak bond, it will also tend to shorten the weak bond. The size of such effects may be large, even one or two tenths of an Angstrom.

Ideally, pcc or some other correction scheme could be used to bring basis set results up to the quality of large basis sets. A minimum in the corrected energies could be sought so as to find equilibrium lengths of weak bonds. Unfortunately, this is a risky calculational process. The counterpoise correction in any form is an approximation of the error, and neither pcc nor cc can be relied on to consistently overestimate or to consistently underestimate BSSE. As mentioned earlier, counterpoise corrections are useful tests of assessing the extent of BSSE among basis set candidates for a particular study, and are best used to select a good basis rather than to correct a deficient one.

Polarization functions have an important impact on the calculated energies and structures of hydrogen bonded complexes. This has to with how they improve the description of the constituent monomers and with how they describe the mutual charge polarization. For the latter, diffuse polarization functions are most important, and certain of the results in TABLE 4.5 show some of the smallest effects of pcc with the multiply polarized bases which included diffuse functions. Latajka and Scheiner [L-14:15,S-20,S-33] have demonstrated in a number of calculations on weak complexes that doubly polarized bases are effective in studying hydrogen bonding with one of the polarization sets being diffuse.

TABLE 4.5

Comparison of SCF and also ACCD interaction energies for two structures of $(HF)_2$ relative to separated monomers [L-12:13]. The two structures were an equilibrium (**1**) and a linear (**2**) arrangement. Energies are in kcal/mol. E refers to SCF or to ACCD values without correction, E(cc) means with standard counterpoise correction, and E(pcc) is with polarization counterpoise correction. An interesting comparison is between the small basis SCF and ACCD results for Structure **1**. Without correction, correlation effects seem quite sizable, amounting to around one kcal. However, after cc and pcc correction, the correlation effects are reduced quite significantly.

Basis Set	*Structure* **1**			*Structure* **2**		
	E	*E(cc)*	*E(pcc)*	*E*	*E(cc)*	*E(pcc)*
SCF Results:						
431G	-8.36	-6.19	-5.67	11.22	15.59	18.02
DZ	-6.55	-5.92	-5.72	12.63	13.92	14.98
TZ	-5.97	-5.43	-5.41	12.61	14.16	14.91
631G*	-5.91	-4.34	-3.83	17.24	21.07	23.61
DZP	-4.29	-3.81	-3.54	17.17	18.02	18.74
6311G**	-4.59	-3.66	-3.33	16.61	18.08	18.84
TZP	-3.90	-3.57	-3.47	17.40	18.05	18.76
TZ2P	-3.45	-3.31	-3.20	17.96	18.38	19.23
Ext.2P	-3.41	-3.30	-3.22	18.12	18.40	19.16
Ext.'3P	-3.17	-3.13	-3.03	18.47	18.64	19.26
ACCD Results:						
431G	-9.12	-6.23	-5.54	13.46	19.08	21.73
DZ	-7.34	-6.13	-5.81	15.05	17.72	18.87
631G*	-7.39	-4.99	-4.33	16.82	22.28	24.97
DZP	-4.69	-3.97	-3.83	16.63	18.81	19.64
TZ2P	-4.23	-3.73	-3.59	17.35	19.22	20.23

A systematic study of three dimer complexes using split-valence bases with several augmentations was carried out by Del Bene [D-31]. A general trend of diminishment of complex stabilization energy with increasing basis augmentation is seen in these calculations. The most important basis enhancement in this study was reported to be diffuse functions on non-hydrogen atoms.

Pcc results in TABLE 4.5 reveal that incompletely polarized basis sets, such as 431G* or 631G*, can exaggerate BSSE in hydrogen bonded complexes because of their imbalance in basis quality between hydrogen atoms and other atomic centers. Quite simply, good hydrogen bases are need to study hydrogen bonding. Another aspect of the results in TABLE 4.5 is that there is little difference between correlated and SCF results for the *incremental* pcc, that beyond cc. For polarized basis sets, the correlation difference in the incremental polarization counterpoise correction amounts to 0.1 to 0.2 kcal/mol. This says that the mutual polarization of the monomers is not dependent or not strongly connected to the correlation effects. On the other hand, there are more noticeable correlation versus SCF differences for cc, with cc being greater for correlated than for uncorrelated energies. Therefore, it is fair to expect that an SCF level check of BSSE will show less than an evaluation of BSSE at a correlated level.

Heavy Elements. Description of small molecules containing first row atoms (e.g. carbon, nitrogen, oxygen, etc.) tends to be simpler than description of molecules containing heavier elements. For instance, even though neither fluorine nor chlorine atoms have formal 3d shell electrons, d-type basis functions play a different role for each atom, being much more important for an accurate treatment of a chlorinated species. Correlation effects may be more complicated, particularly for transition metal systems. The most stringent calculational demands for molecules containing heavy elements seem to be in the evaluation of excitation energies, but of course, structural parameters can not be reliably found if the wavefunction is clearly deficient.

Alkaline earth oxides have been studied by Bauschlicher and coworkers in considerable detail [B-37:40]. BeO, MgO and CaO are ionic and different low-lying states have different partial charges or degree of ionicity. This poses a complication in the calculation of an appropriate electronic wavefunction because it implies importance of non-dynamical correlation and a possible difference in the nature of the correlation among the low-lying states. It was found that a single configuration does not adequately describe the ground state of BeO [B-37]. MCSCF provides a more suitable description. A subsequent CI calculation accounted for dynamical correlation, and as shown by the results for BeO in TABLE 4.6, there was typical bond lengthening from the dynamical correlation effects.

Basis set and correlation effects on the atomization energy and structure of Al_2 and Al_4 have been recently explored by Bauschlicher and Pettersson [B-41]. They used several basis sets, including a [5s 3p] valence double zeta contracted set (DZ) and a [6s 5p] contracted triple set (TZ). Calculations were also carried out with an effective core potential (ECP) replacing the (1s,2s,2p) electrons as described with the TZ basis. A single set of d-type polarization functions (exponent = 0.55) or a double set (exponents = 1.1 and 0.35) augmented these bases. Optimization of the second d-type function gave a more diffuse exponent of 0.2 which was used in the d' or 2d' bases. Selected SCF and CISD results from this study are given in TABLE 4.7. The replacement of the DZ basis with the TZ basis reduces the bond lengths by 0.07-0.08 a.u. at the SCF level. The d-functions yield an even more sizable reduction in the equilibrium bond lengths for both Al_2 and Al_4. The reduction in bond lengths from basis set enlargement or augmentation is also found at the CI level which means there is near additivity in the basis set and correlation reductions in the bond length. The atomization energies are very strongly influenced by correlation effects.

TABLE 4.6

Equilibrium bond length, R_e, in Angstroms and excitation energies, T_e, in cm^{-1}, for low-lying electronic states of BeO [B-39]. Experimental values are those quoted in [B-39].

Spectroscopic state	*MCSCF*		*CI*		*Experiment*	
	T_e	R_e	T_e	R_e	T_e	R_e
X $^1\Sigma^+$		1.359		1.377		1.3309
A $^1\Pi$	10173	1.499	8880	1.508	9406	1.4631
B $^1\Sigma^+$	23298	1.395	20517	1.401	21254	1.3623
$^1\Sigma^-$	44814	1.550	41412	1.593	39120	1.495
$^1\Delta$	44866	1.555	41889	1.593	41365	

TABLE 4.7

Equilibrium bond distance (in a.u.) and dissociation energy (in eV) for Al_2 and Al_4 calculated by Bauschlicher and Pettersson [B-41].

Basis	*SCF*		*CISD*	
	r_e	D_e	r_e	D_e
Al_2 $^3\Sigma_g^-$:				
DZ	5.05	0.10	4.92	0.77
TZ	5.01	0.11	4.92	0.78
TZ + 2d	4.80	0.35	4.69	1.01
H-ECP + 2d'	4.82	0.46	4.76	0.99
Al_4 $^3B_{1u}$ (rhombus):				
DZ	5.30	1.59	5.27	3.20
TZ	5.22	1.68	5.20	3.20
TZ + 2d	5.03	2.38	4.95	3.96
H-ECP + 2d'	5.09	2.54	5.03	3.91
TZ + 2d'	5.10	2.66	5.02	4.00

Chapter Five

DERIVATIVE ELECTRONIC STRUCTURE METHODS AND MOLECULAR PROPERTIES

Many important molecular properties are directly defined as the derivative of an energy. As a particular example, the dipole moment is properly defined as the derivative of the molecular energy with respect to the strength of an applied, uniform electric field. As another case, the force constant associated with a bond is the second derivative of the molecular potential energy with respect to a displacement coordinate along that bond. Polarizabilities and susceptibilities are again properties that are derivatives of various types and orders.

Derivative-related properties can be obtained in several ways. One way is by taking finite differences. If the energy is to be differentiated with respect to some parameter, then a set of calculations can be carried out to find the energy for various choices of the parameter's value. If two such calculations are done, an approximate value of the first derivative is the difference in the two energies divided by the difference in the parameter's values. For instance, an electronic wavefunction and energy of a molecule might be obtained with and without a uniform electric field applied along the x-axis with some specified strength, perhaps 0.0005 a.u. The introduction of the field would be accomplished by adding a one-electron operator to the Hamiltonian, or to the Fock operator. This operator would correspond to the interaction of the electrons with the field, and so it would be the x-axis dipole moment operator multiplied by the specified field strength, 0.0005 a.u. The difference between the "finite field" energy and the energy without the field would be the numerator in a fraction that estimates the first derivative; the denominator would be the field strength, 0.0005 a.u., and the first derivative estimated in this way would be the x-component of the dipole moment vector. The two possible difficulties in a finite difference procedure both have to do with the size of the parameter value increment. It may be so small that the energy difference in the numerator is of the size of the numerical accuracy of the energy values and so is not reliable. Or, the parameter increment may be so large that the energy difference between two points is contaminated by higher derivatives. That is, the estimate may become invalid for a large step size in the parameter. Both these potential difficulties are controllable and do not have to interfere with the quality of the results, but considerable effort may have to be invested to be sure that the final results are, in fact, pure of such numerical inaccuracies.

Another way of obtaining some properties is through computing an expectation value. A dipole moment, using that as one example of a derivative property, might be calculated merely be integrating the system's probability density with the dipole moment operator. That result will be equivalent to the result obtained from invoking the strict definition of the dipole moment as being a derivative in the case where the wavefunction obeys the Hellmann-Feynman theorem [A-7,H-9], or in general, where the wavefunction is completely variationally determined.

A third way of obtaining properties that are derivatives is by analytical differentiation. Procedures for doing this have been the focus of many investigations in recent years. What may be regarded as the underlying idea behind analytical derivative methods in electronic structure amounts to just rigorously differentiating the true quantum mechanical energy. Generally that involves solving a type of eigenfunction equation or a simultaneous system of linear equations. To illustrate how this is accomplished, a straightforward procedure, not specific to electronic wavefunctions, is presented. The subtleties associated with electronic wavefunctions are considered after that, while later chapters review applications results from both analytical and finite difference methods.

Differentiation of the Schrodinger Equation. A molecular Hamiltonian usually has embedded parameters of one sort or another. Within the Born-Oppenheimer approximation, for instance, the nuclear positions are parameters. The parameters that happen to be found in some Hamiltonian will be designated a, b, c, . . .

$$H = H(a, b, c, \ldots) \tag{5-1}$$

The parameter list must be thought of as being entirely general, except that for convenience we will assume all the parameters are independent. If the parameters are not independent, then the discussion pertains to a transformed or contracted list of parameters that are independent. Among the parameters may be geometrical parameters that would typically represent displacement from some chosen structure. Also, there may be parameters corresponding to field strengths or to some type of influencing perturbation.

Basically, all types of parameters may come into play when one considers molecular properties in the most general way. For instance, within the "doubly harmonic" model [H-5], a transition moment for the stretching vibration of a diatomic molecule is a mixed second derivative of the energy; it is a derivative with respect to the strength of a uniform, external electric field and with respect to the displacement coordinate.

If a Hamiltonian has embedded parameters, these must be fixed or set to specific values when a solution to the associated equation is sought. It is convenient to be able to refer to some reference choice or zeroeth order choice as an "equilibrium" specification of the parameters when it comes to working out the derivative Schrodinger equations. In this discussion, that specification will be taken to be when all parameters are zero. This choice is for convenience and is not a restriction since relative parameters may be used in place of any that are non-zero at the "equilibrium." For instance, the parameters for bond lengths and bond angles may be displacement coordinates relative to some reference structure. The specific choice of parameters suggests specifically designating a zeroeth order Hamiltonian.

$$H_0 \equiv H(a=0,b=0,c=0,\ldots) \qquad (5\text{-}1a)$$

The zero subscript will be used for all terms for which the parameters have been set to zero.

The time-independent Schrodinger equation, written two ways, is simply,

$$H\Psi = E\Psi \qquad (H-E)\Psi = 0 \qquad (5\text{-}2)$$

At the equilibrium choice of the embedded parameters, the Schrodinger equation is written as

$$(H_0 - E_0)\Psi_0 = 0 \qquad (5\text{-}2a)$$

The task of differentiating Eqn. (5-2) begins with differentiating the Hamiltonian. The partial derivatives of the Hamiltonian with respect to the parameters are equal to the total derivatives when they are completely independent parameters. The derivatives of operators and wavefunctions will be designated as in

$$H^a = \frac{\partial H}{\partial a} \qquad (5\text{-}3)$$

Though it doesn't necessarily have to occur, any derivative of the Hamiltonian may still be dependent on some of the parameters. Thus, the derivative of a Hamiltonian does not become a specific operator until the parameters are set to some particular values. The "equilibrium" choice is designated in the following way.

$$H_o^a = \frac{\partial H}{\partial a}\Big|_{a=0,b=0,c=0,\,\ldots} \qquad (5\text{-}3a)$$

Second and third derivatives of the Hamiltonian may be designated in a like manner.

The first derivative of the Schrodinger equation with respect to one of the parameters, a, is

$$H^a\,\Psi + H\,\Psi^a = E^a\,\Psi + E\,\Psi^a \qquad (5\text{-}4)$$

This expression, like all subsequent derivative equations, is best used by assuming that the zeroeth order Schrodinger equation has been solved or that its solutions are somehow known. Then, the expression may be "evaluated at equilibrium," meaning that all parameters are set to zero.

$$H_o^a\,\Psi_o + H_o\,\Psi_o^a = E_o^a\,\Psi_o + E_o\,\Psi_o^a \qquad (5\text{-}4a)$$

This equation includes the partial derivative of the energy with respect to the parameter a, i.e. E_o^a. It is also an equation with a very noticeable correspondence to first order perturbation theory, and that suggests how best to extract a solution. Indeed, the general procedure being outlined here officially differs from perturbation theory in only one minor way. A perturbation expansion is in terms of the powers of the parameters, whereas the derivative expansion is a Taylor series type expansion that has each n-th power series term divided by n! relative to the perturbation expansion. (Those factors can convert perturbative energy corrections into energy derivatives and the reverse.) So, Eqn. (5-4a) may be rearranged in exactly the same way as done in an elementary introduction to perturbation theory.

$$E_o^a \Psi_o = \left(H_o - E_o\right)\Psi_o^a + H_o^a \Psi_o \qquad (5\text{-}4b)$$

Integration of this equation using the zeroeth order wavefunctions yields an expression for the first derivative of the energy.

$$E_o^a \langle \Psi_o | \Psi_o \rangle = \langle \Psi_o | H_o - E_o | \Psi_o^a \rangle + \langle \Psi_o | H_o^a | \Psi_o \rangle \qquad (5\text{-}4c)$$

If the zeroeth order wavefunction does, in fact, satisfy Eqn. (5-2a), then the first term in Eqn. (5-4c) is identically zero. That means that the first derivative is obtained as an expectation value of the derivative Hamiltonian. This last statement is one form of the Hellmann-Feynman theorem.

Another useful way of rearranging Eqn. (5-4) is to collect terms involving the unknown derivative function. Again, this follows perturbation theory.

$$(H - E)\,\Psi^a = -\left(H^a - E^a\right)\Psi \qquad (5\text{-}5)$$

This expression is an eigenfunction expression just the same as Eqn. (5-2). However, instead of the operator (H-E) yielding zero when applied to the eigenfunction, it yields another function, the one specified by the right hand side of Eqn. (5-5); it is inhomogeneous. It will be seen that all derivative equations can be put into the same form, differing only in the right hand side functions. Evaluating Eqn. (5-5) at the equilibrium choice of parameters gives another way of writing Eqn. (5-4b).

$$\left(H_o - E_o\right)\Psi_o^a = -\left(H_o^a - E_o^a\right)\Psi_o \qquad (5\text{-}5a)$$

With the result of Eqn. (5-4c) for E_o^a, the only unknown in Eqn. (5-5a) is the function that is the derivative of the wavefunction, Ψ_o^a. Thus, Eqn. (5-5a) serves to determine that function once the derivative of the energy has been obtained.

The Schrodinger equation can be formally differentiated to any order with respect to one parameter or any number of parameters. For example, continuing to second order differentiation, and using another parameter, b, Eqn. (5-4) leads to

$$
\begin{aligned}
H^{ab}\Psi + H^{a}\Psi^{b} + H^{b}\Psi^{a} + H\Psi^{ab} \\
= E^{ab}\Psi + E^{a}\Psi^{b} + E^{b}\Psi^{a} + E\Psi^{ab}
\end{aligned}
\qquad (5\text{-}6)
$$

Rearranging Eqn. (5-6) and integrating with the zeroeth order wavefunction yields an expression for the second derivative of the energy.

$$
\begin{aligned}
E_o^{ab}\left\langle \Psi_o \,|\, \Psi_o \right\rangle = \left\langle \Psi_o \,|\, H_o^{ab} \,|\, \Psi_o \right\rangle &+ \left\langle \Psi_o \,|\, H_o^{a} - E_o^{a} \,|\, \Psi_o^{b} \right\rangle \\
&+ \left\langle \Psi_o \,|\, H_o^{b} - E_o^{b} \,|\, \Psi_o^{a} \right\rangle \qquad (5\text{-}6a) \\
&+ \left\langle \Psi_o \,|\, H_o - E_o \,|\, \Psi_o^{ab} \right\rangle
\end{aligned}
$$

The last term on the right hand side of Eqn. (5-6a) is, of course, zero because of Eqn. (5-2a). Were the differentiation carried out with respect to the parameter a, again and instead of the different parameter, b, then the second and third terms would be identical. The appearance of a factor of 2.0 as these two terms are combined amounts to introducing a binomial coefficient. Indeed, for higher derivatives with respect to the same parameter, binomial coefficients make is simple to collect all like terms and thereby avoid redundant evaluation steps. Another useful point is that even with the parameter a different from b, the second and third terms in Eqn. (5-6a) are complex conjugates of one another, or are the same if all the functions are real. This type of identity will show up again. It comes from Eqn. (5-5a) which says that differentiation of the zeroeth order (H - E) operator can be "swapped" for differentiation of the zeroeth order wavefunction with a change of sign. To show that the second and third terms are equivalent, start with the second term and swap differentiation with respect to a. This leaves the zeroeth order (H - E) operator sandwiched between two first derivative functions. Differentiation with respect to the parameter b can be swapped in the reverse sense. Since there have been two swaps, there is not net change in sign. The result is the complex conjugate of the third term.

Rearrangement of Eqn. (5-6) can put it into a form like that of Eqn. (5-5).

$$(H - E)\,\Psi^{ab} = -(H^{a} - E^{a})\,\Psi^{b} - (H^{b} - E^{b})\,\Psi^{b} - (H^{ab} - E^{ab})\,\Psi \qquad (5\text{-}7)$$

This equation can be evaluated at equilibrium and then solved to obtain the second derivative of the wavefunction. The uniformity of the derivative equations becomes clearer by considering a third derivative equation and then comparing it with Eqns. (5-5) and (5-7).

$$\begin{aligned}(H - E)\,\Psi^{abc} = {} & -(H^{a} - E^{a})\,\Psi^{bc} - (H^{b} - E^{b})\,\Psi^{ac} \\ & -(H^{c} - E^{c})\,\Psi^{ab} - (H^{ab} - E^{ab})\,\Psi^{c} \qquad (5\text{-}8) \\ & -(H^{ac} - E^{ac})\,\Psi^{b} - (H^{bc} - E^{bc})\,\Psi^{a} \\ & -(H^{abc} - E^{abc})\,\Psi\end{aligned}$$

In Eqn. (5-8) and in any similarly organized higher derivative expressions, the right hand side is entirely determined from lower order derivative results. Everything on that side can be collected so that in an order-by-order solution, the right hand side will always be a known function. The equation to be solved has the same form, no matter what level of differentiation.

As in perturbation theory, there is a "2n+1 rule" [H-10,N-3] which means that from the n-th order wavefunctions, energy derivatives up to 2n+1 may be evaluated. The derivative wavefunctions between n and 2n+1 orders are not required explicitly. For example, with the first derivative wavefunctions known explicitly, the third energy derivatives may be evaluated immediately. To see this for the abc derivative of Eqn. (5-8), the equation is evaluated at the equilibrium choice of parameters and then integration is carried out using the zeroeth order wavefunction.

$$\begin{aligned}E^{abc} = {} & \left\langle \Psi_o \,|\, H_o - E_o \,|\, \Psi_o^{abc} \right\rangle + \left\langle \Psi_o \,|\, H_o^{abc} \,|\, \Psi_o \right\rangle \qquad (5\text{-}9) \\ & + \left\langle \Psi_o \,|\, H_o^{a} - E_o^{a} \,|\, \Psi_o^{bc} \right\rangle + \left\langle \Psi_o \,|\, H_o^{b} - E_o^{b} \,|\, \Psi_o^{ac} \right\rangle \\ & + \left\langle \Psi_o \,|\, H_o^{c} - E_o^{c} \,|\, \Psi_o^{ab} \right\rangle + \left\langle \Psi_o \,|\, H_o^{bc} - E_o^{bc} \,|\, \Psi_o^{a} \right\rangle \\ & + \left\langle \Psi_o \,|\, H_o^{ac} - E_o^{ac} \,\middle|\, \Psi_o^{b} \right\rangle + \left\langle \Psi_o \,|\, H_o^{ab} - E_o^{ab} \,|\, \Psi_o^{c} \right\rangle\end{aligned}$$

Assuming that Eqn. (5-2a) has been satisfied, the first term in Eqn. (5-9) vanishes. This means that the third order energy can be obtained without knowing the third order wavefunction. This is an obvious "n+1 rule," where the n-th derivative wavefunctions are sufficient to obtain the n+1 order energy derivatives. Other terms in Eqn. (5-9) involve the second derivatives of the wavefunction, but substitutions using Eqns. (5-5) and (5-7) may eliminate them. As done above for the second derivative expression, Eqn. (5-5a) is used to "swap" differentiation of the operator (H_o - E_o) with differentiation of the zeroeth order wavefunction, with a sign change, as in:

$$\left\langle \Psi_o \mid H_o^a - E_o^a \mid \Psi_o^{bc} \right\rangle = -\left\langle \Psi_o^a \mid H_o - E_o \mid \Psi_o^{bc} \right\rangle \qquad (5\text{-}9a)$$

This result follows from Eqn. (5-5a) by integrating with Ψ^{bc}.

Eqn. (5-7) can be used to "swap" second order differentiation in a like manner. Evaluating Eqn. (5-7) at the equilibrium and then integrating on the right with Ψ_o^a yields the following substitution expression.

$$\left\langle \Psi_o^{bc} \mid H_o - E_o \mid \Psi_o^a \right\rangle = -\left\langle \Psi_o \mid H_o^{bc} - E_o^{bc} \mid \Psi_o^a \right\rangle \qquad (5\text{-}9b)$$

$$-\left\langle \Psi_o^b \mid H_o^c - E_o^c \mid \Psi_o^a \right\rangle - \left\langle \Psi_o^c \mid H_o^b - E_o^b \mid \Psi_o^a \right\rangle$$

This type of substitution can result in elimination of those terms of Eqn. (5-9) that involve the second derivatives of the wavefunction. Substitutions of the type of Eqn. (5-9a) "take out" the differentiation of the operator so that a substitution of the type of Eqn. (5-9b) can be made. The third derivative expression, now recast in terms of the first derivatives of the wavefunction, is,

$$E_o^{abc} = \left\langle \Psi_o \mid H_o^{abc} \mid \Psi_o \right\rangle \qquad (5\text{-}9c)$$

$$+ 2\left\langle \Psi_o^b \mid H_o^c - E_o^c \mid \Psi_o^a \right\rangle + 2\left\langle \Psi_o \mid H_o^{ab} - E_o^{ab} \mid \Psi_o^c \right\rangle$$

$$+ 2\left\langle \Psi_o^c \mid H_o^b - E_o^b \mid \Psi_o^a \right\rangle + 2\left\langle \Psi_o \mid H_o^{ac} - E_o^{ac} \mid \Psi_o^b \right\rangle$$

$$+ 2\left\langle \Psi_o^c \mid H_o^a - E_o^a \mid \Psi_o^b \right\rangle + 2\left\langle \Psi_o \mid H_o^{bc} - E_o^{bc} \mid \Psi_o^a \right\rangle$$

This energy expression uses the second derivatives of the energy, but they are also obtained from the first derivatives of the wavefunction.

This development illustrates that formal differentiation of the Schrodinger equation is easily carried out. The next step, actually computing an energy derivative or solving for a derivative of the wavefunction involves the same complications as in computing the original, or zeroeth order, energy and wavefunction. Thus, basis sets may be employed to solve the derivative equations, or numerical treatments may be used. For electronic wavefunctions, the anti-symmetrization requirement can not be abandoned in the course of differentiation, and so there are special aspects to the differentiation in electronic structure.

Though direct differentiation of the Schrodinger equation leads to the same results as perturbation theory, the differentiation concept holds a certain appeal: Through usual rules of calculus, the process can be generalized to any number or type of parameters and to any order of differentiation. In at least one case [D-18], such an open-ended method has been implemented for electronic wavefunctions.

Basis Set Expansions of Derivative Equations. Basis sets can be employed to solve derivative Schrodinger equations as naturally as employing them to solve the basic Schrodinger equation. The connection between differentiation and perturbation theory, and the well-established use of basis sets in perturbative treatments make this all the more apparent. An organized way of using basis sets, and a way which is quite suited for computational implementation, is to cast operators into their matrix representations [F-1] in the given basis. This needs to be done for the zeroeth order Hamiltonian and for each derivative Hamiltonian operator. The matrix representation of an operator is a matrix of integral quantities. The row-column indices of these quantities identify two particular functions in the basis set, and the quantity itself is the integral of the first function (complex conjugate) times the operator applied to the second function. (Real valued basis functions will be assumed throughout this section.) With this definition, the zeroeth order Schrodinger equation for one state, Eqn. (5-2a), in matrix form is:

$$\left(\mathbf{H}_0 - E_0\mathbf{1}\right)\vec{\mathbf{C}}_0 = 0 \qquad (5\text{-}10)$$

This is the usual matrix eigenvector equation, where $\vec{\mathbf{C}}_0$ is the eigenvector. The coefficients in this vector are the expansion coefficients of the eigenfunction in the given basis set. $\mathbf{H}_0$ is the matrix representation of the "equilibrium" Hamiltonian of Eqn. (5-1a). E_0 (*not boldface*) is the eigenenergy, and **1** is the identity or unit matrix. The first derivative Schrodinger expression, Eqn. (5-5a), when developed in a basis set expansion becomes

$$\left(\mathbf{H}_o - E_o\mathbf{1}\right)\vec{\mathbf{C}}_o^a = -\left(\mathbf{H}_o^a - E_o^a\mathbf{1}\right)\vec{\mathbf{C}}_o \qquad (5\text{-}11)$$

Converting the equations in the first section of this chapter to their basis set forms involves little more than replacing a wavefunction, or derivative wavefunction, with a vector of coefficients, a column vector if to the right of an operator, and replacing an operator by its matrix representation.

Comparing Eqns. (5-10) and (5-11) reveals that the equations have the same form except that there is a non-zero column vector on the right hand side of Eqn. (5-11). It turns out that all higher derivative expressions have the same inhomogeneous form, and the matrix expression that needs to be solved in every case has the following form.

$$\left(\mathbf{H}_o - E_o\mathbf{1}\right)\vec{\mathbf{C}}_o^\alpha = \vec{\mathbf{X}}^\alpha \qquad (5\text{-}12)$$

α represents some arbitrary derivative without regard to order. A general algorithm for solving the coupled linear equations of Eqn. (5-12) is all that is necessary, and there are many standard algorithms for this purpose. The column vector on the right hand side of Eqn. (5-12) will be determined in every case from lower order results.

The energy derivatives can be found from each equation by multiplying on the left with $\vec{\mathbf{C}}_0^\dagger$. Doing this corresponds to using the "n+1 rule," as illustrated with the first derivative expression, Eqn. (5-11).

$$E_o^a = \vec{\mathbf{C}}_o^\dagger \mathbf{H}_o^a \vec{\mathbf{C}}_o \qquad (5\text{-}13)$$

Here, the derivative value is obtained without using the first derivative of the wavefunction; it is only the n=0 order wavefunction that is used explicitly. The "2n+1 rule" requires the same manipulations as discussed in the previous section. It presents no added complication when used with a basis set expansion if the basis is not dependent on the parameters with respect to which the differentiation is being carried out. If the basis set is dependent on the parameters, then derivatives to the 2n+1 order of the integrals over the basis functions are required. King and Kormornicki [K-3] have given a very general and nicely organized development of the relationships leading to the 2n+1 rule, and at the same time have derived expressions for errors in derivatives from using imperfectly optimized wavefunctions.

In electronic structure calculations, it is not unlikely for a basis set to be dependent on the parameters. The most obvious case is with geometrical parameters. The atomic orbital basis functions used to construct molecular orbitals are generally chosen to follow the atomic centers. That means that the functions are dependent on the molecular geometry, and consequently there will be non-zero derivatives, with respect to the geometrical parameters, of the usual one- and two-electron integrals. In the case of parameters such as an electric field strength, however, there is no functional dependence of the standard types of basis functions. The derivatives of all the basis functions with respect to this parameter are zero.

Sadlej [S-15:18] has recommended use of basis sets that *are* dependent on the perturbation because that may afford using a smaller basis set. Sadlej and coworkers have done this for electric field properties through incorporating a specific field dependence into Gaussian basis functions. Hudis and Ditchfield [H-11] have more recently suggested a different way of selecting field dependent bases, and both schemes seem quite promising. Ditchfield had much earlier accomplished the same thing for the challenging problem of solving for NMR chemical shifts [D-19].

Without considering normalization, derivative wavefunctions cannot be completely determined. The derivative Schrodinger equations do not serve to fully specify the derivative functions, but the normalization condition provides another derivative equation set that does. Alternatively, the normalization condition may be incorporated as a constraint. If the zeroeth order Schrodinger equation were solved for all states, the column vectors could be arranged in a square matrix, which we will designate $\mathbf{C}_0$ (*no arrow*), and each derivative eigenvector for a particular state could be defined in terms of this basis using a vector, $\vec{\mathbf{U}}$, that gives the expansion coefficients in terms of the zeroeth order functions instead of in terms of the basis functions. For instance,

$$\mathbf{C}_o \vec{\mathbf{U}}_o \equiv \vec{\mathbf{C}}_o \qquad (5\text{-}14a)$$

$$\mathbf{C}_o \vec{\mathbf{U}}_o^{\,a} \equiv \vec{\mathbf{C}}_o^{\,a} \qquad (5\text{-}14b)$$

$$\mathbf{C}_o \vec{\mathbf{U}}_o^{aa} \equiv \vec{\mathbf{C}}_o^{aa} \qquad (5\text{-}14c)$$

The derivative eigenvectors for all states may be arranged column-by-column into square arrays, **U** (*no arrow*), and then the zeroeth order transformation is the identity, i.e. $\mathbf{U}_o = \mathbf{1}$. The introduction of the **U** vectors or matrices is a basis set transformation that turns out to be convenient.

Eqn. (5-12) may be written in terms of elements of a **U** vector.

$$\left(\mathbf{H}_o - E_o \mathbf{1}\right) \mathbf{C}_o \vec{\mathbf{U}}_o^{\alpha} = \vec{\mathbf{X}}^{\alpha} \qquad (5\text{-}15)$$

Applying the operator to the first column of $\mathbf{C}_0$, though, yields a zero column vector (Eqn. (5-10)). Thus, the first element of $\vec{\mathbf{U}}_o^{\alpha}$ is multiplied by zero, and so its value is not determinable from Eqn. (5-15). The normalization condition, just as in perturbation theory, provides an extra condition which does determine this element.

Normalization in an orthonormal basis set expansion is expressed as,

$$\mathbf{C}_o^{\dagger}\, \mathbf{C}_o = \mathbf{1} \qquad (5\text{-}16)$$

If the basis set is not orthogonal or if it may become non-orthogonal with a non-zero choice of one of the parameters, then the normalization condition that needs to be used is,

$$\mathbf{C}_o^{\dagger}\, \mathbf{S}_o\, \mathbf{C}_o = \mathbf{1} \qquad (5\text{-}17)$$

where **S** is the matrix of basis function overlap. Differentiation to first order yields

$$\mathbf{C}_o^{a\dagger}\, \mathbf{C}_o + \mathbf{C}_o^{\dagger}\, \mathbf{C}_o^{a} = 0 \qquad (5\text{-}18)$$

$$\mathbf{C}_o^{a\dagger}\, \mathbf{S}_o \mathbf{C}_o + \mathbf{C}_o^{\dagger}\, \mathbf{S}_o^{a} \mathbf{C}_o + \mathbf{C}_o^{\dagger}\, \mathbf{S}_o \mathbf{C}_o^{a} = 0 \qquad (5\text{-}18a)$$

It is straightforward to write the expressions arising from differentiating the normalization condition to any order uniformly. Also, these equations may be written specifically for individual states (vectors) rather than the whole set. The substitutions of Eqn. (5-14) are conveniently used for these expressions, too, and in the end the complete derivative eigenvectors are obtained. For example, from Eqn. (5-18a), the element that could not be determined from Eqn. (5-16) is found.

$$\mathbf{U}_o^{a\dagger}\,\mathbf{C}_o^{\dagger}\,\mathbf{S}_o\,\mathbf{C}_o \;+\; \mathbf{C}_o^{\dagger}\,\mathbf{S}_o^{a}\,\mathbf{C}_o \;+\; \mathbf{C}_o^{\dagger}\,\mathbf{S}_o\,\mathbf{C}_o\,\mathbf{U}_o^{a} \;=\; 0 \qquad (5\text{-}19)$$

$$=\; \mathbf{U}_o^{a\dagger} \;+\; \mathbf{C}_o^{\dagger}\,\mathbf{S}_o^{a}\,\mathbf{C}_o \;+\; \mathbf{U}_o^{a} \;=\; 0 \qquad (5\text{-}19a)$$

$$[\,\mathbf{U}_o^{a\dagger}\,]_{11} \;+\; [\,\mathbf{U}_o^{a}]_{11} \;=\; -\left[\,\mathbf{C}_o^{\dagger}\,\mathbf{S}_o^{a}\,\mathbf{C}_o\,\right]_{11} \qquad (5\text{-}19b)$$

(This assumes that the state of interest in Eqn. (5-16) is associated with the first column position in $\mathbf{C}_0$.) The set of derivative normalization equations and derivative Schrodinger equations does completely specify the derivative eigenvectors in a basis set expansion.

Derivatives of Numerical Wavefunctions. Numerical wavefunctions are generally those represented by a set of amplitudes at points in the space spanned by the wavefunction. The quality of the representation depends somewhat on the spacing of the points. Finding numerical wavefunctions involves integrating a differential Schrodinger equation. In principle, a numerical procedure can be applied to a derivative Schrodinger equation just as well as to a zeroeth order Schrodinger equation, though this does not seem to be a common practice.

McCullough has reported dipole polarizabilities of diatomics [M-12;C-15] that have been obtained using a semi-numerical Hartree-Fock procedure specifically for diatomic molecules [M-13:14]. The procedure is semi-numerical in that there is an implicit truncation in the wavefunction representation. Essentially Hartree-Fock limit results are obtainable, and the dipole polarizabilities that McCullough has reported provide basis set limit information for the molecules studied. However, the polarizabilities were obtained from introducing a finite field, and so this is not strictly a derivative numerical method.

An interesting case that illustrates how derivative numerical methods may be developed is that of the vibrational Schrodinger equation for a two-body system. Cooley has outlined the numerical method (*Numerov-Cooley*) for finding wavefunctions for any specified two-body potential [C-9]. It is straightforward to show that the derivative equations can be expressed in a similar form that is uniform for all orders of differentiation. They can be solved numerically as well.

The general vibrational Schrodinger equation is written as

$$\frac{1}{2\mu}\,P^{(2)}(R) \;=\; (U(R) - E)\,P(R) \qquad (5\text{-}20)$$

where R is the radial or bond displacement coordinate and μ is the reduced mass. P(R) is the wavefunction and U(R) is the potential function. $P^{(2)}(R)$ is the second derivative of P with respect to R. This, of course, corresponds to the kinetic energy operator in the Hamiltonian acting on the wavefunction. We consider U(R) to have embedded parameters, which as before, may be field strengths or other perturbational parameters. First order differentiation with respect to one parameter, a, followed by differentiation with respect to another parameter, b, yields the following examples of derivative vibrational Schrodinger equations.

$$\frac{1}{2\mu} P^{(2)\,a}(R) = (U^{a}(R) - E^{a})\,P(R) + (U(R) - E)\,P^{a}(R) \qquad (5\text{-}21)$$

$$\begin{aligned}\frac{1}{2\mu} P^{(2)\,ab}(R) &= (U^{ab}(R) - E^{ab})\,P(R) + (U(R) - E)\,P^{ab}(R) \qquad (5\text{-}22)\\ &\quad + (U^{a}(R) - E^{a})\,P^{b}(R) + (U^{b}(R) - E^{b})\,P^{a}(R)\end{aligned}$$

Formal differentiation and generation of derivative Schrodinger equations can be continued as far as desired, and as before, there is a uniform way of expressing all such equations.

$$\frac{1}{2\mu} P^{(2)\,\alpha}(R) = (U(R) - E)\,P^{\alpha}(R) - E^{\alpha}\,P(R) + X^{\alpha}(R) \qquad (5\text{-}23)$$

Again "α" represents an arbitrary derivative such as "ab" in Eqn. (5-22). $X^{\alpha}(R)$ is a function which is fixed and known from all lower order derivative energies and derivative wavefunctions. At the point of seeking a solution to Eqn. (5-23), it is necessary to specify the parameter values, to set them to their "equilibrium values." Zero subscripts will designate that this has been done.

The "n+1" rule for these energy derivative expressions is

$$E_{o}^{\alpha} = \left\langle P_{o}(R) \,|\, X_{o}^{\alpha}(R) \right\rangle \qquad (5\text{-}24)$$

"2n" and "2n+1" rules follow just as in the prior sections. Eqn. (5-24) means is that integration of the X(R) function with the zeroeth order wavefunction yields the energy derivative. Considering the case where "α" is the first derivative with respect to the strength of a uniform field, it is easy to show that the corresponding X(R) is simply the dipole moment function of R multiplied by the zeroeth order wavefunction. This means that the first derivative of the energy, which is the dipole moment of the vibrational state, is the vibrational average of the dipole moment function. This is a Hellmann-Feynman theorem result where an expectation value is the same as an energy derivative. For higher orders, though, merely integrating with the zeroeth order vibrational probability density (i.e., taking an expectation value) will not generally yield the same thing as a true derivative value.

The numerical solution of the vibrational Schrodinger equation is accomplished by partitioning the coordinate R into small segments and finding the value of the wavefunction at each segment. This amounts to converting the differential equation into a difference equation. The first step is combining power series expansions for P(R) at two points on either side of a third. The expansions are both done about the middle point since this eliminates every other term in the combined power series expansion. All the terms depend, with increasing order, on the segment length. Since this can be made very small, the power series expansion may be truncated. Using guesses for the value of P(R) at the closest-in segment and at the farthest-out segment, the difference equations can be used to integrate (or find succeeding segments' P(R) values) inward and outward. Iterative adjustment in the eigenenergy is dictated by matching the inward and outward P(R) functions [C-9]. For the derivative equations, the zeroeth order eigenenergy is already known, and there is no longer a need to iterate. The only change is the incorporation of the X(R) function and this is simple in computation [D-21].

Derivative Hartree-Fock Theory. Direct differentiation of electronic wavefunction and energies can be accomplished by the approaches that have been discussed. Configuration interaction (CI) is a linear basis set expansion where the basis functions are electron configurations. The derivative process for basis set expansions can be employed almost immediately, with important details having to do mainly with computing the requisite integral quantities. Of course, that's a serious task and it has only been through many different algorithmic developments that real progress on derivatives of CI wavefunctions has been achieved. The usual starting point for electronic structure studies, SCF level wavefunctions, is different because the Fock operator is basis-dependent. While the orbitals are expanded linearly in a basis set, the eigenequation has a higher level dependence on the basis. By looking at SCF differentiation in some detail, certain of the complications in obtaining derivatives of correlated wavefunctions will appear clearer.

The earliest investigations of derivatives of SCF energies were generally discussed in the language of perturbation theory, which as mentioned, is entirely equivalent to the language of differentiation, that being the author's choice. It has become generally accepted terminology to identify low-order differentiation of the SCF energy as a coupled-perturbed Hartree-Fock (CPHF) procedure. McWeeny was one of the first to recognize that derivative properties could be obtained analytically by perturbative expansion of the Hartree-Fock equation [M-15]. Stevens, Pitzer and Lipscomb [S-21] developed a perturbative expansion starting from the basis set form of the Hartree-Fock-Roothaan equations and were calculating electrical and magnetic properties in 1963. Langhoff, Karplus and Hurst [L-16] tested and distinguished forms of perturbed Hartree-Fock, leaving CPHF as the complete form. "Uncoupled" forms, which are largely unused today, amounted to a neglect of certain terms.

Gerratt and Mills [G-5] generalized the formulation of Stevens et al. [S-21] so that geometrical derivatives could be obtained with CPHF. This step was important because the usual basis sets are dependent on the geometrical parameters. Atomic basis functions "follow" the nuclei. With this development, first derivatives of the orbitals could be obtained for nuclear displacement perturbations. Pulay pioneered the contemporary treatments of energy gradients, first derivatives with respect to geometrical coordinates, and their use in finding potential minima [P-8]. In a series of papers, McWeeny and coworkers gave explicit expressions through several low orders for energy derivatives [D-22:24] following a density matrix organization [M-3,M-17] of the problem.

Certain of the ideas from early work have been collected into a uniform procedure for differentiating the Hartree-Fock equations with an orbital basis set expansion. This is the derivative Hartree-Fock (DHF) theory of Dykstra and Jasien [D-18] which may be regarded as infinite order generalization of CPHF if one prefers the language of perturbation theory. Unique in this theory is the intrinsic capability to continue to any order of differentiation, provided that any necessary integrals over the atomic basis functions are at hand. DHF is the SCF-specific form of the ideas presented at the start of this chapter. The uniformity of the SCF derivative equations was already noted for first and second order by Dupuis [D-25], and for evaluation of up to second and third order, DHF is not unlike other methods that follow alternate formulations and extensions to other types of problems [G-7,M-16;O-4:5;P:9-10;T-7;Y-3]. The DHF formulation will be explained as one means of understanding the derivatives of SCF wavefunctions. Aspects related to using multi-configuration and open-shell reference wavefunctions, which are formally just as straightforward, are left out for the sake of conciseness.

As before, it is a convenient notation to use a,b,c, ... for specific parameters and to place them as superscripts when a quantity has been differentiated with respect to one or more of them. "α" is used for an arbitrary derivative, which means an arbitrary list of a's, b's, c's, and so on. One simple but very effective logic procedure developed for DHF keeps track of the derivatives. An integer list is constructed for each particular derivative and there is one integer in the list for each parameter. Most DHF calculations to date have been to obtain multipole polarizabilities, and so those parameters serve as a good example set. For first and second multipole polarizabilities, there will be nine field or electrical potential parameters, three associated with the first moment and six with the second moment. One way of designating and ordering them is F_x, F_y, F_z, F_{xx}, F_{xy}, F_{xz}, F_{yy}, F_{yz}, and F_{zz}. These are assigned order numbers one through nine, respectively. TABLE 5.1 illustrates the simple connection between the derivative integer lists and specific derivatives for this example situation.

The integer lists are useful for computing the lower order pieces in the derivative equations. It is a general result that for a derivative given by a list [i, i', i", . . .], the lists for the elements in any contributing low-order product terms must add to give this list. This fact facilitates searching for the low-order terms. From the lists in TABLE 5.1, sums of lists can be formed. A specific example would be the calculation of the [2 0 0 0 1 0 0 0 0] derivative. To identify low order terms that would be used in products to find this derivative, sums of lists may be checked.

$$\begin{array}{r} [0\,0\,0\,0\,1\,0\,0\,0\,0] \\ +\,[2\,0\,0\,0\,0\,0\,0\,0\,0] \\ \hline [2\,0\,0\,0\,1\,0\,0\,0\,0] \end{array} \qquad \begin{array}{r} [1\,0\,0\,0\,0\,0\,0\,0\,0] \\ +\,[1\,0\,0\,0\,1\,0\,0\,0\,0] \\ \hline [2\,0\,0\,0\,1\,0\,0\,0\,0] \end{array}$$

In this example, two combinations of two lists have been found that sum to the list of the particular derivative being sought. Each is a "match" and in the discussion to follow, certain summations will be restricted to such matches.

The Hartree-Fock-Roothaan equation uses the overlap matrix **S**, a matrix of orbital expansion coefficients, **C**, an orbital eigenvalue matrix, **E**, and the Fock operator matrix, **F**.

$$\mathbf{F}\,\mathbf{C} = \mathbf{S}\,\mathbf{C}\,\mathbf{E} \qquad (5\text{-}25)$$

TABLE 5.1

Integer lists associated with derivatives in a nine-parameter, multipole polarizability DHF calculation.

Integer list	*Associated Derivative Element*
0 0 0 0 0 0 0 0 0	Zeroeth order
1 0 0 0 0 0 0 0 0	x-component of the first moment
0 1 0 0 0 0 0 0 0	y-component of the first moment
0 0 1 0 0 0 0 0 0	z-component of the first moment
0 0 0 1 0 0 0 0 0	xx-component of the second moment
0 0 0 0 1 0 0 0 0	xy-component of the second moment
0 0 0 0 0 1 0 0 0	xz-component of the second moment
0 0 0 0 0 0 1 0 0	yy-component of the second moment
0 0 0 0 0 0 0 1 0	yz-component of the second moment
0 0 0 0 0 0 0 0 1	zz-component of the second moment
2 0 0 0 0 0 0 0 0	x,x dipole polarizability
1 1 0 0 0 0 0 0 0	x,y dipole polarizability
1 0 1 0 0 0 0 0 0	x,z dipole polarizability
1 0 0 1 0 0 0 0 0	x,xx dipole-quadrupole polarizability
. . .	
0 0 0 2 0 0 0 0 0	xx,xx quadrupole polarizability
0 0 0 1 1 0 0 0 0	xx,xy quadrupole polarizability
. . .	
3 0 0 0 0 0 0 0 0	x,x,x dipole hyperpolarizability
2 1 0 0 0 0 0 0 0	x,x,y dipole hyperpolarizability
. . .	
0 0 0 0 0 0 0 0 3	zz,zz,zz quadrupole hyperpolarizability
4 0 0 0 0 0 0 0 0	x,x,x,x dipole second hyperpolarizability
. . .	

Though closed shell configurations will be assumed wherever it is necessary to be specific about the type of wavefunction, the development is general so long as **F** is a matrix whose appropriate off-diagonal elements are the single substitution Hamiltonian elements that would be zero by Brillouin's theorem for the particular reference wavefunction. Differentiation of Eqn. (5-25) leads to the following.

$$\mathbf{F}^a\mathbf{C} + \mathbf{F}\mathbf{C}^a = \mathbf{S}^a\mathbf{C}\mathbf{E} + \mathbf{S}\mathbf{C}^a\mathbf{E} + \mathbf{S}\mathbf{C}\mathbf{E}^a \qquad (5\text{-}26)$$

As in the basis set expansion form of the derivative Schrodinger equations, the next step is to introduce a set of matrices that represent the derivative orbitals in terms of the zeroeth order orbitals rather than in terms of the atomic basis functions.

$$\mathbf{C}_o^\alpha \equiv \mathbf{C}_o\mathbf{U}_o^\alpha \qquad (5\text{-}27)$$

Finding these **U** matrices is equivalent to finding the derivative **C** matrices.

Multiplying Eqn. (5-26) on the left and right with $\mathbf{C}_o^\dagger$ and substituting with Eqn. (5-27), the first derivative Hartree-Fock equation becomes,

$$\mathbf{C}_o^\dagger\mathbf{F}_o^a\mathbf{C}_o + \mathbf{C}_o^\dagger\mathbf{F}_o\mathbf{C}_o\mathbf{U}_o^a = \qquad (5\text{-}28)$$
$$\mathbf{C}_o^\dagger\mathbf{S}_o^a\mathbf{C}_o\mathbf{E}_o + \mathbf{C}_o^\dagger\mathbf{S}_o\mathbf{C}_o\mathbf{U}_o^a\mathbf{E}_o + \mathbf{C}_o^\dagger\mathbf{S}_o\mathbf{C}_o\mathbf{E}_o^a$$

A simplification results from the fact that $\mathbf{C}_o^\dagger\mathbf{S}_o\mathbf{C}_o = \mathbf{1}$ and that $\mathbf{C}_o^\dagger\mathbf{F}_o\mathbf{C}_o = \mathbf{E}_o$,

$$\mathbf{E}_o\mathbf{U}_o^a - \mathbf{U}_o^a\mathbf{E}_o = \mathbf{C}_o^\dagger\mathbf{S}_o^a\mathbf{C}_o\mathbf{E}_o - \mathbf{C}_o^\dagger\mathbf{F}_o^a\mathbf{C}_o + \mathbf{E}_o^a \qquad (5\text{-}29)$$

This equation is the standard CPHF equation and it is sufficient for finding the elements of $\mathbf{U}_o^a$ wherever the corresponding elements of $\mathbf{E}_o^a$ (or **E**) are zero. For instance, for a closed shell wavefunction, all off-diagonal elements of **E** between occupied and virtual orbitals are zero. So for that block, Eqn (5-29) serves to determine those off-diagonal block elements of the **U** matrix. The diagonal blocks are not obtained. Because of the constraint of orthogonality, the entire set of molecular orbital coefficients are not independently variable, and it is the constraint of orbital orthonormality that yields the diagonal blocks.

It is convenient to define two new matrices that are derivative operator matrices transformed to the orbital basis; their rows and columns correspond to zeroeth order molecular orbitals.

$$\mathbf{R}_o^\alpha \equiv \mathbf{C}_o^\dagger\mathbf{S}_o^\alpha\mathbf{C}_o \qquad (5\text{-}30a)$$

$$\mathbf{G}_o^\alpha \equiv \mathbf{C}_o^\dagger\mathbf{F}_o^\alpha\mathbf{C}_o \qquad (5\text{-}30b)$$

In terms of these two matrices, the first derivative equation (Eqn. (5-29)) becomes

$$\mathbf{E}_o \mathbf{U}_o^a - \mathbf{U}_o^a \mathbf{E}_o = \mathbf{R}_o^a \mathbf{E}_o - \mathbf{G}_o^a + \mathbf{E}_o^a \tag{5-31}$$

As may be obvious from the general discussion at the start of this chapter, there is a uniform structure for every derivative equation.

$$\mathbf{E}_o \mathbf{U}_o^\alpha - \mathbf{U}_o^\alpha \mathbf{E}_o = \mathbf{R}_o^\alpha \mathbf{E}_o - \mathbf{G}_o^\alpha + \mathbf{E}_o^\alpha + \mathbf{X}_o^\alpha \tag{5-32}$$

where **X** is a residual matrix that may be constructed from lower order results. Specifically,

$$\mathbf{X}^\alpha = \sum_{[\mu+\nu+\tau=\alpha]} \mathbf{R}^\mu \mathbf{U}^\nu \mathbf{E}^\tau f(\mu,\nu,\tau) \quad - \sum_{[\mu+\nu=\alpha]} \mathbf{G}^\mu \mathbf{U}^\nu f(0,\mu,\nu) \tag{5-33}$$

The brackets on the summation indexes in Eqn. (5-33) mean that the sums are, in the case of the first one, over μ, ν, and τ but restricted so that the sums of their integer lists, as in Table 5.1, match the integer list of α. The scalar factors f(I,J,K) are binomial coefficients which provide the necessary factors when there is multiple differentiation with respect to one or more parameters. For instance, in the first sum, if **R** were differentiated with the respect to parameter a n-times, if **U** were differentiated n'-times, and if **E** were differentiated n"-times, a factor would have to be applied and its value would be F(n,n',n").

$$F(n,n',n'') = \binom{n+n'}{n''}\binom{n+n'+n''}{n''} \tag{5-34}$$

There would be a factor for each parameter:

$$f(I, J, K) \equiv F(n, n', n'')\, F(m, m', m'')\, F(l,l',l'') \dots \tag{5-35}$$

where

$$[\,I\,] = [\,n \;\; m \;\; l \; \dots\,]$$

$$[\,J\,] = [\,n' \;\; m' \;\; l' \; \dots\,]$$

$$[\,K\,] = [\,n'' \;\; m'' \;\; l'' \; \dots\,]$$

These factors are easy to obtain by a "table look-up" procedure once the integer lists have been compared. It should be clear that **X** matrices can be obtained from matrices determined from lower order differentiation. All that's necessary is to check the integer lists and find the "matches" with the possible sums.

The diagonal blocks of the U matrices are obtained from differentiating the orbital orthogonality condition. The first order and general order expressions are

$$\mathbf{U}_o^{a\dagger} + \mathbf{U}_o^{a} + \mathbf{R}^{a} = 0 \tag{5-36}$$

$$\mathbf{U}_o^{\alpha\dagger} + \mathbf{U}_o^{\alpha} + \mathbf{R}_o^{\alpha} + \mathbf{Y}_o^{\alpha} = 0 \tag{5-37}$$

where **Y** is similar to **X** and depends on products of lower order matrices.

$$\mathbf{Y}^{\alpha} \equiv \sum_{[\mu+\nu+\tau = \alpha]} \mathbf{U}^{\mu}\,\mathbf{R}^{\nu}\,\mathbf{U}^{\tau}\, f(\mu,\nu,\tau) \tag{5-38}$$

This result may also be obtained from the idempotency of the one-electron density which is usable through all orders of differentiation, too [D–23:24].

The evaluation of the energy derivative values from the orbital derivative functions involves certain of the details of the derivative Fock operators. This is a good point to explain specifically what a matrix such as $\mathbf{F}^a$ means and how it is constructed. The Fock operator matrix is sum of three matrices, a one-electron operator **h**, a Coulomb operator **J**, and an exchange operator **K**. The Coulomb and exchange operators are dependent on the one-electron density matrix **D**, which is twice the idempotent density matrix "**R**" which was used in Chapter Three. (At this point, the zero subscript denoting the "equilibrium choice of parameters" will be suppressed since it would appear on all the matrices used in the next set of equations.)

$$\mathbf{F}(\mathbf{D}) = \mathbf{h} + \mathbf{J}(\mathbf{D}) - \frac{1}{2}\mathbf{K}(\mathbf{D}) \tag{5-39}$$

The derivative of the **F** operator is found by differentiating each of the terms in Eqn. (5-39).

From the definition of the Coulomb operator, the derivative operator is found in terms of the derivatives of the two-electron integrals and the derivatives of the density matrix elements. For instance,

$$\mathbf{J}(\mathbf{D})^{a} = \mathbf{J}^{a}(\mathbf{D}) + \mathbf{J}(\mathbf{D}^{a}) \tag{5-40}$$

$$\mathbf{J}(\mathbf{D})^{ab} = \mathbf{J}^{ab}(\mathbf{D}) + \mathbf{J}^{a}(\mathbf{D}^{b}) + \mathbf{J}^{b}(\mathbf{D}^{a}) + \mathbf{J}(\mathbf{D}^{ab}) \tag{5-41}$$

In general, a derivative Coulomb operator is obtained as a sum.

$$\mathbf{J}(\mathbf{D})^{\alpha} = \sum_{[\mu+\nu=\alpha]'} \mathbf{J}^{\mu}(\mathbf{D}^{\nu})\, f(0,\mu,\nu) \tag{5-42}$$

In Eqn. (5-42), the restriction on the summation is different than in prior equations, and this difference is distinguished with a prime symbol on the brackets that show the summation restriction, i.e. $[\mu+\nu=\alpha]'$. This difference is that μ and ν may be the zeroeth order result, which means they may be the integer list [0 0 0 . . .]. In the restricted summations of earlier equations, this initial or zeroeth order list was not included. Derivative **J** and **K** operators are constructed alike and it is practical to combine their construction just as would be done in constructing the Fock operator for a conventional SCF calculation.

The construction of individual terms in the right hand side of Eqn. (5-42) is accomplished in the following way, which comes about from chain-rule differentiation.

$$\left[\mathbf{J}^{\mu}(\mathbf{D}^{\nu})\right]_{st} = \sum_{pq} \mathbf{D}^{\upsilon}_{pq}\, (st\,|\,pq)^{\mu} \tag{5-43}$$

$$\mathbf{D}^{\alpha} = \sum_{[\mu+\nu=\alpha]'} \left\{ \mathbf{U}^{\mu\dagger}\mathbf{D}^{\nu} + \mathbf{D}^{\mu}\mathbf{U}^{\nu} \right\} \tag{5-44}$$

The separation and construction of the derivative Fock operators in this way corresponds to the what Takada, Dupuis and King termed "skeleton" Fock matrices [T-7]. If the basis set is not dependent on the parameters, then the derivative two electron integrals, $(st\,|\,pq)^{\mu}$, are identically zero and the derivative Fock operators are much simpler to set up. In any situation, the derivative Fock operator matrix may be written as

$$\mathbf{F}^{\alpha} = \mathbf{h}^{\alpha} + \mathbf{J}(\mathbf{D})^{\alpha} - \frac{1}{2}\mathbf{K}(\mathbf{D})^{\alpha} \tag{5-46}$$

As with the zeroeth order Hartree-Fock equations, the dependence of the derivative Fock operator on the derivative wavefunction (via **D** and **U** matrices) means that the solution may be reached iteratively. From Eqn. (5-32), an element by element iterative correction equation is,

$$U^{\alpha}_{mr}\,(E_{mm}-E_{rr}) \;=\; R^{\alpha}_{mr}E_{rr} \;-\; G^{\alpha}_{mr} \;+\; X^{\alpha}_{mr} \qquad (5\text{-}47)$$

$\mathbf{G}^{\alpha}$ is computed initially taking **U** (initial) to be zero. Then Eqn. (5-47) is used to find a new value of the **U** elements in the off-diagonal blocks where **E** is strictly zero. A similar element by element expression for the diagonal blocks comes from Eqn. (5-37).

The energy derivatives are obtained from differentiating the energy expression. For the specific case of a closed-shell wavefunction, the energy is given as

$$E \;=\; \frac{1}{2}\,\mathrm{Trace}\left\{\mathbf{D}\,(\mathbf{h}+\mathbf{F})\right\} \qquad (5\text{-}48)$$

Differentiating this once with respect to the parameter a will mean that E^{a} may be computed from $\mathbf{D}^{a}$, $\mathbf{F}^{a}$, and $\mathbf{h}^{a}$. However, identities corresponding to the "n+1 rule" result in a simplification, and it can be shown that only the zeroeth order density and wavefunction is needed to evaluate the first derivatives.

$$E^{a} \;=\; \frac{1}{2}\mathrm{Trace}\left\{\mathbf{D}\left(\mathbf{h}^{a} + \mathbf{J}^{a}(\mathbf{D}) - \frac{1}{2}\mathbf{K}^{a}(\mathbf{D})\right)\right\} \qquad (5\text{-}49)$$

Higher energy derivatives may be evaluated by successive differentiation and use of the "n+1" or "2n+1" rules. Nee, Parr and Bartlett developed the powerful "2n" and "2n+1" rules in this context in 1976 [N-3]. Their result has been generalized to multiple parameters in the DHF implementation by Dykstra.

The general derivative approach outlined here represents an important advance in electronic structure methodology because all the necessary steps have been put into a procedure which is uniform for all levels of differentiation. A computer program implementing all the ideas that have led to this point need not have routines that are specific to the order of differentiation. The whole task is done at once.

Schaefer and coworkers have presented a number of interesting reports of methods for obtaining derivatives of SCF energies [G-6,H-12,O-4:6,S-22,Y-3]. These approaches have been employed in numerous applications studies and have been generalized to about fourth order of differentiation and to general types of reference wavefunctions including MCSCF. These reports give derivative expressions directly in terms of individual one- and two-electron integral quantities. While the matrix organization that has been used in this chapter provides one of the best ways of seeing uniformity in the expressions for all orders of differentiation, the integral-by-integral development is helpful in another way, that of showing how identities among integral quantities might be exploited.

For geometrical energy derivatives, computation and processing of the two-electron integrals is a sizable task. A two-electron integral quantity is invariant to simultaneous translation or rotation of all (basis function) centers involved in that integral quantity. Letting i, j, k, . . . refer to atomic basis functions, the total derivative of the two-electron integral $(ij \mid kl)$ with respect to a geometrical parameter a is simply

$$(ij \mid kl)^a = (i^a j \mid kl) + (ij^a \mid kl) + (ij \mid k^a l) + (ij \mid kl^a) \qquad (5\text{-}50)$$

where i^a means that in the integral, the i-atomic basis function has been replaced by the function that is the derivative of that function with respect to the parameter a. If the geometrical parameter happens to be identical translation of all centers, then by the translational invariance, the total derivative integral is zero [K-2]. The individual terms on the right hand side of Eqn. (5-50), however, are not necessarily zero, but are now related to each other. That relation may be useful for evaluating derivatives with respect to certain other geometrical parameters. Through rotational and translational invariance properties, and through molecular symmetry, the task of evaluating derivative two-electron integrals has been reduced dramatically. Kahn demonstrated relationships arising from rotational invariance [K-4], and Vincent [V-3:4], Simons and coworkers [B-20;J-5], Schlegel, Binkley and Pople [S-23], Taylor [T-8], Dupuis and King [D-26], and Schlegel [S-24] have brought the derivative integral evaluation to a very high level of sophistication and efficiency.

Derivatives of Correlated Wavefunctions. Correlated wavefunctions are usually expansions in a basis of electron configurations, and so the general ideas for treating basis sets may be employed. However, a configurational basis is dependent on the molecular orbitals, the molecular orbitals are constructed from atomic basis functions, and the atomic orbitals may be dependent on the embedded parameters. Thus, differentiating a correlated energy is complicated. It may involve obtaining derivatives of the expansion coefficients, derivatives of the molecular orbitals (as done in DHF or CPHF), and as always, derivatives of the integrals over the basis functions.

Configuration interaction is a linear basis set expansion. Derivative equations for CI are formally straightforward. They are those given in the earlier section of this chapter on linear basis set of expansions. The complications from the configurational dependence on the molecular orbitals, and then on the basis functions, enter only into the derivative Hamiltonian matrix, such as $\mathbf{H}_0^a$ in Eqn. (5-11). For instance, the derivative of the element $[\mathbf{H}_0]_{11}$ of a CI matrix, where the row and column choice of "1" is meant to refer to an SCF reference configuration, is the first derivative of the SCF energy. It is in this way that SCF energy derivatives and eventually orbital function derivatives, as obtained with a CPHF or DHF procedure, all enter into the process of differentiating the CI eigenvalue equations. There has been considerable success in obtaining derivatives of CI wavefunctions. Pople and coworkers [K-5] reported an analytic first derivative method for CID wavefunctions in 1980 at the same time that Schaefer and coworkers [B-21] reported their CI analytic first derivative method. Both studies reported how equilibrium geometries had been rapidly obtained by knowing the energy gradients, and this success opened the door to the current era of electronic structure studies where derivative methods are extensively employed.

Further elaboration on the details of derivative CI methods would have to tie in with aspects of the computational implementations, and that goes beyond the scope of this chapter. Several papers have provided quite general discussions of the problem, such as those by King and Komornicki [K-3], Handy and Schaefer [H-10], Jorgensen and Simons [J-6], and Simons, Jorgensen and Helgaker [S-25].

Derivatives of correlated wavefunctions obtained from many-body perturbation theory have been obtained. There is a significant difference from CI, however, since the MBPT expansion coefficients are not determined variationally. They are not found by an eigenequation and so that condition is not available for direct differentiation. Even so, the elements that enter the MBPT energy expression may be differentiated, and methods have been found to obtain through third derivatives of second order (MBPT(2) or MP2) energies [H-13:14,P-11]. Coupled cluster wavefunctions, which may be viewed as an infinite order many body perturbation result, have yielded to analytic energy differentiation by Bartlett and coworkers [F-3,S-30], with a more recent scheme by Schaefer and coworkers [S-31]. Important in these development is the formal demonstration of how the differentiation of the expansion coefficients or amplitudes may be avoided.

Overall, formal understanding and practical methods for energy derivatives in molecular structure have reached a very significant point. Efficient calculation of numerous properties has become possible for a wide range of chemical problems. It is likely that algorithmic improvements will be found that make the procedures even more attractive, or in some case, extend the level of differentiation. What needs to be considered as such developments take place is the significance of the derivatives themselves. Where they correspond closely to experimentally measurable properties, their values and the methods for obtaining them are essential products of theoretical investigation. Where the correspondence is indirect, it may be more fruitful to combine derivative results with more conventional (finite perturbation) surface information to make the connection with measurement a stronger one. Predicting a vibrational *transition* frequency may be more useful than the geometrical gradients of a potential around the equilibrium.

Chapter Six

MOLECULAR VIBRATIONS

Interesting information obtainable from potential energy surface calculations or from gradient calculations at stationary points is that of how a molecule's structure is subject to deformation with increasing internal energy. This is given by knowing the shape of a surface around a minimum. Experimental investigation is sometimes motivated by the prospect of deducing just such potential surface information for its own sake. In the reverse sense, a calculated surface, or a local surface or a surface of properties might be used to calculate the parameters or constants that arise in the analysis of vibrational spectra. When an accurate calculation of such vibrational parameters and constants can be carried out prior to their measurement, the calculation could naturally serve to aid spectra interpretation and analysis. This is particularly so for exotic species with few chemical analogs, and this has happened in several cases. Thus, there is a very definite and important role for electronic structure calculations in vibrational spectroscopy, and the full impact of calculational tools in this area is still to come.

Electronic structure calculations can map out a potential surface, or a region of it, in a point by point fashion, with energy gradients and force constants obtained after fitting the surface to some type of function. Alternatively, the analytical differentiation methods that have been developed in the last several years can be employed to find the energy gradients and force constants at particular points, such as an equilibrium structure. If a functional representation of the surface is required, the geometry derivative information may be incorporated into the fit of the surface. Because of the power of differentiation or gradient methods, calculation of equilibrium force constants has become standard, and there is a sizable body of calculational results. From normal mode analysis using computed equilibrium force constants, harmonic frequencies have been obtained as well.

Computing true transition energies requires energy derivatives beyond the second ones (force constants), or requires that surface points span more than the immediate region of the equilibrium in order to account for anharmonicity. The difference between harmonic frequencies and fundamental transition frequencies is often several percent. For calculation of either harmonic or of transition frequencies, the concern in an electronic structure calculation is simply how to accurately determine the shape of the surface and the way it is changing.

Vibrational Transitions in Diatomics. The most complete, currently available understanding of the calculation of vibrational potentials, transition frequencies and vibrational state properties is for diatomic species. For two-body systems an exact vibrational treatment is easily carried out via the Numerov-Cooley numerical method [C-9:10], and so all the error may be associated with the quality of the potential. The Numerov-Cooley method can generate a whole manifold of vibrational state energies and transition frequencies. Of course, while diatomics serve as good test systems to see how transition frequencies are affected by the electronic structure level used to generate the potential, the important surface features that couple vibrational motions in polyatomic systems can not be checked.

TABLE 6.1 lists calculations of the fundamental vibrational transition frequencies for a small set of diatomics. The error range at the DZ/SCF level is the widest of any of the levels listed. At all SCF levels, the most common feature is an overestimation of the transition frequencies. As discussed already, this is partly because the SCF approximation exaggerates the electron density in the bonding regions. As the bond is stretched, the SCF potential tends to rise too sharply. Non-dynamical correlation, at the least, is required for a more correct shaping of the potential. Because SCF potentials tend to be too steep, the vibrational levels tend to be somewhat too far apart in energy, and that means an overestimation of the transition frequencies. The same holds for the equilibrium frequencies: SCF usually overestimates, though it is possible for them to be less in error since they "sample" but one point on the potential curve.

The overestimation of the frequencies at the SCF level is often more with DZP bases than with DZ bases. This follows the trend in bond length predictions discussed in Chapter Four in a usual chemical sense. Contraction of a bond upon some type of substitution or change in coordination usually goes along with an increase in the force constant and an increase in the vibrational frequency. In a similar way, a change in the level of theoretical treatment that leads to a bond length contraction will likely lead to a frequency increase as well.

Correlation effects continue the correspondence between bond length and vibrational frequency determination. In Chapter Four, it was shown that correlation effects usually lengthen a bond. As the results in TABLE 6.1 show, when correlation effects are first incorporated, the vibrational frequencies are diminished. The most accurate calculations of vibrational transition frequencies of diatomics have been obtained at the most complete electron correlation levels available, and these are the coupled cluster methods.

TABLE 6.1

Vibrational frequencies (in cm^{-1}) of diatomic molecules. Equilibrium (ω_{eq}) frequencies are the harmonic frequencies evaluated at the equilibrium for the given potential curve. Transition frequencies were obtained from the difference of vibrational state energies determined numerically for the given potential curve.

Molecule	*Basis*	*SCF*	*MBPT(2)*	*CISD*	*CCD/ACCD*	*Expt.[H-5:8]*
H_2 (ω_{eq})	DZ	4713	4598	4417		
	(4s2p) [B-6]			4376		
	(5s3p1d)	4599		4394		4395
H_2 ($v=0\rightarrow1$)	DZ	4559	4405	4167		
	(4s2p) [B-6]			4164		
	(5s3p1d)	4379		4165		
HF (ω_{eq})	DZ	4233	3832	3810	3774	
	DZP	4499	4198	4257	4212	
	ELP[a]	4447	4089	4177	4156	4139
HF ($v=0\rightarrow1$)	DZ	4082	3661	3673	3594	
	DZP	4369	4015	4073	4026	
	ELP[a]	4324	3921	4009	3977	3961
CO (ω_{eq})	DZ	2264	1871	2095	2039	
	DZP	2417	2090	2256	2208	2170
CO ($v=0\rightarrow1$)	DZ	2241	1845	2088	2020	
	DZP	2395	2064	2233	2185	2143
N_2 (ω_{eq})	DZ	2590	1833			
	DZP	2704	2094	2436		2360
N_2 ($v=0\rightarrow1$)	DZ	2567	1782			
	DZP	2680	2054	2414		
F_2 (ω_{eq})	DZ	1317	848			
F_2 ($v=0\rightarrow1$)	DZ	1304	581			
	TZP				939	892

[a] The ELP basis, described in Chapter Seven (p. 144), is multiply polarized.

Vibrational transition frequencies, as opposed to equilibrium frequencies, are dependent on the shape and features of the potential curve even when it reaches somewhat above the energy of the vibrational state. The tunneling of vibrational wavefunctions into classically forbidden regions means that these wavefunctions sample the potential farther up. Generally, a potential needs to be known accurately at least one or two vibrational quanta above the energies of the vibrational states being investigated.

In vibrational spectroscopy, transition frequencies are the measured quantities. With a set of diatomic transition frequencies, a useful expression is obtained by fitting them to a polynomial in the variable $(v+\frac{1}{2})$, where v is the vibrational quantum number [H-5,K-8]. The constants in this expression characterize the potential, and it is often the goal of *ab initio* calculations to obtain values for these constants to compare with experiment.

$$G(v) = \omega_e (v+\tfrac{1}{2}) - \omega_e\chi_e (v+\tfrac{1}{2})^2 + \omega_e y_e (v+\tfrac{1}{2})^3 + \ldots \qquad (6\text{-}1)$$

This is the term value expression for the vibrational states; a usual energy level expression, E(v), differs by there being a factor of hc in every term. G(v) gives the frequency or state energy in wavenumbers relative to the bottom of the potential (i.e., $V(r_e) = 0$) were the potential to be deduced from the state energies. The constants are taken to be equilibrium values. The anharmonicity constants, $\omega_e\chi_e$, $\omega_e y_e$ and so on are normally reported as products, not as χ_e, y_e, etc.

Fine precision comparison between experimental and computed values for the constants in Eqn. (6-1) may be subject to certain problems. As discussed in Chapter Two, the number of vibrational frequencies used and the truncation of the expansion affect the values of the Eqn. (6-1) constants that would be derived from measured spectra, or from directly calculated spectra. Force constants, the derivatives of the energy with respect to the stretching coordinate, may be related to the constants in Eqn. (6-1) by carrying out an anharmonic oscillator analysis using more and more terms in a power series expansion of the potential energy. Truncating at a harmonic potential relates ω_e to $k_e = V''(r_e)$, the harmonic force constant, while quadratic terms are needed to relate the first anharmonicity to the the potential derivatives [K-8]:

$$\omega_e\chi_e = \frac{1}{24\,\mu} \left\{ 5\left(\frac{V'''(r_e)}{V''(r_e)}\right)^2 - 3\left(\frac{V''''(r_e)}{V''(r_e)}\right) \right\} \qquad (6\text{-}2)$$

If a specific functional form is assumed for the potential, such as a Morse potential, then a few experimental term values (transition frequencies) can serve to generate a potential through fitting to Eqn. (6-1) and relating to the anharmonicity parameters in the chosen potential via Eqn. (6-2).

The energies or frequencies can also be expressed relative to the v=0 state by simply subtracting the term value for the v=0 state.

$$G_0(v) = G(v) - G(0) \tag{6-3}$$

With $G_0(v)$, it is convenient to collect terms in the following way.

$$\omega_o = \omega_e - \omega_e\chi_e + \frac{3}{4}\omega_e\chi_e + \ldots \tag{6-4}$$

$$\omega_o\chi_o = \omega_e\chi_e - \frac{3}{2}\omega_e y_e + \ldots \tag{6-5}$$

$$G_o(v) = \omega_o v - \omega_o\chi_o v^2 + \omega_o y_o v^3 + \ldots \tag{6-6}$$

In this operational analysis, $v = -\frac{1}{2}$ represents a fictitious choice for the vibrational quantum number value where the energy of the system is the same as the minimum potential energy.

Harmonic frequencies for real chemical species differ from the zero point energies by a noticeable amount. For HCl, ω_e is 2890 cm^{-1} while ω_0 is 2938 cm^{-1} [H-5]. This means that anharmonicity already is important in the lowest vibrational state. It will be more important for higher states because of the non-linear dependence on the vibrational quantum number of the anharmonicity terms in Eqn. (6-1). Differences between anharmonicity parameters such as $\omega_e x_e$ and $\omega_0 x_0$, though, tend to be less noticeable because of the normally rapid decrease from $\omega_e x_e$ to $\omega_e y_e$ and so on. For polyatomics, the harmonic frequencies again correspond to the classical frequencies of the system for infinitesimally small amplitude displacements from equilibrium. The distinctions between harmonic frequencies, frequencies of the ground state, and transition frequencies are important ones when calculated results are compared with measured values.

Harmonic Frequencies and Force Constants. There are quite a few studies of harmonic frequencies of polyatomics. A 1980 paper by Yamaguchi and Schaefer [Y-4] presented interesting comparative results for a handful of small molecules, H_20, CH_4, H_2CO, HCN and NH_4^+. They used primarily DZ and DZP bases, but also a basis which was essentially TZ2P, though only singly polarized on hydrogen centers. Harmonic frequencies were obtained at both the SCF level and CISD levels, and TABLE 6.2 gives certain of the values that they obtained. The characteristic overestimation for stretching and breathing modes at the SCF level is apparent in these results. Generally, augmenting the DZ basis with polarization functions (DZP basis) increased the frequencies. Further improvement to the extended basis diminished the frequency values in most cases.

An interesting result in the Yamaguchi and Schaefer study is that DZ/CI values were found to be the most reliable, even though DZP/CI is a higher level of treatment. As already discussed several times, this can be a consequence of cancellation of neglected effects. Yamaguchi and Schaefer made a further observation that though the DZP/CI errors tended to be greater than the DZ/CI errors, the DZP/CI error tended to be much more systematic. The errors at the higher level gave frequencies that were uniformly greater than the experimental values. This means that systematic adjustment of the calculated values may sometimes yield reliable values.

Pulay and coworkers [P-12] systematically examined convergence in correlation and basis set effects on the force constants of HCN, ammonia and HF. An idea that Pulay advances is that comparisons of vibrational results from different *ab initio* methods should be comparisons of force constants, not just frequencies. This may be the most appropriate comparison when several force constants (energy derivatives) have been found. At the same time, if *transition* frequencies were calculated, their comparison provides an overall measure of the potential surface quality that a limited set of force constants does not. This is especially true if a manifold of transition frequencies is calculated, for it is difficult for a potential surface to be improperly shaped and yet yield a large set of vibrational states accurately. (For polyatomic systems treated by normal mode analysis, the comparing force constants instead of transition frequencies circumvents the problems of mode coupling, and so is a common practice.)

Pulay and coworkers [P-12] consider a bond stretching force to be composed of a valence electronic part and a core (plus nuclear) electronic part. They suggest that the core contribution is more sharply changing around the equilibrium than the valence part and that most of the potential's anharmonicity near the equilibrium results form this contribution. The physical idea behind this is that the atomic cores are small, positively charged electron distributions. For the most part, there is just a simple 1/R repulsion between the cores of two atoms. The second derivative of this potential, 2 R^{-3}, is the force constant and is clearly quite distance dependent. It might also be said that core-valence attraction may be changing as rapidly, and as an attractive force, it will partly balance the core-core repulsion.

TABLE 6.2

Ab initio harmonic frequencies in cm^{-1} reported by Yamaguchi and Schaefer [Y-4]. The frequencies are listed by the molecular point group symmetry representation of the normal mode. Listed as experimental values are harmonic frequencies inferred from measured transition frequencies for water [B-22], formaldehyde [D-27], and methane [G-8].

	DZ/SCF	*DZP/SCF*	*TZ2P/SCF*	*DZ/CI*	*DZP/CI*	*TZ2P/CI*	*Expt.*
Water							
a_1	4028	4164	4128	3710	3967	3937	3834
a_1	1710	1751	1757	1649	1693	1688	1647
b_1	4204	4287	4234	3880	4088	4043	3943
Formaldehyde							
a_1	3223	3149	3028	3074			2944
a_1	1878	2006	1703	1869			1764
a_1	1651	1656	1544	1596			1563
b_1	1324	1335	1194	1243			1191
b_2	3315	3226	3112	3155			3009
Methane							
a_1	3177	3174	3152	3001	3116		3026
e	1698	1671	1671	1571	1601		1583
t	3306	3294	3250	3129	3257		3157
t	1506	1457	1458	1407	1397		1367

Pulay and coworkers have argued that to evaluate force constants properly, it is necessary that the core-core contribution be correct. Since this contribution is distance dependent, the true equilibrium separation should be used [P-12] even if that is not the equilibrium separation predicted at the chosen level of calculation. This seems particularly appropriate when a low level of treatment has been employed and the errors in the equilibrium geometry may be sizable. Among well-correlated, large basis set calculations with well-described cores, the errors are smaller and their sources are less apparent. It is important to recognize that obtaining force constants and equilibrium bond lengths, both to high accuracy, is difficult. As Pulay et al. [P-12] point out, assuming a typical Morse potential, a 1% contamination of the force constant results from only about a 0.002 Angstrom error in the point of evaluation, the equilibrium distance.

Though the accuracy of a calculated force constant may be very dependent on accurately locating the potential minimum, a main point of Pulay's work [P-12], it is possible for calculated transition frequencies to be less dependent on how well the equilibrium is determined. Consider the vibrational wavefunctions of a diatomic with a flat-bottomed potential. Then, consider a slight change in that flat potential bottom, such as "tipping" it one way or the other, that leaves the vibrational wavefunctions and state energies little affected. Such a change, though, could make a difference in the location of the minimum in view of the flatness of this hypothetical diatomic. Consequently, there could be a noticeable change in the harmonic force constant *without* there being a noticeable change in the transition frequencies. The subtle point, here, is the same one mentioned in Chapter Two concerning the extent of physical significance of an "equilibrium" structure when discussing a quantum mechanical system that one knows is never at rest. Certainly, the equilibrium is of much more calculational than physical significance. For vibrations, knowing the equilibrium is most essential for knowing other *equilibrium* properties (e.g., force constants).

Anharmonicity. Anharmonicity effects, those arising from everything in the potential other than the harmonic forces, are of interest for precise determinations of vibrational energies. The biggest sources of anharmonicity are usually potential terms that are cubic in the geometrical parameters and often these alone are referred to as the anharmonic terms. Quartic contributions to the potential can be important, and as one ascends the ladder of vibrational levels, still higher order terms are required for accurate descriptions.

In a study of methane, Pulay, Meyer and Boggs [P-13] found that SCF level cubic force constants were in good agreement with those deduced from experimental measurements. This suggests that neglected correlation effects on cubic force constants are small. In the 1983 study by Pulay, Lee and Boggs [P-12] it was firmly concluded that electron correlation has little effect on cubic and quartic stretching force constants. Ermler et al. [E-2] found in recent detailed treatments of the vibrational states of water that for anharmonic force constants, SCF yields better agreement with corresponding correlated values for the harmonic constants. Gaw and Handy [G-9] have reported that the errors in SCF anharmonic force constants usually attributed to lack of correlation effects are actually due to errors in fitting SCF surfaces. They used gradient techniques to be certain of the numerical reliability of their SCF anharmonic constants and again concluded that SCF yields good values for other than the harmonic constants.

This body of results on anharmonicities, which is in line with Pulay's ideas about proper description of core-core contributions to the potential, tends to justify a practical strategy for calculating vibrational parameters. It is to carry out correlated calculations to find the harmonic force constants, but use only SCF to find whatever anharmonicities are sought. Since the anharmonicities in the potential are higher order derivatives of the energy, this process offers considerable computational savings and probably sacrifices little in terms of reliability.

Recently, Bartlett et al. [B-47] have carried out a very thorough and very important study of the vibrations and force fields of water. This was done with a high quality basis of 39 Slater type orbitals and comparisons were made between SCF and correlated levels through CCSDT. At the highest level of treatment, agreement between calculated and experimental values for fundamental, overtone and combination transition frequencies was superb. Certain of their results are shown in TABLE 6.3 The mean error for water vibrations at the highest level was 22 cm^{-1} or 0.6%. Correlation effects, even through the inclusion of triple substitutions, produce their most significant change in the harmonic force constants as opposed to affecting the anharmonicities, as shown in TABLE 6.4. These results strongly support Pulay's thinking, and they show that it is meaningful to evaluate the harmonic force constants at the true equilibrium rather than at the equilibrium for the given level of calculation. The substantial range (about 15% of the mean) in the symmetric stretching force constant of water from the various levels of treatment is reduced to a 1% variation when the force constant is evaluated at the experimental equilibrium for all levels.

Calculated Force Constants and Vibrational Frequencies. Calculation of force constants has become routine, and a survey of several calculations helps to illustrate the capabilities of calculational tools. An especially fine example of *ab initio* calculation of vibrational data is the 1982 study of diacetylene carried out by Botschwina [B-23]. To find an equilibrium structure, an essentially triple-zeta basis SCF calculation was carried out and then a small empirical adjustment, based on corresponding acetylene results, was made. Derivatives of a fitted SCF potential surface gave an initial set of force constants. The diagonal quadratic stretching force constants were empirically adjusted using four experimental fundamental frequencies. Botschwina found that the vibrational parameters obtained for diacetylene were similar to those of cyanoacetylene, as might be expected. The force constants obtained are listed in TABLE 6.4.

Botschwina continued his study of diacetylene in a very useful way. The potential represented by the calculated force constants was used in an approximate vibrational Hamiltonian. Low-lying vibrational state energies were obtained by diagonalizing the matrix representation of this Hamiltonian in a basis of harmonic

TABLE 6.3

Vibrational transition energies (in cm^{-1}) of water isotopomers calculated by Bartlett et al. [B-47] from a CCSDT-1 potential energy surface. Transitions are from the ground state (0,0,0). For certain of the transitions, the Fermi-type interactions have been removed.

Excited State			H_2O		HDO		D_2O		HTO		T_2O	
ν_1	ν_2	ν_3	*Calc.*	*Obs.*[a]	*Calc.*	*Obs.*[a]	*Calc.*	*Obs.*[a]	*Calc.*	*Obs.*[a]	*Calc.*	*Obs.*[a]
1	0	0	3652	3652	2721	2727	2669	2668	2296	2300	2235	2237
0	1	0	1625	1595	1430	1403	1200	1178	1357	1324	1013	995
0	0	1	3747	3756	3700	3707	2782	2788	3708	3717	2362	2367
2	0	0	7218	7211	5352	5364	5293	5292	4530		4439	
0	2	0	3217	3156	2837	2779	2382	2340	2692		2013	
0	0	2	7397	7425	7231		5509		7246		4683	
1	1	0	5262	5227	4138	4120	3862		3638		3244	
1	0	1	7232	7244	6410	6416	5364	5374	6004		4537	4537
0	1	1	5351	5331	5108	5090	3971	3956	5052		3368	3358
1	1	1	8821	8807	7805		6546	6533	7333		5538	

[a] See [B-47] for references for experimental values.

TABLE 6.4

Harmonic and first anharmonic spectroscopic parameters (in cm^{-1}) for the vibrations of water [B-47].

	SCF	*CISD*	*MBPT(4)* [a]	*CCSD*	*CCSDT-1*	*Expt.* [b]
ω_1	4131.8	3930.5	3865.2	3866.2	3829.8	3832.2
ω_2	1770.6	1701.9	1687.6	1688.4	1677.0	1648.5
ω_3	4235.5	4035.0	3975.3	3974.5	3939.5	3942.5
χ_{11}	-38.4	-40.7	-42.4	-42.5	-43.3	-42.6
χ_{22}	-20.2	-17.3	-17.0	-17.0	-16.8	-16.8
χ_{33}	-43.8	-46.6	-48.0	-47.9	-48.9	-47.6
χ_{12}	-13.5	-13.7	-14.3	-14.0	-14.9	-15.9
χ_{13}	-152.2	-159.7	-163.8	-164.5	-167.4	-165.8
χ_{23}	-18.6	-20.1	-21.0	-20.3	-21.4	-20.3

[a] SDQ configurations included. [b] [B-48]

oscillator product functions. Thus, both harmonic and anharmonic (transition) frequencies were obtained, and these have been listed in TABLE 6.5. Anharmonicity in the fundamental stretching transitions amounts to a few percent of the harmonic frequencies. Botschwina also calculated infrared intensities. Using correlated wavefunctions, information was obtained on the dipole moment dependence on the stretching coordinates near equilibrium. By integrating with the harmonic oscillator product functions and then transforming the representation of the dipole moment to the basis of the final vibrational states, the transition moments were obtained. Botschwina found rather good agreement among the transition moments computed in this way and the transition moments obtained with a doubly harmonic analysis. In the doubly harmonic analysis, all vibrations are treated as harmonic oscillators and the dipole moment is taken to be a linear function in each displacement coordinate. Botschwina's results led to a prediction of a significant enhancement in a triple bond stretching intensity upon deuterium substitution.

TABLE 6.5

Vibrational force constants and frequencies obtained by Botschwina [B-23] for diacetylene. Force constants are in units of Joules per Angstrom squared (or cubed) times 10^{-18} and frequencies are in cm^{-1}. r, s, t, u, v are used to label the bond stretching displacement coordinates, going from one end of HCC-CCH to the other.

Harmonic force constant matrix

	r	s	t	u	v
r	6.402				
s	-0.111	15.613			
t	-0.015	0.647	6.934		
u	0.003	-0.230	0.647	15.613	
v	0.003	0.003	-0.015	-0.111	6.402

Diagonal cubic and quartic force constants

r (v)	-39.1	198
s (u)	-99.5	497
t	-41.1	203

Harmonic stretching frequencies

	HCCCCH	HCCCCD	DCCCCD	
ω_1	3464	3464	2679	(sym. C H)
ω_2	2213	2173	2092	(sym. C C)
ω_3	882	867	853	(C-C)
ω_4	3465	2676	2673	(asym. C H)
ω_5	2048	1961	1914	(asym. C C)

Anharmonic stretching frequencies

ν_3	874	859	845
$2\nu_3$	1742	1716	1684
$\nu5$	2022	1932	1885
$\nu2$	2184	2143	2059
$3\nu_3$	2610	2577	2523
$3\nu_3$	2910	2597	2731
$\nu_3+\nu_5$	2901	2797	2906
$\nu_2+\nu_3$	3057	3008	2906
ν_1	3328	3329	2608
ν_4	3329	2606	2602

Hydrides, AH_n, have been the subject of quite a number of studies of vibrational parameters. Gaw and Handy [G-10] carried out SCF calculations for water and ammonia and once again showed that anharmonic constants were accurately obtained at the SCF level. From their results, it is interesting to see the sizable effect that nitrogen 3d polarization functions have on one, low frequency vibration. Polarization functions play a major role in properly determining the pyramidal equilibrium structure of ammonia, and so a drastic effect on an inversion-like vibration is not surprising. The reported harmonic frequencies are in TABLE 6.6. Using a model vibration-rotation Hamiltonian, rotation-vibration constants and λ–doubling constants were also calculated in this study.

Another AH_n species, the methyl radical was the subject of an interesting study by Botschwina and coworkers [B-14]. They generated a potential energy surface for the symmetric stretching motion, or breathing, and for the out of plane bending, or inversion, using spin-unrestricted SCF energies and spin-unrestricted correlated energies obtained with SCEP and employing the CEPA-1 approximation for higher order effects. The potential was fit to a sixth order polynomial in the breathing coordinate and a tenth order polynomial in the curvilinear bending coordinate. Cubic and quartic cross terms were included in this two-dimensional surface. A large basis of harmonic oscillator product functions was used to find vibrational state energies for the two vibrations. The results agreed nicely with experimental values that existed. The Raman active symmetric stretch frequency which had not been measured was predicted from these calculations along with rotational constants for the low-lying vibrational states. A CEPA-1 dipole moment surface was calculated and then transition moments were calculated. From these *ab initio* calculations, a most

TABLE 6.6

SCF calculated harmonic vibrational frequencies (in cm-1) of ammonia obtained by Gaw and Handy [G-10].

	DZ Basis	*DZ+d Basis*	*Expt. [B-32]*
ω_1	3775.0	3706.3	3506
ω_2	585.3	1187.8	1022
ω_{3a}	3992.2	3851.2	3577
ω_{4a}	1800.2	1841.3	1691

comprehensive, high quality set of predictions of spectroscopic constants of the methyl radical was produced. TABLE 6.7 lists the force constants as obtained at the SCF and correlated levels and certain of the vibrational term energies.

Calculated vibrational frequencies have been used to unravel a number of chemical questions. Knowing the frequencies means the zero-point vibrational contributions to the molecular stability are known. From that, more complete knowledge of relative stabilities comes about. Schaefer and coworkers [H-15] pursued this in studying H_2SiC isomers. The lowest energy isomer was silylidene where the silicon is formally a radical site, doubly bonded to CH_2. Much higher in energy is silaacetylene, HSiCH, and above that is a vinylidene radical structure. Zero point energies contributed to the understanding of how the silaacetylene isomer had a barrier to rearrangement into the most stable structure, a point first made by Gordon and Pople [G-12].

A challenging application of *ab initio* vibrational methods was the study by Fogarasi, Boggs and Pulay on the ethynyl radical, HCC [F-4]. In this system, an excited electronic state lies around 2000 cm^{-1} above the ground state, and so calculations were aimed at obtaining vibrational frequencies of both states. CI calculations were carried out with a 6-311G** basis and a pointwise potential surface was mapped out. Harmonic force constants were rescaled downward by several percent on the basis of like calculations done on HCN where accurate force constants are known. For the ground electronic state, the C-C stretching frequency and the C-H stretching frequency that were calculated were about 200 cm^{-1} below the experimental values of Jacox [J-7]. Neglected anharmonicity effects, were they to be included, could only worsen the discrepancy. The calculations carried out for the first excited electronic state showed it to be lower than previous studies had indicated. Its structure and stretching vibrational frequencies were computed. A number of possibilities were considered in detail to resolve the discrepancy between experiment and theory including the possibilities that transitions to the excited state had been observed instead of fundamental ground state transitions or that matrix effects were sizable in the laboratory measurements. The theoretical results, showing a small diminishment in the stretching frequencies upon electronic excitation, are summarized in TABLE 6.8.

Vibrational frequencies have been calculated for stable small molecules, exotic molecules, and large molecules alike. Fox et al. [F-5] calculated structures and harmonic frequencies for Al-CH_n species. Botschwina has given very detailed

TABLE 6.7

Vibrational force constants and state energies for the methyl radical as calculated by Botschwina, Flesch and Meyer [B-24]. The values listed as "experimental" are from or are based on reported transition frequencies as discussed in [B-24]. The units for the force constants are the same as in TABLE 6.5. Frequencies are in cm^{-1}.

Potential Term	*UHF-SCF*	*CEPA-1*
Symmetric Stretch Force Constants:		
n = 2	6.193	5.726
n = 3	-19.8	-18.6
n = 4	56.8	53.8
n = 5	-177	-166
n = 6	611	576
Curvilinear Symmetric Out-of-plane Bending Force Constants:		
n = 2	0.0827	0.118
n = 4	7.68	6.81
n = 6	-140	-130
n = 8	3584	3472
n = 10	64438	64438

Vibrational Term Energies

($v_{stretch}$, v_{bend})	Calculated	Experimental
(0, 1)	597.9	606.4
(0, 2)	1288.1	1288.1
(0, 3)	2039.7	2019.2
(0, 4)	2839.4	2791
(1, 0)	3067.4	
(1, 1)	3652.0	
(0, 5)	3688.2	
(1, 2)	4343.6	
(0, 6)	4559.9	
(1, 3)	5092.0	

TABLE 6.8

Calculated harmonic stretching frequencies of HCC in cm^{-1} [F-4].

	Ground State	*Excited State*
C-H stretch	3450	3340
C-C stretch	2044	1740

vibrational data for a series of C, N, P containing molecules [B-25:28], among many others. Pulay and coworkers have obtained force constants for numerous organic molecules including benzene, glyoxal, oxetane and pyridine [P-14:16,B-33]. Even something as unusual as triprismane has been studied [D-28]. And that is just a *small* sampling of what has been done. Clearly, *ab initio* calculations are serving as a serious tool for examining vibrational properties of molecules.

Vibration-Rotation Coupling. Resolution of rotational fine structure in vibrational spectroscopy provides the most detailed parameters about internal molecular motion. In principle, calculations can be used to obtain these parameters from the potential surface. Vibration-rotation interaction constants can be related to cubic force constants [G-7] and so can be evaluated directly using energy gradient methods. Gaw et al. find that the vibration-rotation constants are well determined at the SCF level [G-7]. Rotation can be fully treated along with vibration by using a suitably constructed Hamiltonian. Whitehead and Handy [W-5] showed how to carry out a variational basis set expansion of the vibrational-rotational states for a triatomic using the Watson Hamiltonians, while Estes and Secrest [E-1] have provided a comprehensive theory for calculating vibrational-rotational states for general molecular systems. A fitted potential energy surface as obtained form *ab initio* calculations is required.

The generalizations about basis set and correlation requirements that have been discussed so far do not hold as well for weak complexes or for molecules with many low frequency vibrations. In weak complexes, basis set superposition effects are so troublesome that reliable trends are not apparent. When vibrational frequencies are sought for the purpose of evaluating the molecular stability with zero-point vibrational contributions, though, the errors for weak modes are no more important (no more sizable) than the errors for strong modes. The extra difficulty comes in trying to precisely calculate a weak bond or low frequency vibration. An error size of only a few percent requires a serious calculation.

Perhaps the biggest step remaining for the *ab initio* determination of vibrational frequencies and constants for molecules is the generalization of accurate means for finding vibrational states and vibrational-rotational states using the potential information from electronic structure. Energy surfaces and surfaces of gradients are all calculable and ready to use in studying spectroscopic problems. In many cases, though, the next step, finding transition frequencies, just has not been taken. Generally applicable methods for internal nuclear motion would also make it possible to properly determine the vibrational effects on molecular properties such as polarizabilities, as has been done for diatomics [D-21].

While gradient methods have been responsible for much of the current computational capability for understanding molecular vibration, it may be that conventional potential surface generation will have a bigger role in high precision studies of vibration. The reason for this is that a power series expansion about an individual geometry point in terms of displacement coordinates may need to be continued to very high order to get a representation capable of describing a surface at energies many vibrational quanta above the ground state. It is in low order models of vibration, such as a harmonic model or perturbed harmonic model, that energy gradients provide sufficient and complete information. If the wavefunctions and energies of high-lying vibrational states are sought to an accuracy of 10 cm^{-1}, it will be necessary to know the shape and surface features of the potential energy surface quite high in energy. Undoubtedly, the ideal matching of ideas will be to select points on a surface and obtain energies and gradients at those points. This will provide more information on the surface and how it is shaped than the set of energies alone. What will have to be developed is the strategy for optimum selection of the points. Attention to subtle basis set effects will also be required to achieve very high accuracy.

Chapter Seven

ELECTRICAL PROPERTIES

One of the most important accomplishments of electronic structure theory has been the capability to determine molecular properties. From the very start of investigation of molecules by calculation, that has been a serious goal. Correlations of structures and properties, or of stabilities and properties, are clearly subject to direct and unlimited examination by calculation. In recent years, sophisticated techniques have been developed that make it possible to compute virtually any type of property and to achieve very high accuracy in the values obtained.

One important class of properties that characterize a molecule, the electrical properties, are those properties that relate to a molecule's response to electric fields and electric charges. Some of these are measured directly in various spectroscopic experiments, and some are determined indirectly or are inferred form bulk properties. Some that are calculable have never yet been measured or derived from measurement.

Electrical properties are important in many ways. They explain the longest range interaction between molecules, the electrostatic attraction or repulsion of the molecular charge distributions. This long-range attraction is a fundamental part of what makes a van der Waals or a weak hydrogen bond [D-32]. The same type of interaction may play a role in the orientation or ordering of molecules physisorbed on a surface. Also, the electrical interaction dictated by molecular electrical properties may provide a crucial orienting force for selecting reaction pathways in complex molecular species. The measurement of certain electrical properties can be a probe of how electronic structure and molecular structure are affected by transformations, reactions, substitutions, and external perturbations. Finally, electrical properties can help in understanding and sometimes in devising new spectroscopic methods.

Definitions of Electrical Properties. Classical electrostatics is a starting point for discussing the definitions of molecular electrical properties and their computation. The classical interaction energy for placing a point charge, q_i, at the spatial position (x_i,y_i,z_i) in an electric potential, $V(x,y,z)$, is the product of the charge and the value of the potential at the position of the charge. This product is a term in the classical or quantum mechanical Hamiltonian for the system. The energy for placing a distribution of N fixed point charges in an electric potential is just the sum of the interaction energies for each of the individual point charges.

$$E_{int} = \sum_{i}^{N} q_i V(x_i,y_i,z_i) \qquad (7\text{-}1)$$

The potential function V may be expressed as a power series expansion in terms of the spatial coordinates. Any center for the expansion may be chosen, though a convenient choice is simply the coordinate system origin, (0,0,0). Letting $V_o = V(0,0,0)$, the power series expansion for an arbitrary electric potential, V, is,

$$\begin{aligned} V(x,y,z) = {} & V_o + x\frac{\partial V}{\partial x}\Big|_o + y\frac{\partial V}{\partial y}\Big|_o + z\frac{\partial V}{\partial z}\Big|_o \\ & + \frac{1}{2}x^2\frac{\partial^2 V}{\partial x^2}\Big|_o + xy\frac{\partial^2 V}{\partial x\partial y}\Big|_o + \ldots \qquad (7\text{-}2) \\ & + \frac{1}{6}x^3\frac{\partial^3 V}{\partial x^3}\Big|_o + \ldots \end{aligned}$$

The partial derivatives of the potential, evaluated at the origin or the center of the expansion, are the electric field vector components (V_x, V_y, V_z) where $V_x \equiv \frac{\partial V}{\partial x}\Big|_o$. The electric field gradient tensor components are V_{xx}, V_{xy}, etc. As Applequist has very nicely worked out [A-8:10], it is quite helpful to organize these field terms into a *polytensor* [A-8]. This is useful for seeing the generality of the multipole expansion, and it provides an organization that is quite effective for developing computer programs. The field (or potential) polytensor is a column vector of the derivatives of V.

$$\mathbf{V} = \begin{bmatrix} V_o \\ V_x \\ V_y \\ V_z \\ V_{xx} \\ \cdots \end{bmatrix} \qquad (7\text{-}3)$$

$$\mathbf{V}^T = \begin{bmatrix} V_o & V_x & V_y & V_z & V_{xx} & V_{xy} & V_{xz} & V_{yx} & V_{yy} & \cdots & V_{xxx} & V_{xxy} & \cdots \end{bmatrix}$$

This ordering of the elements in **V** is anticanonical, which means that the indices change like an odometer, the right-most index changing fastest. It is important to notice that V_{xy} and V_{yx} are both included in **V** even though they are identical in value. This is by choice, but as will be seen later, it is a practical choice.

The power series expansion of the potential gives rise to the usual multipole expansion when it is substituted into Eqn. (7-1).

$$\begin{aligned} E_{int} &= V_o \sum_i q_i + V_x \sum_i q_i x_i + \ldots \\ &\quad + \frac{1}{2} V_{xx} \sum_i q_i x_i^2 + V_{xy} \sum_i q_i x_i y_i + \ldots \qquad (7\text{-}4) \\ &\quad + \frac{1}{6} V_{xxx} \sum_i q_i x_i^3 + \ldots \end{aligned}$$

The summations in Eqn. (7-4) correspond to *moments of the charge distribution*. These can be arranged in a polytensor, **M**, where the factors in the interaction energy expression are absorbed into the definition of the polytensor elements.

$$\mathbf{M} = \begin{bmatrix} M_o \\ M_x \\ M_y \\ M_z \\ M_{xx} \\ \ldots \end{bmatrix} \qquad (7\text{-}5)$$

$$M_o = \sum q_i \qquad M_x = \sum q_i x_i$$

$$M_{xx} = \frac{1}{2} \sum q_i x_i^2 \qquad M_{xy} = \frac{1}{2} \sum q_i x_i y_i$$

$$M_{xxx} = \frac{1}{6} \sum q_i x_i^3$$ and so on.

The interaction energy becomes a simple dot product of the two rank one Cartesian polytensors.

$$E_{int} = \mathbf{M}^T \bullet \mathbf{V} \qquad (7\text{-}6)$$

(Applequist and others define a field polytensor, **F**, which is the negative of **V**, and then the interaction energy is the negative of the dot product of the moment tensor and this polytensor.)

The elements of **V** constitute a set of parameters. Adjustment of any one parameter's value amounts to prescribing a different choice for V(x,y,z). (At this point, constraints due to the symmetry of the system or the Laplace equation are ignored.) Eqn. (7-4) represents a potential energy term in the classical Hamiltonian for a system of point charges in an external potential. Correspondence of the dynamical variables (e.g., x_i, y_i, ...) with their quantum mechanical operators generates the quantum mechanical interaction Hamiltonian that may be used for atomic and molecular systems. That interaction Hamiltonian will consist of component moment operators, which are just one-electron operators, scaled by the parameters making up the polytensor **V**. This means that the derivative methods outlined in Chapter Five can be employed directly. There exists a Hamiltonian with embedded parameters, and the derivatives with respect to these parameters are the electrical properties, the quantities that characterize a molecule's response to an external field.

Laplace's equation can be considered a constraint on the external field, $V_{xx} + V_{yy} + V_{zz} = 0$. Differentiating this condition leads to constraints on higher order elements of **V**, constraints that may be stated in a general way.

$$V_{xx\mu\nu\tau\ldots} + V_{yy\mu\nu\tau\ldots} + V_{zz\mu\nu\tau\ldots} = 0 \qquad (7\text{-}7)$$

These constraints may be built into the definitions of the multipole moments as done by Buckingham [B-19,B-29:30] and McLean and Yoshimine [M-18]; these are the *traceless* forms. The constraint has the effect of making several elements redundant, and so the list of unique elements is the most concise with this form. Another form is the *traced Cartesian* form where no constraint is invoked and no factors are introduced. A third form is what will be labelled herein as the *Cartesian polytensor* form. It differs from the traced form in the introduction of the factor $(n!)^{-1}$ where n is the order of the particular multipole moment. (**M** has already been defined in Cartesian polytensor form.) Other definitions are possible, too, but these three probably include the most commonly used and the most conveniently organized. To keep these forms distinguished, Roman letters will be used for the traced forms beyond the dipole. Q is for the second moment, and R is for the third moment. The dipole moment is the same in all three forms, and is designated μ. Greek letters will be used for the traceless forms, θ for quadrupole moments and Ω for octupole moments. "M" with a particular subscript (e.g., M_x, M_{xx}) will be used to designate elements in the polytensor form. As long as the form is made clear, the terms second moment and quadrupole moment, or third moment and octupole moment, may be used interchangeably. Otherwise, it seems to be common practice to reserve the use of quadrupole and octupole etc. for traceless tensor values.

As with most properties, several systems of units are in use for reporting electrical properties. From the standpoint of an electronic structure calculation, atomic units are an automatic choice. TABLE 7.1 lists conversion factors from atomic units for quite a number of electrical tensor properties. The system of units has nothing to do with the form of the tensors, so the conversion factors apply to traceless, traced and polytensor forms alike.

Calculation of Permanent Moments. The elements of each moment of a charge distribution may depend on the directionality of the coordinate system and on the chosen center of the multipole moment expansion. Any moment element that has an odd-order dependence on x or y or z will change sign upon reversing the direction of that coordinate axis. Apart from direct calculation, chemical intuition often suggests the direction of the dipole moment vector for a simple molecule, and so specification of the coordinate axis directions tends to be overlooked when values are reported. For higher moments, it is easier for confusion to set in if the axes are not specified. The choice of the evaluation center may affect the value of moment elements for all but the first non-vanishing moment (non-vanishing everywhere). This is really a consequence of how the moments are transformed by a translation of the evaluation center. For instance, if R_{xxx} were to be re-evaluated with the origin shifted in the x-direction by an amount x_o, the desired value could be obtained form the values of R_{xxx} and lower order moments at the orignal center.

$$
\begin{aligned}
R_{xxx}^{\text{new point}} &= \sum q_i (x_i - x_o)^3 = \sum q_i \left(x_i^3 + 3x_i x_o^2 - 3x_i^2 x_o - x_o^3 \right) \\
&= R_{xxx} - 3\, x_o\, Q_{xx} + 3\, x_o^2 \mu_x - x_o^3 \sum q_i \qquad (7\text{-}8)
\end{aligned}
$$

If the total charge, the x-component of the dipole, and the xx-component of the second moment tensor were all zero, then R_{xxx} would be independent of x_o which means it would be independent of the choice of the evaluation center. In the traced form or the polytensor form, it is particularly easy to see that until there is a non-vanishing component in one direction, the next higher moment's component in that direction does not depend on the choice of the evaluation center.

TABLE 7.1

Conversion factors for molecular electrical properties from atomic units (a.u.) to the units listed. These conversion factors are based on values of fundamental constants from Cohen and Taylor [C-16]. The general formula for a conversion factor from atomic units to S.I. units (Coulomb,meter,joule) is

$$A^{n+2m+3k+\ldots} \; U \left(\frac{Q}{U}\right)^{n+m+k+\ldots}$$

where $A = 0.529217706 \times 10^{-10}$ m is 1 a.u. of length, $Q = 1.6021892 \times 10^{-19}$ C is 1 a.u. of charge and $U = 4.3598124 \times 10^{-18}$ J is 1 a.u. of energy. The integers in this expression are the orders of dependence of the moments in increasing order. For instance, for the dipole moment, $n = 1$ and all other integers are zero. For the dipole-quadrupole polarizability, the conversion factor is found by using $n = 1$ and $m = 1$ with all other integers zero.

1 V = 1 J/C

Electric charge (zeroeth moment)

1.602189×10^{-19} C (Coulomb)
4.803242×10^{-10} $cm^{3/2} g^{1/2} sec^{-1}$

Dipole (first) moment

8.478418×10^{-30} C m
2.541765×10^{-18} $cm^{5/2} g^{1/2} sec^{-1}$
2.541765 D (Debyes)

Quadrupole (second) moment

4.486584×10^{-40} C m^2
1.345044×10^{-26} $cm^{7/2} g^{1/2} sec^{-1}$
1.345044 B (Buckinghams)

Octupole (third) moment

2.374197×10^{-50} C m^3
7.117664×10^{-35} $cm^{9/2} g^{1/2} sec^{-1}$

Hexadecapole (fourth) moment

1.256371×10^{-60} C m^4
3.766505×10^{-43} $cm^{11/2} g^{1/2} sec^{-1}$

Dipole polarizability

$1.648778 \times 10^{-41}\ C^2\, m^2\, J^{-1}$

$0.148185\ Å^3$

Dipole-quadrupole polarizability

$8.724947 \times 10^{-52}\ C^2\, m^3\, J^{-1}$

$7.841588 \times 10^{-2}\ Å^4$

Quadrupole-quadrupole and dipole-octupole polarizability

$4.617042 \times 10^{-62}\ C^2\, m^4\, J^{-1}$

$4.149589 \times 10^{-2}\ Å^5$

Quadrupole-octupole polarizability

$2.443233 \times 10^{-72}\ C^2\, m^5\, J^{-1}$

$2.195867 \times 10^{-2}\ Å^6$

Octupole-octupole polarizability

$1.292903 \times 10^{-82}\ C^2\, m^6\, J^{-1}$

$1.162003 \times 10^{-2}\ Å^7$

Dipole hyperpolarizability

$3.206334 \times 10^{-53}\ C^3\, m^3\, J^{-2}$

$4.149589 \times 10^{-2}\ Å^5$

Second dipole hyperpolarizability

$6.235278 \times 10^{-65}\ C^4\, m^4\, J^{-3}$

$1.162003 \times 10^{-2}\ Å^7$

Dipole-dipole-quadrupole hyperpolarizability

$1.696719 \times 10^{-63}\ C^3\, m^4\, J^{-2}$

$2.195867 \times 10^{-2}\ Å^6$

Electric field strength

$5.142250 \times 10^{9}\ V\, cm^{-1}$

Electric field gradient

$9.717447 \times 10^{17}\ V\, cm^{-2}$

Undue physical significance should not be inferred from manipulations using the translation properties of the moments. Consider a hypothetical system that for one particular evaluation center has only two non-zero moment components, the x-component of the dipole and the xx-component of the second moment. If the evaluation center were shifted along the x-axis, the system could then have non-zero axial components of the third moment, of the fourth moment and so forth. The translation would have "smeared" the original dipole and quadrupole into all the higher moments. This only means that truncation of a moment expansion goes hand-in-hand with choosing the evaluation center.

The permanent moments are strictly defined as the first derivatives of the molecular energy with respect to corresponding parameters in the **V** polytensor. The second and higher derivatives are the polarizabilities. Within the Born-Oppenheimer approximation, moments and polarizabilities are computed at fixed geometrical arrangements of the nuclei.

Calculated values of the permanent moments of a molecular charge distribution differ from the value of the total energy in their sensitivity to features of the electronic wavefunction. There is also different sensitivity among the moments. With increasing moment order, there is greater weighting of the electron density away from the evaluation center. If the center is at some location in the midst of the molecular skeleton, then this means that higher order moments are more dependent on the fringe region electron density than lower order moments, or than the energy. As a result, there may be a more noticeable need for diffuse functions in the atomic basis sets with higher order moments. Electron correlation effects will have a role in high precision calculations of permanent moments, though the effects can be exaggerated if the basis sets are deficient.

Early CI calculations of Green [G-4] showed an improvement in dipole moments of small molecules from incorporating electron correlation effects at the CISD level. Generally, where SCF results were found to be in error relative to measured values by tenths of Debyes, correlated values were in error by only hundredths of Debyes. It is quite clear that electron correlation should affect the electric moments because as has been discussed earlier, the correlation of electron motions does change the on-average electron distribution somewhat. An interesting case in Green's study and in several earlier studies was carbon monoxide. The dipole moment of CO is small, and so the relative effect of correlation seems dramatic: It can change the sign. FIGURE 7.1 helps to illustrate how this comes about and also points out other aspects of the correlation effect. This figure is a segment of the dipole moment function of CO as calculated by Jasien [J-4]. These calculations were done at the SCF level and at the CISD level (via SCEP). The curves show that correlation shifts the dipole moment curve downward by about a tenth of a Debye. The dipole moment of CO happens to become zero very near the equilibrium bond length, and so this correlation refinement to the dipole has the unique consequence of changing the sign of the moment at equilibrium. The size of the correlation effect in this case is typical even for molecules with dipole moments of one or two Debye. Thus, it is important that the sign reversal that has ben found in numerous, different calculations on CO not be construed to mean either that the sign of an SCF-determined multipole is suspect or that it is sharply in error.

Green's calculations [G-4] on CO led to a conclusion about how correlation effects come into play in the determination of a permanent moment. This idea was that the singly substituted configurations in the CI expansion, in particular, gave a very big share of the (small) net correlation effect. The dipole moments that Green reported were based on expectation value calculations using the correlated electron density from the CI wavefunctions. The single substitution effects could be computed

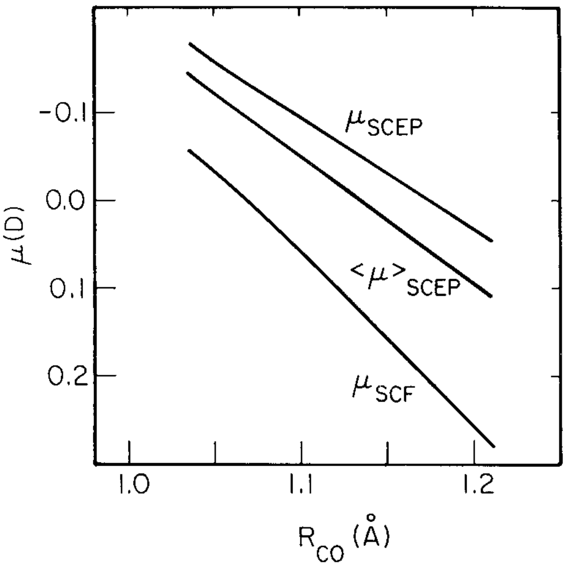


FIGURE 7.1

Calculated dipole moment curves for CO [J-4] obtained with a TZ2P basis set. The bottom line is the SCF result. The middle line is the dipole moment curve obtained as an expectation value form the one-electron density of a CIDS (via SCEP) wavefunction. Above that is an analytically calculated (derivative) dipole moment curve for the CIDS wavefunction. The equilibrium bond length of CO is around 1.13 Angstroms which is where the dipole is near zero.

separately from the entire correlation effect. In more recent times, Raghavachari and Pople [R-9] explained that this apparent role of the single substitutions was related to the particular manner of evaluating the dipole. Since a CISD wavefunction for anything but a two-electron system does not satisfy the Hellmann-Feynman theorem, there is a difference between an expectation value result, which is an integration of the electron density with the moment operator, and a derivative result, where the moment is obtained as the first derivative with respect to an applied field. For a CISD wavefunction for CO, the difference between the two types of results is small, as illustrated in FIGURE 7.1. However, for a CID wavefunction, the difference is larger. Thus, the sizable role of the single substitutions in an expectation evaluation is really a consequence of how the single substitutions bring the correlated wavefunction closer to satisfying the Hellmann-Feynman theorem.

Correlation will have an increasingly noticeable effect on permanent moments away from the molecular equilibrium structure. This, of course, is just a non-dynamical correlation effect arising from the inability of an SCF wavefunction to describe bond breaking. In the dissociation of hydrogen fluoride into neutral ground state atoms, for example, the true dipole moment function will begin to increase as the bond is stretched away from equilibrium. In a rough sense, this comes about just because there is an increase in the separation of the partially charged atomic centers. Somewhere this curve must turn over and diminish to zero because that is the asymptotic limit for separated neutral atoms. As shown in FIGURE 7.2, the SCF dipole moment continues to rise well beyond the point where it should turn over. Correlation effects, including higher order effects brought in at the coupled cluster level, improve the picture nicely.

Basis set choices for accurate multipole moment calculation should be governed by at least three concerns. First, polarization functions are almost always important. The level of polarization functions depends somewhat on the problem. For very small molecules, the polarization functions may need to be continued to an *l*-value equal to or greater than the sum of the highest *l*-value of the occupied valence orbitals and the order of the moments sought. For extended molecules, this requirement might be relaxed without serious effect if the moments are arising more from the distribution of numerous partially charged atomic centers, a rough feature that may override detailed electronic structure features at each atom. A second concern in basis set selection should be the need for diffuse basis functions, both valence and polarization type. This becomes increasingly important with the order of the moments, and several sets of diffuse functions may already be required for high precision determination of an octupole moment. Again, the requirements may be relaxed

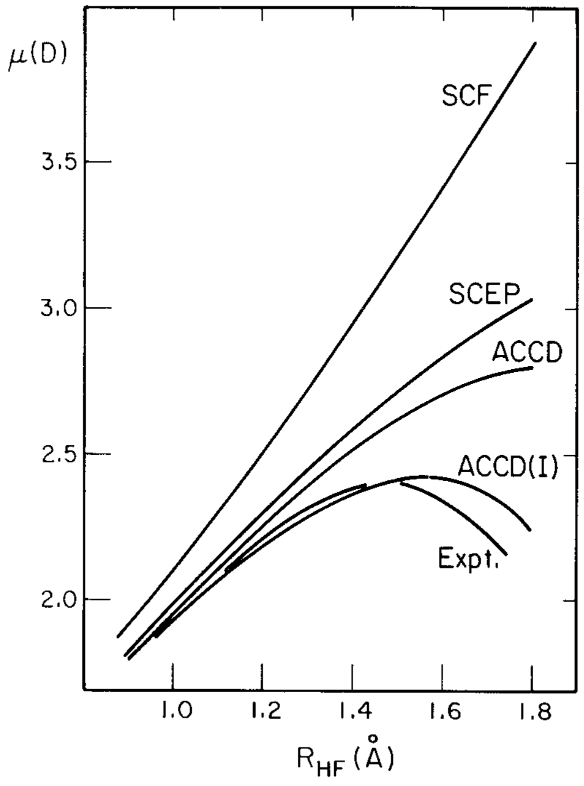


FIGURE 7.2

Calculated dipole moment curves of hydrogen fluoride using a large, triply polarized basis [J-2]. The equilibrium separation is 0.9168 Angstroms. The curve labelled "SCEP" is a CIDS expectation value result. The ACCD and ACCD(I) curves are expectation values using the electron densities of ACCD wavefunctions truncated at double substitutions. Brueckner orbitals were obtained in the ACCD(I) calculation. The experimental curve is that developed by Sileo and Cool [S-26] but shifted by 0.007 Debye to bring it into agreement with a more recent determination of the equilibrium dipole moment [G-13].

somewhat for large molecules, though it is difficult to say from existing experience exactly where that is acceptable. Finally, it is important that balance be maintained in the quality of basis sets for the different types of atoms making up a system. Without equivalent quality, there is an almost automatic artifact in the charge distribution and in its moments. A simple type of augmentation of basis sets is shown for light elements in TABLE 7.2.

The quadrupole moment of the nitrogen molecule has been studied in numerous calculations. A representative selection of these results is given in TABLE

TABLE 7.2

Diffuse and polarization function augmentation to triple-zeta valence sets for the calculation of electrical properties [L-10]. These augmented sets are referred to as "ELP" (electrical properties) sets. In addition to the s and p functions listed, Li through Ne are also augmented with three d functions with exponents of 0.9, 0.13, and 0.02. For Li, the augmentation is to a 5s contracted valence set.

Element	*Exponents of Uncontracted Gaussian Functions*	
H	s: 0.06	p: 0.9, 0.1
Li	s 0.008	p: 5.0, 1.0, 0.15, 0.02
B	s: 0.035	p: 0.02, 0.0035
C	s: 0.05	p: 0.03, 0.005
N	s: 0.06	p: 0.04, 0.006
O	s: 0.06	p: 0.05, 0.007
F	s: 0.06	p: 0.06, 0.008
Ne	s: 0.07	p: 0.07, 0.009

7.3. The partial wave SCF result of McCullough [M-20] represents the best idea of the Hartree-Fock limit. This value has been approached in several large basis set calculations, but since no variation condition applies, values may be scattered above and below the limit value. There is unfortunately, substantial sensitivity to the choice of exponents of the polarization functions. The calculations of Mulder et al. [M-19] reveal that f functions may add 0.05 a.u. to the quadrupole moment, but this is somewhat subject to how complete the s,p,d sets are. Correlation effects were recently evaluated at the fourth order MBPT level by Chernusak et al. [C-17], at the CISD and MP2 levels by Amos [A-11:12], and at the ACCD level by Dykstra, Liu and Malik [D-29]. The correlation effect seems to be to add -0.2 a.u. The ACCD result given in TABLE 7.3 is quite close to the experimental value; however, this is partly fortuitous since the ACCD value does not include any vibrational averaging effects, a point which will be returned to later. Also, there is probably some cancellation of lingering correlation effects and f-function effects (neglected when using the ELP bases). Nonetheless, it is encouraging to see that a reasonably accurate moment value is obtained with a well-chosen s,p,d set.

The assessment of basis sets effects on electrical properties is at a crucial stage. It is very important to be able to select basis sets that will give uniformly accurate results from one molecule to the next. It is clear that electrical properties are

TABLE 7.3

Quadrupole moment values for the nitrogen molecule. The x-axis is the molecular axis and values are given in a.u. The bond length for the calculated values is 1.094 Angstroms (1.068 a.u.).

Q_{xx}	Q_{yy}	$\theta = Q_{xx} - Q_{yy}$	
		-0.945	SCF (5s4p2d) [M-19]
		-1.00	SCF (5s4p2d) [A-11]
-8.666	-7.780	-0.886	SCF-ELP basis [D-29]
		-0.904	SCF-partial wave [C-17]
		-0.940	SCF-partial wave [M-20]
		-1.23	CIDS (5s4p2d) [A-11]
		-1.149	MBPT(4) (8s5p2d1f) [C-17]
-8.780	-7.695	-1.085	ACCD ELP basis [D-29]
		-1.09	Expt. [B-31]

more demanding of basis set flexibility than are force constants, and so the number of basis sets that one might test can be quite large. Complicating the problem is that one basis may yield a value too low and another too high; there is no bounded order of improvement. Thus, the path to developing uniformly reliable basis sets probably will require completeness tests with increasing *l*-type functions. This means establishing a valence set such that the moments are unaffected by any further augmentation, uncontraction, or expansion involving the same *l*-type functions. Then, *l* +1 type functions can be added and this part of the basis expanded to "saturation" or virtual completion before going on to *l* +2, and so on. From any such complete basis, one can work backwards and find what smaller set of s,p,d,... functions best mimics the large set both in terms of the net value of the moments and also in terms of other features that characterize the quality of the wavefunction. While very large basis sets have been employed in quite a number of permanent moment calculations, there is still room for more systematic basis set assessments. For instance, the true importance of f-functions can only be established with tests that insure that the f's are not partly correcting deficiencies in p or d sets. Rarely has this been done, even in studies proclaiming the importance of f-functions.

TABLE 7.4 is a collection of permanent moment values for a number of small molecules. These and other comparisons among calculations with different bases indicate that the extent of lingering basis set effects after reaching the equivalent of a doubly polarized triple zeta set will tend to be around 5% or 0.05 a.u., whichever is greater. Correlation effects may amount to 20% or so, and often less. They may be exaggerated because of a small basis. These estimates of reliability are based on a reading of currently available calculational results, and should be taken as no more than an empirical guess of accuracy.

TABLE 7.4

Low order permanent moments (in a.u.) of small molecules. ELP basis results are from [D-29].

Molecule	*Property*	*Value*	*Value Obtained From:*
H_2	θ_{xx}	0.3207	DZ basis SCF
		0.2954	DZ basis CISD
		0.4266	DZP basis SCF
		0.3910	DZP basis CISD
		0.4898	ELP basis SCF
		0.4512	ELP basis CISD
		0.4944	[5s3p1d] SCF
		0.4531	[5s3p1d] CISD
CH_4	M_{xx}	-3.1337	ELP basis SCF
		-3.1545	ELP basis ACCD(S)
	Ω_{xyz}	2.5153	ELP basis SCF
		2.4725	ELP basis ACCD(S)
HF	μ_x	0.7588	DZP basis CISD
		-0.7665	ELP basis SCF
		-0.7153	ELP basis ACCD(S)
	θ_{xx}	1.7949	DZP basis CISD
		1.7787	ELP basis SCF
		1.7499	ELP basis ACCD(S)
	Ω_{xxx}	-2.5794	ELP basis SCF
		-2.4581	ELP basis ACCD(S)
HCCH	θ_{xx}	5.4256	ELP basis SCF
		4.9249	ELP basis ACCD(S)

Calculation of Polarizabilities and Hyperpolarizabilities. While the permanent moments are first derivatives of the energy with respect to elements of **V**, polarizabilities are simply the second derivatives. Hyperpolarizabilities are third and higher derivatives, though it is acceptable to refer to all second and higher derivatives with respect to the elements of **V** as polarizabilities. The names of the specific polarizabilities are associated with the moments because there is a one to one association of the moment elements and the elements of the **V** polytensor. Thus, one may refer to dipole-quadrupole polarizability elements, dipole-octupole-octupole (hyper)polarizability elements, and so on. For "diagonal" types, such as the quadrupole-quadrupole polarizability, the moment name is normally not repeated; it would be called just the quadrupole polarizability. There are traced and traceless forms, and there are at least two possible sign conventions. The Greek letters, α, β, γ, and δ, are often used to designate, respectively, the polarizability and the first, second, and third hyperpolarizabilities associated only with the dipole. Buckingham introduced the use of Roman letters for other polarizabilities [B-30] (e.g., A for dipole-quadrupole, C for quadrupole-quadrupole, and B for dipole-dipole-quadrupole).

Dipole polarizabilities are usually the most important of the polarization properties, and this is because the simple shift of charge density in one direction, dipole polarization, is the most sizable effect of the perturbing fields that molecules typically encounter. A general dipole polarizability may be defined as a derivative of the dipole moment with respect to components of a uniform field, evaluated at zero field. It is possible to use the elements of **V**, which are V_x, V_y and V_z, as the field components but it is a more common convention to have the field defined with the negative of these elements. To distinguish these two forms, a polytensor **F** is defined to be

$$\mathbf{F} = -\mathbf{V} \qquad (7\text{-}9)$$

Though easiest to follow for just dipole polarizabilities, a general definition can be written for all multipole polarizabilities [A-9].

$$\mathbf{P}^{(t+1)} = \frac{\partial^t \mathbf{M}}{\partial \mathbf{F}^t}\bigg|_o \qquad (7\text{-}10)$$

where **M** is taken to be a function of **F** and where the derivative is evaluated at **F** = 0. Eqn. (7-10) is a concise statement of the definitions of many tensor properties. The rank or order of a particular **P** tensor is (t+1), and so there will be (t+1) subscripts identifying an individual element of **P**. The case where t=1 corresponds to polarizability, and **P** is then second rank. Each element would be labelled by two indices corresponding to specific elements from **M** and **F**. For example,

$$\left[\mathbf{P}^{(2)}\right]_{x,xx} = \frac{\partial M_x}{\partial F_{xx}}\bigg|_o \qquad (7\text{-}11)$$

If t=2 in Eqn. (7-10), then the elements would be labelled by an index corresponding to an element of **M** and two indices corresponding to the two elements of **F** with respect to which differentiation is being done. (At this point it is important to recognize that defining the polarizabilities, **P**, as derivatives with respect to elements of **V**, not **F**, will lead to a sign difference for polarizabilities, second hyperpolarizabilities and higher odd power derivatives of Eqn. (7-10). The choice of definition or convention is important to designate.)

FIGURE 7.3 shows how the polarizability polytensor, $\mathbf{P}^{(2)}$, may be thought of in terms of individual polarizability tensors, those with specific names, such as the dipole-quadrupole polarizability. The symmetry of elements of $\mathbf{P}^{(2)}$ with respect to permutation of indices arises form the permutation symmetry of the permanent moment elements that label the rows and columns (e.g., $M_{xy} = M_{yx}$).

The hyperpolarizability tensor, $\mathbf{P}^{(3)}$, is a third rank or three index tensor. Again, there are pieces associated with more commonly thought of tensors. For instance, the first diagonal cube is the dipole hyperpolarizability β.

Basis set and electron correlation effects require very careful consideration in the evaluation of polarizabilities and hyperpolarizabilities. A large number of studies have appeared that provide good indications of what these effects are and how to judge the requirements for a high quality calculation. For correlation effects, though, mostly just dipole polarizabilities and hyperpolarizabilities have been studied. Finite field methods have been used far more often than analytical derivative methods with correlated wavefunctions, and a finite uniform field (yielding dipole polarizabilities) is a lower dimension problem than a finite non-uniform field. Most correlation studies also have been on small molecules, mainly LiH, HF,CO, N_2 and H_2O. In some cases correlation effects are difficult to assess because of the interplay of basis set and correlation effects. From large basis set results where lingering basis set effects should be small, it appears that correlation often affects $\mathbf{P}^{(2)}$ values by about 10% for small, covalent molecules, assuming that what is seen for the dipole polarizability applies to the higher multipole elements of $\mathbf{P}^{(2)}$. It is probably too early to know if the same can be said about large molecules. It is possible that the correlation effect could be less as polarization becomes more and more an interatomic, valence shift of

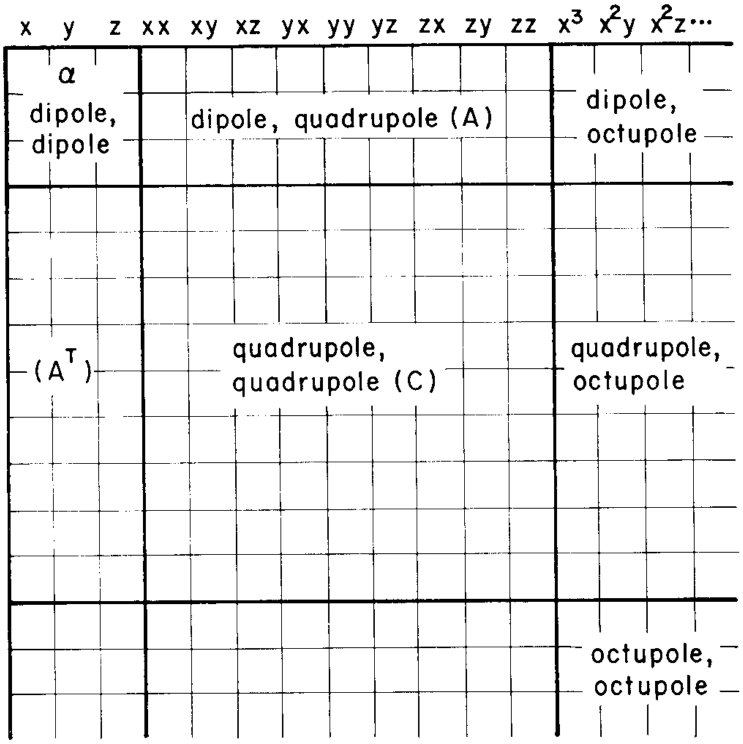


FIGURE 7.3

Schematic representation of the Cartesian polytensor multipole polarizabilities, $\mathbf{P}^{(2)}$, defined by Eqn. (7-10). This second rank polytensor has each element labelled by an element of the first rank moment polytensor, **M**. These labels are shown for the columns at the top of the figure. The diagonal block in the upper left corner is the dipole-dipole polarizability tensor, designated α. To the right are the elements of the dipole-quadrupole polarizability. The elements that would be found in this block can be transformed into the traceless tensor usually designated A. The transpose of this block is found just below the dipole-dipole block. The second diagonal block is the quadrupole-quadrupole polarizability. Its elements can be transformed into what is usually designated as a C (traceless) tensor. The $\mathbf{P}^{(2)}$ tensor can be continued to all orders of multipoles. The next diagonal block, for instance, is the octupole-octupole polarizability. This would be a 27 x 27 block since there are 27 octupole (third moment) elements in **M**.

charge. Polarization of that sort would be little affected by correlation. Another conclusion that may be drawn form the existing studies is that the correlation effect on the dipole polarizability seems to increase with the degree of ionic character. This is most likely associated with non-dynamical correlation effects needed to describe the ionic electronic wavefunction.

The dipole hyperpolarizability of small molecules seems to be more sensitive to correlation than the polarizability. Correlation effects of 20-50% have been reported, and for that reason it is quite possible that each higher order hyperpolarizability becomes more sensitive to correlation. However, this is not too firmly established as a general rule. Polarizabilities and hyperpolarizabilities are quite sensitive to the fringe or tail regions of the electron distribution because normally this is where an external field may shift charge density most easily. Correlation may play an indirect role, affecting the polarizability because of how the fringe density adjusts to the correlation effects in the higher-density, strongly correlated central regions, and not so much because of correlation in the fringe regions. Expressed in a different way, the least polarizable regions of the charge density, the regions close to nuclear centers, are also the regions of greatest electron correlation. A system where the correlation of the electrons in the close-in regions does not happen to cause a change in the fringe or tail electron distribution might not show a sizable correlation effect on polarizabilities and hyperpolarizabilities. This might be more and more the case as molecule size increases, but that remains to be fully tested. One thing that is certain is that tests of the correlation effects on hyperpolarizabilities need to be done with very large basis sets to insure that the calculated correlation effect is not just a compensation for a basis deficiency.

A very carefully presented study of nitrogen's permanent moments and selected polarizabilities by Maroulis and Thakkar [M-23] made an important point about correlation effects on polarizabilities. A relatively small correlation refinement in one particular element can become a large relative difference in a polarizability *anisotropy*, because an anisotropy is a difference of elements. Anisotropy gives the orientational differentiation of a molecule's response to electric potentials. TABLE 7.5 is a summary of results obtained by Maroulis and Thakkar.

Karlstrom et al. [K-9] have reported very high level results for the dipole polarizability of LiH with SCF and correlated CASSCF treatments. TABLE 7.6 lists certain of their results along with values form a smaller basis SCF study. The net effect of correlation is about 15% on the axial and perpendicular elements of the α tensor. However in this case, the polarizability anisotropy, the difference between the parallel and perpendicular elements, was found to be largely independent of the correlation effects. Earlier calculations of Gready et al. [G-14] with a smaller basis showed a much larger correlation effect at the CISD level, though the same insensitivity of the anisotropy to correlation.

Several studies have been reported showing the correlation effects on dipole polarizabilities of hydrogen fluoride. Bartlett and Purvis [B-34] carried out finite field calculation at the SCF and MBPT(4)-SDQ levels and tested five large basis sets. Their results, included in part in TABLE 7.7, led them to conclude that there was a 7% correlation effect on the dipole moment, a 12% effect on the dipole polarizability, a

TABLE 7.5

SCF and correlated polarizabilities of N_2 obtained by Maroulis and Thakkar [M-23] in a.u. The bond length for these calculations was 2.07432 a.u. The basis was a [6s4p3d1f] contracted set. z is the molecular axis.

Property	*SCF Value*	*SDQ-MBPT(4) Value*
α_{zz}	14.960	14.774
α_{xx}	9.788	10.126
$\overline{\alpha}$	11.512	11.675
$\Delta\alpha$	5.172	4.648
γ_{zzzz}	808	1172
γ_{xxxx}	563	639
γ_{xxzz}	254	319
$\overline{\gamma}$	665	830
$\Delta_1\gamma$	935	1916
$\Delta_2\gamma$	-154	-103

22% effect on the hyperpolarizability, and a 30% effect on the axial element of the second hyperpolarizability. As with LiH, the anisotropy seems to be independent of the correlation effects. Sekino and Bartlett [S-27] have examined the dipole polarizabilities in a recent finite field study and they compared several levels of

TABLE 7.6

Calculated polarizabilities of LiH in a.u. For each calculation, the contracted basis sets employed are shown as [Li/H].

α_{xx}	α_{yy}	$\Delta\alpha$	β_{xxx}	β_{xyy}	*Calculation*
22.3	24.0	-1.7	353.	138.	[6s4p3d/4s2p] SCF [D-29]
22.1	25.4	-3.3			[8s6p3d/7s5p] SCF [G-14]
26.3	29.3	-3.0			[8s6p3d/7s5p]CASSCF [G-14]

correlation treatment, such as fourth order MBPT with singles, doubles and quadruples, and then with triples, too. They also carried out calculations at the level of CCSD and CCSD with triples included through fourth order. They used an extended basis that included f-functions on fluorine and obtained what must be the most critically calculated electrical properties of HF. Their results show small differences between coupled cluster results and fourth order MBPT. A somewhat more noticeable difference comes form the inclusion of triple substitutions which affect β_{xxx} by over 5%.

As shown by the property values for hydrogen fluoride, some of which are collected in TABLE 7.7, calculational results demonstrate a sooner convergence with respect to basis size in the correlation effects than in the SCF property values. This is consistent with the earlier suggestion that correlation plays an indirect role because of its primary influence on the close-in electron distribution. The diffuse valence and polarization functions needed for SCF level polarizability evaluations make little difference in the close-in regions of high electron correlation.

Amos has reported finite field SCF and CI dipole and dipole-quadrupole polarizabilities of carbon monoxide [A-14]. The basis set was essentially a doubly polarized triple zeta set. Over a range of separation distances, correlation made the system more polarizable, altering SCF values by 6-7%. In a study of the water molecule, Purvis and Bartlett found that correlation affected the dipole hyperpolarizability by 50% [P-17]. For the polarizability, the correlation effect was about 9%, which is in line with what has been seen for other small molecules. However, there was an equally sharp basis set sensitivity in the four basis sets they tested and there is undoubtedly an interplay of basis set and correlation effects. Certain of their results are shown in TABLE 7.8. They concluded that the most important correlation effects were due to double substitutions. An example of the correlation contribution by perturbative order is for β_{zzz}. The incremental contributions at second, third and fourth order were found to be -3.78, 2.08 and -1.63 a.u.

Basis set quality is a more difficult consideration for the evaluation of multipole polarizabilities than correlation effects. In a fair number of reported studies, there is a lingering error from basis set quality that is larger than the correlation effect. Making basis set selection complicated is that there are several features to consider, not just the total number of functions. Diffuse functions, tight functions, s functions, p functions, d functions, and so on might all be chosen to augment the basis. Their effects are not necessarily additive nor independent.

TABLE 7.7

Calculated polarizabilities of HF in a.u. at a bond length of 1.7328 a.u. The number of contracted functions ([F/H]) are listed for each calculation. An experimental measurement of the dipole polarizability anisotropy, was reported by Muenter, and the value was 0.220 Angstrom^3 = 1.48 a.u. [M-21]. Experimental values of 6.40 a.u. for α_{xx} and 5.08 for α_{yy} are listed in the paper by Sekino and Bartlett [S-27] following the measurements of Dudley and Ward [D-30].

α_{xx}	α_{yy}	$\Delta\alpha$	β_{xxx}	β_{xyy}	γ_{xxxx}		
SCF RESULTS:							
5.72	4.45	1.27	- 9.2		260	[7s5p3d/5s3p]	[B-34]
5.73	4.51	1.22	- 8.4	0.0	250	[6s5p4d/4s2p]	[B-34]
5.76	4.48	1.28	- 8.5	0.0	280	[6s5p4d/5s3p]	[B-34]
5.740	4.445	1.295				[6s5p3d/4s3p]	[A-13]
5.612	4.320	1.292	- 8.27	0.10	263	[7s5p3d/4s2p]	[D-29]
5.764	4.473	1.291	- 8.548	-0.044	280	[5s3p4d2f/5s3p]	[S-27]
CISD RESULTS:							
6.325	5.093	1.232				[6s5p3d/4s3p]	[A-13]
SDQ-MBPT(4) RESULTS:							
6.31	5.11	1.20	-10.8		350	[7s5p3d/5s3p]	[B-34]
6.32	5.22	1.10	- 9.2	0.6	340	[6s5p4d/4s2p]	[B-34]
6.39	5.18	1.21	- 9.7	0.6	390	[6s5p4d/5s3p]	[B-34]
6.315	5.119	1.196	- 9.524	- 0.614	380	[5s3p4d2f/5s3p]	[S-27]
CCSD (+ T-4TH ORDER) RESULTS:							
6.428	5.253	1.175	- 9.838	- 0.802	400	[5s3p4d2f/5s3p]	[S-27]

The 1976 report of Werner and Meyer [W-6] is one of the most important and comprehensive examinations of basis set construction for dipole polarizabilities. For the first row atoms they obtained the d-exponents that maximize the polarizability and found that they were well-fitted by the formula 0.0034 x $(Z - 1.16)^2$, where Z is the atomic number. Values are given in TABLE 7.9. To improve the flexibility of the polarization set, a 2d set was derived by using the optimal d-exponent in one function multiplied by 2, and in another function multiplied by 2/3. Thus, the ratio in the d-

TABLE 7.8

Calculated dipole polarizability and hyperpolarizability of water [P-17]. The basis ("D" in [P-17]) was a (6s5p4d) contracted set on oxygen and a (4s2p) set on hydrogen. The O-H bond length was 1.811 a.u. and the bond angle was 104.5°. Values are in atomic units.

	SCF	*SDQ-MBPT(4)*
α_{zz}	8.47	9.46
α_{yy}	9.18	9.87
α_{xx}	7.95	9.30
β_{zzz}	-5.2	-9.2
β_{zyy}	-12.9	-10.0
β_{zxx}	-0.5	-3.7
γ_{zzzz}	700	1230
γ_{yyyy}	460	630
γ_{xxxx}	1400	2580
γ_{zzyy}	270	400
γ_{zzxx}	360	630

exponents for this 2d set was three. The next most important d-function was the energy optimized function which was about eight times the polarizability optimal d-exponent. These 3d sets, with exponents in the ratio 1:3:4, were considered to be the minimal to reproduce the valence-shell energy, the dipole moment and the dipole polarizability with high accuracy. The d-sets of the "ELP" bases in TABLE 7.2 cover a wider range of values since the ratio between exponents is about six. They may not be as sufficient as the Werner-Meyer bases for simultaneously reproducing all three quantities. The most important augmentation to the valence parts of the basis, s and p functions, was found to be diffuse functions with the ratio of exponents being about three and a half. Christiansen and McCullough [C-18] suggested that dipole polarizabilities accurate to a few percent could be obtained if a double-zeta quality basis were augmented with one set of tight polarization functions, and a diffuse function of each type. A ratio of about four was recommended for choosing the exponent of the diffuse function relative to the original set. It is probably the case that hyperpolarizabilities require still one more diffuse set of functions to achieve the same accuracy.

TABLE 7.9

Optimal d-function exponents for dipole polarizabilities of first row molecules from Werner and Meyer [W-6].

	Ne	HF	H_2O	NH_3	CH_4
d-exponent:	0.34	0.21	0.15	0.11	0.08

An interesting examination of basis set effects on polarizabilities is the case of the magnesium atom, and results from a set of calculations are shown in TABLE 7.10. A good quality valence basis was selected, and then augmented with three almost even-tempered (equal ratio) exponent s-functions and p-functions. A total of seven uncontracted d-functions were added. The ratio of exponents used to select this set was just greater than three, in line with Werner and Meyer's conclusions. Most of the dipole polarizability and quadrupole polarizability of the magnesium atom arises from the outer two electrons in the 3s suborbital. This is because of how diffuse this orbital is relative to the core. With this heavily augmented set, designated "7a" in TABLE 7.10, there is little sensitivity to further augmentation of the s, p or d sets and little sensitivity to uncontracting core functions. Several test calculations verified this. In other words, this set is very near an s,p,d basis limit for the three properties listed, the dipole polarizability, the quadrupole polarizability and the dipole-dipole-quadrupole hyperpolarizability.

Other basis augmentations shown in TABLE 7.10 are successively smaller sets, all the way down to the "0a" set which is not augmented. Each of the sets, 1a to 6a, were selected by finding the exponents of the augmented functions and the relative number of s, p and d augmenting functions to produce values of all the dipole and quadrupole polarizabilities and hyperpolarizabilities that were closest to the 7a basis result. This is an attempt to find smaller bases that provide the flexibility and balance of the limiting basis as required for this specific set of properties.

It is rather striking how well results from small basis sets can match those of the near limit basis. The 1a set produces values that differ form the 7a set by 2%, 6%, and 5% for the three tensor elements, yet the 1a set has only two augmenting functions. This is especially interesting since without augmentation, the results are extremely poor. By looking at the series of basis sets, it becomes clear that moderately diffuse p and d functions are the first most important functions for the polarizabilities, as would be expected. A tighter d-function (exponent = 1.0) makes the next significant

TABLE 7.10

The effect of basis set augmentations on the polarizabilities of the magnesium atom. Values are in a.u. and are SCF-level, having been obtained with derivative Hartree-Fock (DHF). The core basis was a contracted set: (13s8p/7s5p). The exponents of the s, p, and d functions that augmented this core basis are listed. The quadrupole polarizability element is in traced Cartesian form, and so is the element of the dipole-dipole-quadrupole polarizability. The total number of basis functions is listed in parentheses.

Basis	*Augmentation*	$\alpha_{x,x}$	$C_{xx,xx}$	$B_{x,x,xx}$
7a (76)	s: 0.025, 0.008, 0.0025 p: 0.032, 0.010, 0.003 d: 5.0, 1.4, 0.4, 0.12, 0.033, 0.009, 0.0023	-81.542	-643.0	-12495.
6a (70)	s: 0.025, 0.008, 0.0025 p: 0.032, 0.010, 0.003 d: 2.8, 0.7, 0.175 0.044, 0.011, 0.003	-81.599	-646.1	-12431.
5a (60)	s: 0.025, 0.008 p: 0.032, 0.010 d: 2.8, 0.7, 0.175, 0.044, 0.010	-81.664	-645.6	-12434.
4a (54)	s: 0.025, 0.008 p: 0.032, 0.010 d: 2.2, 0.55, 0.14, 0.035	-81.665	-644.8	-12406.
3a (44)	s: 0.025 p: 0.03 d: 1.0, 0.2, 0.04	-82.373	-662.3	-12752.
2a (37)	p: 0.03 d: 0.28, 0.04	-83.177	-677.1	-12938.
1a (31)	p: 0.03 d: 0.04	-83.436	-678.6	-13070.
0a (22)		-52.742	-20.3	-1360.
3b	s: 0.025 p: 0.03 d: 2.7, 0.5, 0.09	-82.642	-479.2	-10440.

Basis	*Augmentation*	$\alpha_{x,x}$	$C_{xx,xx}$	$B_{x,x,xx}$
3c	s: 0.025 p: 0.03 d: 1.8, 0.35, 0.07	-81.689	-540.2	-10929.
2b	p: 0.03 d: 2.7, 0.5	-62.552	-45.3	-3776.
2c	p: 0.03 d: 0.4, 0.06	-77.393	-479.1	-9270.
1b	d: 0.06	-58.788	-470.5	-3061.

improvement. From then on, the optimal basis improvement comes about by spreading the range of exponents for the s, p and d sets while diminishing the ratio between exponents of different functions. For the d set, the ratio of exponents goes from 5.0 in 3a to 4.0 in 4a and to almost 3.0 in 7a. The decreasing ratio implies a smoother description from the linear combination of atomic functions, while the increasing exponent range implies better accuracy far-out and close-in. With this natural type of basis enhancement, there is little variation in the polarizabilities and basis set convergence, along this special "path" through the basis set possibilities, is very direct.

At the end of TABLE 7.10 are results with several other basis sets. These results illustrate the sensitivity of the smaller basis sets to the choice of the exponents. Horrible results are obtained without sufficiently diffuse sets. Other tests, not listed, show that imbalanced augmentation of one *l*-type set over another can sharply affect the values obtained. This means that small, polarized bases can be useful for evaluating electrical properties only if optimally chosen. As would be expected, the smaller the basis the greater the sensitivity to the particular values of the exponents and to the relative numbers of s, p and d functions.

A detailed study of basis set effects on the electrical properties of hydrogen fluoride was carried out by Bishop and Maroulis [B-35]. They concluded that the polarization functions that should be added for the evaluation of polarizabilities should be those optimized for the corresponding molecular ions. This will force the functions to be diffuse. The problem with this idea is that its effectiveness is really for the low order multipoles and multipole polarizabilities. The nature of the anion's electronic structure does not dictate how the neutral species will respond to a sharply changing field. The results that Bishop and Maroulis reported [B-35] include those from basis sets with 96 contracted functions for the simple hydrogen fluoride molecule, and so provide a good deal of information about large basis set values for that system.

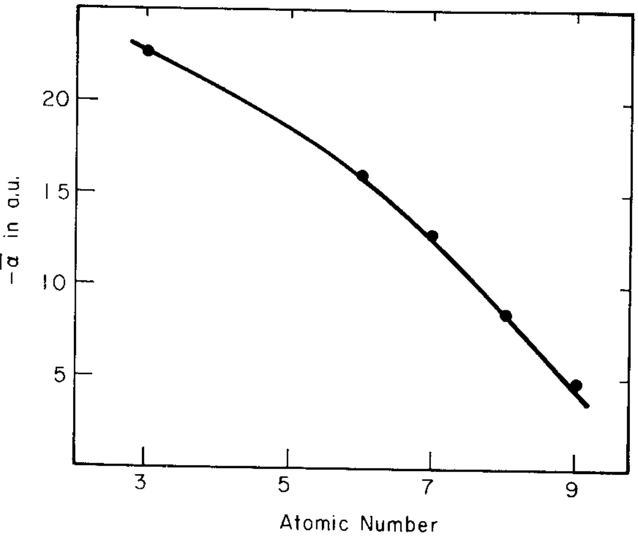


FIGURE 7.4

Isotropic dipole polarizability in a.u. of LiH, CH_4, NH_3, H_2O, and HF plotted against the atomic number of the first row element. The values were obtained from comparable basis DHF calculations [L-10].

From the growing number of calculations of molecular electrical properties, correlations with structure and bonding begin to emerge. For instance, the isotropic dipole polarizabilities of first row hydrides show a regular decline with atomic number. This is shown in FIGURE 7.4. The isotropic dipole polarizabilities for hydrides containing two first row atoms reveals an interesting pattern, too. The polarizability of an ABH_n molecule is well-estimated (to about 15-20%) by the sum of the isotropic polarizability of the A-hydride and the B-hydride, diminished by 6 a.u. if A and B are doubly bonded and 12 a.u. if A and B are triply bonded. There is a kind of additivity of polarizability. For example, the isotropic dipole polarizability of HCN, calculated to be 16.6 a.u., is well approximated as the sum of the like-calculated isotropic polarizability of CH_4, 16.0, and NH_3, 12.8, less 12 a.u. for triple bonding, and this value is 16.8 [D-29, L-10].

TABLE 7.11 is a collection of molecular multipole polarizability and hyperpolarizability tensor values. These give an idea of what is typical for small molecules. Unless otherwise indicated, the values are in the traced Cartesian form with evaluation centers as indicated. Applequist has given the general formula for relating the Cartesian tensor forms to the traceless forms [A-9]. From among his specific examples are the following relations between traceless tensors and elements of **M** and $\mathbf{P}^{(2)}$. These formulas use the convention that a summation over all components is implied by a repeated index.

TABLE 7.11

Calculated multipole polarizabilities and hyperpolarizabilities (in a.u.) of small molecules at equilibrium structures. Results are DHF/ELP basis values from [D-29] unless otherwise indicated. Only symmetry-unique values are listed. The x-axis is the highest symmetry axis.

Molecule	*Polarizability* $\mathbf{P}^{(2)}$ *tensor elements and values*					
Be [7s3p2d]	x,x	-44.14				
	xx,xx	-38.44	xx,yy	-13.52	xy,xy	-12.46
H_2	x,x	-6.443	y,y	-4.440	xx,xx	-3.672
	yy,yy	-2.031	xx,yy	-0.780	xy,xy	-1.386
CH_4	x,x	-16.00	x,yz	6.562		
	xx,xx	-18.51	xx,yy	-2.202	xy,xy	-10.03
NH_3	x,x	-13.19	y,y	-12.65	x,xx	0.470
	x,yy	0.913	y,xy	1.514	y,yy	-1.883
HF	x,x	-5.612	y,y	-4.320	x,xx	1.905
	x,yy	-0.068	y,xy	0.230		
CO	x,x	-14.21	y,y	-11.09		
	x,xx	-6.321	x,yy	-0.567	y,xy	-4.630
N_2	x,x	-14.83	y,y	-9.66		
HCN	x,x	-22.40	y,y	-13.75		
	x,xx	5.532	x,yy	-0.114	y,xy	0.567
	xx,xx	-38.95	xx,yy	-0.201	xy,xy	-11.98
	yy,yy	-12.36	yy,zz	-4.948	yz,yz	-3.704
F_2	x,x	-14.555	y,y	-5.277		
	xx,xx	-11.39	xx,yy	-0.918	xy,xy	-3.981
	yy,yy	-2.910	yy,zz	-1.203	yz,yz	-0.854
trans-N_2H_2	x,x	-23.91	x,y	-2.984	y,y	-17.38
	z,z	-13.25				
cis-N_2H_2	x,x	-25.03	y,y	-17.01	z,z	-13.56
H_2O	x,x	-8.313	y,y	-9.077	z,z	-7.839
H_2O_2	x,x	-19.90	x,y	1.902	y,y	-12.41
	z,z	-10.90				

Molecule	*Hyperpolarizability* $\mathbf{P}^{(n>2)}$ *tensor elements and values*					
H_2	x,x,xx	57.15	x,x,yy	13.07	y,y,xx	13.63
	x,y,xy	20.96	y,y,yy	40.46	y,y,zz	26.29
	y,z,yz	8.59				
CH_4	x,y,z	-11.03				
	x,x,xx	-161.0	x,x,yy	-35.57	x,y,xy	-70.33
	x,xx,yz	-21.38	x,xy,xz	-41.20	x,yy,yz	-26.40
	xx,xx,xx	-480.6	xx,xx,yy	-71.01	xx,xy,xy	-129.7
	xx,yy,zz	11.61	xy,xy,zz	-22.80	xy,xz,yz	-55.07
NH_3	x,x,x	9.126	x,y,y	7.801	y,y,y	-9.798
HF	x,x,x	8.274	x,y,y	-0.100	x,x,x,x	-262.9
	x,x,y,y	-80.77	y,y,y,y	-312.8	y,y,z,z	-104.26
	x,x,x,x,x	2309	x,x,x,y,y	243.5	x,y,y,y,y	91.06
	x,y,y,z,z	30.35				
CO	x,x,x	30.81	x,y,y	5.026	x,x,xx	138.3
	x,x,yy	25.40	x,y,xy	42.34	y,y,xx	21.69
	y,y,yy	89.17	y,y,zz	25.82	y,z,yz	31.68
HCN	x,x,x	7.346	x,y,y	2.255	x,x,xx	-201.1
	x,x,yy	-42.67	x,y,xy	-67.81	y,y,xx	-16.46
	y,y,yy	-143.4	y,y,zz	-49.61	y,z,yz	-46.90
	x,x,x,x	-1561	x,x,y,y	-581.5	y,y,y,y	-1647
	y,y,z,z	-549.0				
F_2	x,x,xx	-57.03	x,x,yy	-13.32	x,y,xy	-20.63
	y,y,xx	-9.642	y,y,yy	-24.69	y,y,zz	-9.060
	y,z,yz	-7.816				
H_2O	x,x,x	5.472	x,y,y	10.03	x,z,z	0.545
	x,x,x,x	-794.0	x,x,y,y	-288.6	x,x,z,z	-343.4
	y,y,y,y	-475.2	y,y,z,z	-300.1	z,z,z,z	-1309
H_2O_2	x,x,x	-2.201	x,y,z	-0.008	y,y,z	-6.373
	z,z,z	-1.799				

$$\mu_{\alpha} = M_{\alpha} \tag{7-12a}$$

$$\theta_{\alpha\beta} = 3\,M_{\alpha\beta} - \delta_{\alpha\beta}\,M_{\nu\nu} \tag{7-12b}$$

$$\Omega_{\alpha\beta\gamma} = 15\,M_{\alpha\beta\gamma} - 3\left(\delta_{\alpha\beta}\,M_{\nu\nu\gamma} + \delta_{\alpha\gamma}\,M_{\nu\beta\nu} + \delta_{\beta\gamma}\,M_{\alpha\nu\nu}\right) \tag{7-12c}$$

$$\begin{aligned}\Phi_{\alpha\beta\gamma\delta} = {} & 105\,M_{\alpha\beta\gamma\delta} + 3\,M_{\mu\mu\nu\nu}\left(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}\right) \\ & -15\left(\delta_{\alpha\beta}M_{\nu\nu\gamma\delta} + \delta_{\alpha\gamma}M_{\nu\beta\nu\gamma} + \delta_{\alpha\delta}M_{\nu\beta\gamma\nu} + \delta_{\beta\gamma}M_{\alpha\nu\nu\gamma}\right. \\ & \left. + \delta_{\beta\delta}M_{\alpha\nu\gamma\nu} + \delta_{\gamma\delta}M_{\alpha\beta\nu\nu}\right)\end{aligned} \tag{7-12d}$$

$$\Pi_{\alpha,\beta\gamma} = 3\,P_{\alpha,\beta\gamma} - \delta_{\beta\gamma}\,P_{\alpha,\nu\nu} \tag{7-13a}$$

$$\Pi_{\alpha,\beta\gamma\delta} = 15\,P_{\alpha,\beta\gamma\delta} - 3\,(\delta_{\gamma\delta}P_{\alpha,\beta\nu\nu} + \delta_{\beta\delta}P_{\alpha,\nu\gamma\nu} + \delta_{\beta\gamma}P_{\alpha,\nu\nu\delta}) \tag{7-13b}$$

$$\Pi_{\alpha\beta,\gamma\delta} = 9\,P_{\alpha\beta,\gamma\delta} - 3\left(\delta_{\alpha\beta}P_{\mu\mu,\gamma\delta} + \delta_{\gamma\delta}P_{\alpha\beta,\nu\nu}\right) + \delta_{\alpha\beta}\delta_{\gamma\delta}P_{\mu\mu,\nu\nu} \tag{7-13c}$$

The traceless polarizability tensors, Π, are exactly the same as the tensors usually referred to with the letters A (dipole-quadrupole), B (dipole-dipole-quadrupole), and C (quadrupole-quadrupole) [M-18], except for C. The Π tensor in Eqn. (7-13c) is equal to 3C, not C.

For neutral molecules, the dipole polarizabilities and dipole hyperpolarizabilities to all orders are invariant to the choice of the moment center. This can be seen by following the quantum mechanical development of energy derivatives as discussed in Chapter Five. For a neutral molecule, a shift in the evaluation center will add a constant, the total electronic charge times the distance of the position shift, to the dipole moment component operator. In a matrix representation of this operator, the constant will enter as a multiple of the identity or unit matrix. The constant will affect only the first derivatives of the energy but not any higher derivatives or any derivative wavefunctions. This is equivalent to the effect of adding a constant to a Hamiltonian: The energy eigenvalue changes by the value of this constant, but not the wavefunction. And actually, the shift in the evaluation center will not even change the dipole moment because the contribution of the electrons will be offset by the like contribution of the total nuclear charge times the distance of the position shift. (The first non-vanishing moment is invariant.) Other multipole polarizabilities and hyperpolarizabilities may be invariant in certain cases because of particular molecular symmetry, though these invariances are not as simple to notice.

The changes that may occur in $\mathbf{P}^{(2)}$, $\mathbf{P}^{(3)}$, and so on, from shifting the evaluation center are prescribed by the changes in the moments or the moment operators. If a particular origin translation leads to

$$M_i' = M_i + a M_j \tag{7-14}$$

then the energy derivatives in the translated coordinate system are related to the energy derivatives in the original system in the following way.

$$\frac{\partial}{\partial V_i'} = \frac{\partial}{\partial V_i} + a \frac{\partial}{\partial V_j} \tag{7-15}$$

A simple example is a translation of the evaluation center along the x-axis, x' = x + b. For a neutral molecule, the xx-component of the Cartesian second moment tensor becomes, by definition,

$$M_{xx}' = M_{xx} - b M_x \tag{7-16}$$

Now, a corresponding diagonal polarizability element will be obtained in terms of polarizability elements in the unshifted system by using Eqn. (7-15).

$$\frac{\partial^2}{\partial V_{xx}'^{\,2}} = \left(\frac{\partial}{\partial V_{xx}} - b \frac{\partial}{\partial V_x} \right) \left(\frac{\partial}{\partial V_{xx}} - b \frac{\partial}{\partial V_x} \right)$$

$$= \frac{\partial^2}{\partial V_{xx}^2} - 2 b \frac{\partial^2}{\partial V_{xx} \partial V_x} + b^2 \frac{\partial^2}{\partial V_x^2} \tag{7-17a}$$

$$P_{xx,xx}^{(2)\,'} = P_{xx,xx}^{(2)} - 2 b P_{xx,x}^{(2)} + b^2 P_{x,x}^{(2)} \tag{7-17b}$$

Notice that Eqn. (7-16) is dependent on the definition of the permanent moments. If the $n!^{-1}$ factor for the n^{th} order moment elements in **M** were not present, a factor of -2b instead of -b would multiply the dipole moment component. As suggested by this example, lower order moment polarizabilities are required to shift the evaluation center. Alternatively, a shift in the evaluation center will mix polarizabilities associated with different multipoles. It will not mix polarizabilities and hyperpolarizabilities, since these are derivatives of different order.

Vibrational Motion and Electrical Properties. Equilibrium or near equilibrium electrical properties, such as those considered so far in this chapter, provide an idea of what a molecule's electrical properties are like. However, it is important to realize that because of vibrational and rotational motion, a molecule's response to even a static field is not precisely what is implied by these values. A more complete picture comes from realizing that the electrical properties are sensitive to the geometry of a molecule. This is illustrated by the contours in FIGURES 7.5 and 7.6 which are for the dipole polarizability and hyperpolarizability of HCN. They show how these properties change with the two bond stretching coordinates. Both β_{xxx} and β_{xyy} have zero contours passing through regions not too distant from the equilibrium geometry. This indicates that the hyperpolarizability of HCN may change sign in the course of some low-energy vibrational excursion. Furthermore, there will be differences between each vibrational level in how the surfaces of properties are sampled because of vibrational motion. One can also see from the fact that the contour lines are nearly vertical that there is a naturally greater sensitivity of these properties to the C-N bond length than to the C-H bond length.

To understand the consequences of internal motion on electrical properties, it is necessary to see that the way a molecule vibrates is actually affected or changed by the presence of an external electrical field, though this change may be small. The energy of interaction from a field with the molecule's permanent moments and *electronic* polarizabilities varies with the molecular geometry because those moments and polarizabilities vary with the molecular geometry. Thus, the field gives rise to changes in the stretching and bending potentials via the interaction potential energy. A change in the vibrational motion can give rise to what may be called a "vibrational polarization" just a change in the electronic wavefunction from applying a field was associated with "electronic polarization." The vibrational polarization contributes to the overall electronic-vibrational state electrical properties, and does so in a way that is not merely vibrational averaging of the *electronic* properties [L-17].

A starting point for working out the complete role of vibration in determining electrical properties is to consider a diatomic molecule in the harmonic oscillator approximation, where the stretching potential is taken to be quadratic in the displacement coordinate. Within the *doubly harmonic model* [H-5:7,K-8], the various electrical properties are taken to be just linear functions of the displacement coordinate. This turns out to be most reasonable in the vicinity of an equilibrium structure, though it breaks down at large separations. Letting x be a coordinate giving the displacement from equilibrium of a one-dimensional harmonic oscillator, the dipole moment, dipole polarizability and dipole hyperpolarizability, within the doubly harmonic model, may be written in the following way.

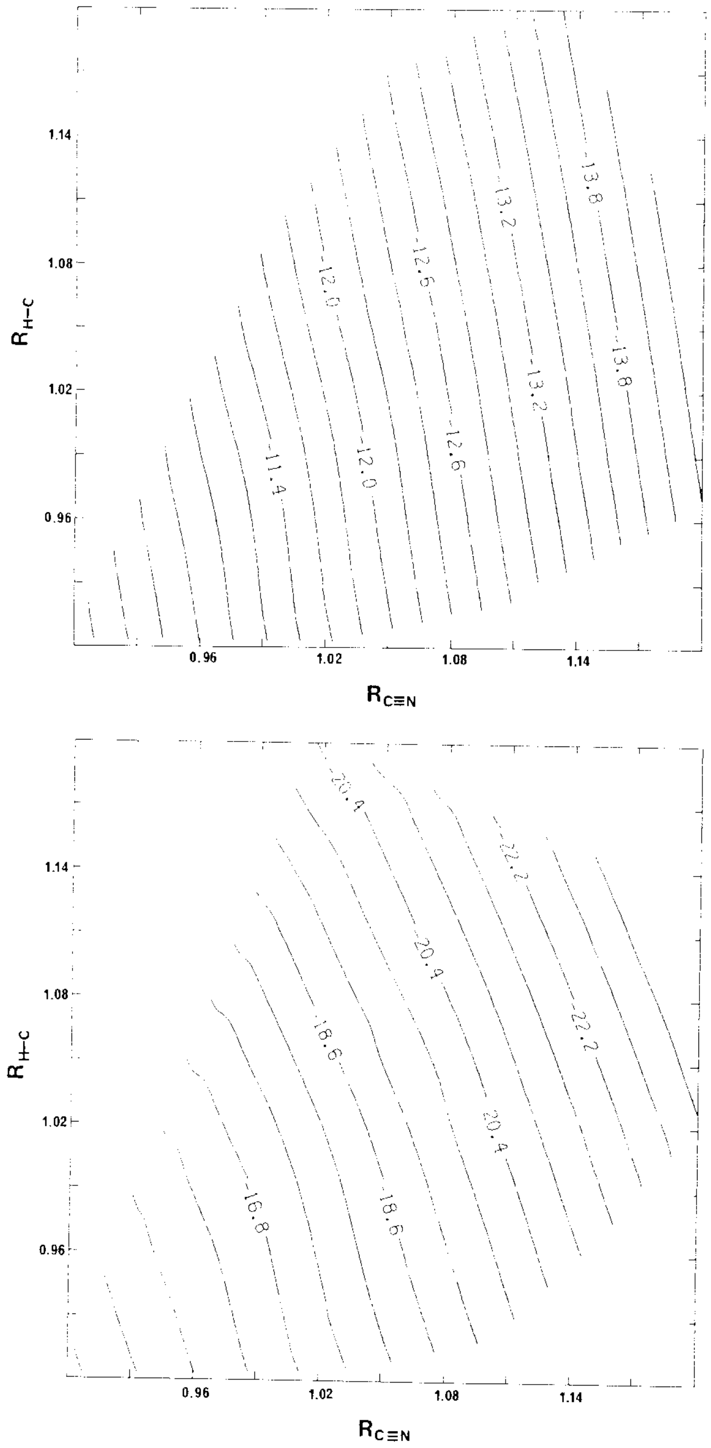
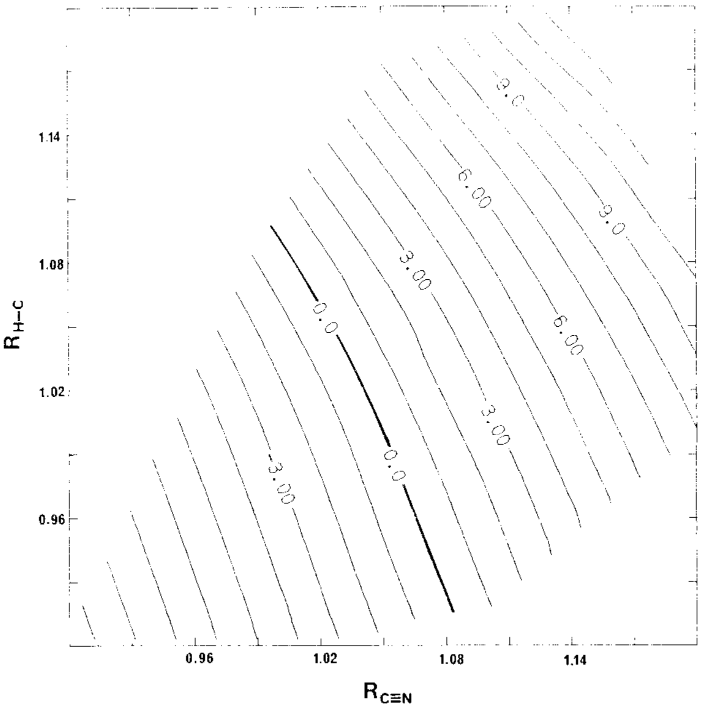


FIGURE 7.5

Contour plot of the components of dipole polarizability tensor of HCN as a function of the two bond lengths. Contours are in a.u. and the bond lengths are given in Angstroms. These values were calculated [D-29] with the DHF program using the ELP bases discussed earlier in this chapter. The top figure is the axial or parallel (x,x) component and the lower figure is the perpendicular (y,y) component.



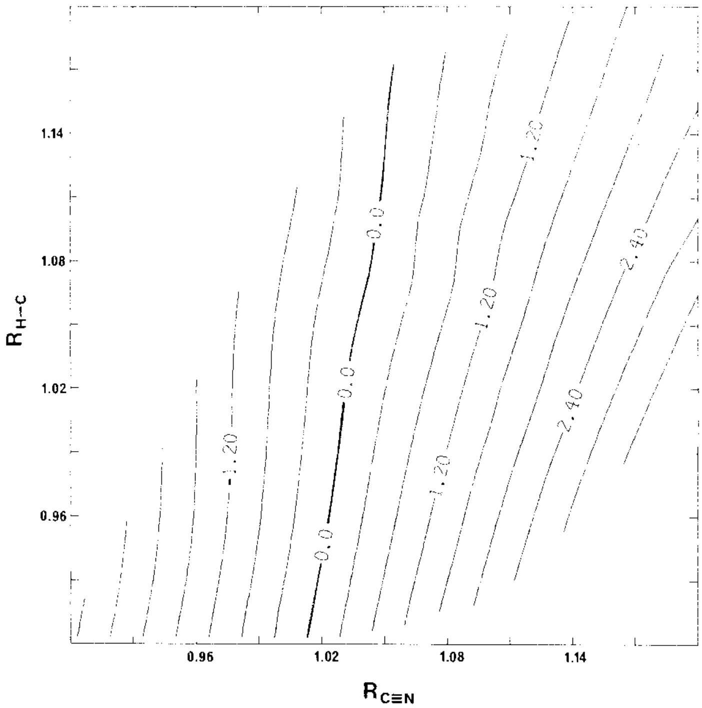


FIGURE 7.6

Contour plots of the components of the dipole hyperpolarizability tensor of HCN as a function of the two bond lengths. The top figure is the axial (x,x,x) component and the lower figure is the perpendicular (x,y,y) component.

$$\mu^{dh}(x) = m_o + m\,x \tag{7-18}$$

$$\alpha^{dh}(x) = \alpha_o + a\,x \tag{7-19}$$

$$\beta^{dh}(x) = \beta_o + b\,x \tag{7-20}$$

"dh" will identify doubly harmonic property functions. An external uniform field, along the x-axis, and of strength F, will alter the doubly harmonic stretching potential with a potential that is linear in x.

$$V'(x) = a' + b'\,x \tag{7-21}$$

$$a' = -(\mu_o F + \tfrac{1}{2}\alpha_o F^2 + \tfrac{1}{6}\beta_o F^3 + ...) \tag{7-22a}$$

$$b' = -(mF + \tfrac{1}{2}a\,F^2 + \tfrac{1}{6}b\,F^3 + ...) \tag{7-22b}$$

The effect of V'(x) when added to a potential, V(x), that is quadratic in x is to change the location of the minimum and the minimum energy. It will not change the curvature, and so it will not change the vibrational frequency or the spacing between levels. The actual change in the minimum energy is $[a' - b'^2/4c]$ where c is the quadratic coefficient in V(x). This energy change is, of course, experienced by all the vibrational energy levels; all are shifted down or up by the same amount for a given field strength.

The definition of electrical properties as derivatives of the molecular energy can be applied to electronic-vibrational states just as well as to pure electronic states at a specific nuclear arrangements as discussed so far. Continuing with the doubly harmonic model, the derivatives with respect to F are,

$$\mu = \mu_o \tag{7-23}$$

$$\alpha = \alpha_o + m^2/2c \tag{7-24}$$

$$\beta = \beta_o + 3\,m\,a/2\,c \tag{7-25}$$

$$\gamma = \gamma_o + (4\,m\,b + 3\,a^2)/c \tag{7-26}$$

These properties are for the entire vibrational state manifold of the doubly-harmonic oscillator. There happens not to be any difference from state to state. The properties are equilibrium values plus corrections that result from the shift in the equilibrium position arising from application of a field. This shift in the equilibrium, either a stretching or a contraction, is the physical picture of vibrational polarization.

The simple analysis that has been presented is useful in several ways. For one, if the dipole moment is not dependent on x (i.e., if m = 0), then the vibrational motion will not affect α or β. So, within the doubly harmonic model, the vibrational state dipole polarizability of a molecule such as N_2, but not a molecule such as CO, will be identical with the equilibrium or pure electronic value.

Two steps must be taken to go from the doubly harmonic model to treatment of a realistic system. One is to allow for the potential to be anharmonic, and the other is to allow the properties to be more complicated than just being linear in the vibrational coordinate. Via computation, one may take one or the other step first. Removing the harmonic approximation on the moments and polarizabilities first, one sees that as soon as the property functions become non-linear, the effect of an external field will be more than just changing the equilibrium separation distance. It will also change the shape or curvature at the minimum, and elsewhere. This means the spacing between vibrational levels will be affected. The vibrational polarization will then be more involved than shifting the equilibrium; it will be dependent on the vibrational quantum number. Thus, the properties will no longer be alike for the different vibrational states. The effects from the electrical properties being non-linear are often referred to as "electrical anharmonicity" effects [S-28,P-18].

Changes in properties due to allowing a potential to be anharmonic are referred to as "mechanical anharmonicity" effects [S-28, P-18]. A principal manifestation of mechanical anharmonicity is that it makes vibrational state averages of properties different from the values at equilibrium even for electrically harmonic properties. Even for a slightly anharmonic stretching potential, V(x), the expectation value, $\langle x \rangle_n$, varies with the quantum number n, and so the expectation value of any property proportional to x (linear in x) varies with n as well. Mechanical anharmonicity also affects vibrational polarization, and typical anharmonicity of a bond stretching potential will slightly enhance vibrational polarization. Because a typical anharmonic potential, $V(x) = ax^2 - bx^3$, is not as steep at displacements greater than x = 0 than the harmonic potential $V(x) = ax^2$, an applied field may shift the equilibrium further. This implies the possibility of a greater vibrational contribution to the polarizability because of mechanical anharmonicity.

The development in Chapter Five showed that first derivatives may be obtained as expectation values if the wavefunctions are eigenfunctions of the zeroeth order Hamiltonian. Assuming that such vibrational wavefunctions have been found, then the vibrational state first derivative properties (i.e., the electrical multipole moments) are properly found as simple vibrational averages. In line with this, there are no additional terms in Eqn. (7-23) for the dipole moment of the model system discussed above. Polarizabilities and hyperpolarizabilities especially are not strictly vibrational averages. Vibrational polarization (with or without electrical anharmonicity) enters into the determination of second and higher derivative properties.

To completely determine the pure vibrational effects on electrical properties, it is necessary to obtain derivatives of vibrational state energies. These state energies must be total energies, including the electronic energy, not relative vibrational energies. Finite field methods can be applied, wherein the vibrational state energies are recomputed with particular fields (or generally, electrical potentials or arbitrary form) acting to modify the vibrational potential via the electrical moments and polarizabilities [M-24]. One analytical approach has been developed, so far: For diatomics, it is possible to carry out the differentiation of the vibrational state energies and wavefunctions analytically using the derivative Numerov-Cooley (DNC) method of Dykstra and Malik [D-21] that was mentioned in Chapter Five. This method follows the basic Numerov-Cooley method [C-9] in converting the differential Schrodinger equation and derivative Schrodinger equations of the one-dimensional oscillator into difference equations that can be solved exactly.

FIGURE 7.7 shows the vibrational wavefunctions calculated by the Numerov-Cooley method for the ground and first excited vibrational states of hydrogen fluoride. The isolated molecule stretching potential used to find these wavefunctions is from a large basis ACCD calculation of the electronic energy at about a dozen geometry points. This potential is quite realistic as assessed by the accuracy of the vibrational transition energies. Among the lowest three states, all transitions are within ten cm^{-1} of measured frequencies. Purely electronic properties were obtained at most of the potential curve points, and an analytical representation of each was found by low order polynomial fitting. The moments were obtained at the ACCD level, and the polarizabilities were at the SCF level and obtained with DHF. These property functions are derivative Hamiltonians for the vibrational motion problem, where the differentiation is with respect to elements of the electrical potential polytensor (i.e., field, field gradient, etc.). With the DNC analysis, derivative vibrational wavefunctions and derivatives of the electronic-vibrational state energies were computed.

Shown in FIGURE 7.7 are derivative vibrational wavefunctions where the differentiation is with respect to an external field applied along the molecular axis. The first derivative of the $v = 0$ wavefunction is very much like the unperturbed $v = 1$ wavefunction. This is not surprising when one considers that within the doubly harmonic model, the first derivative of any v' state wavefunction is a linear combination only of the $v' + 1$ and $v' - 1$ wavefunctions. For $v' = 0$, this allows only the $v' + 1$ state. The extent to which this derivative wavefunction does *not* resemble the $v = 1$ wavefunction is a measure of the effects of mechanical and electrical anharmonicity in this problem. Inspection of the first derivative of the first excited vibrational state shows

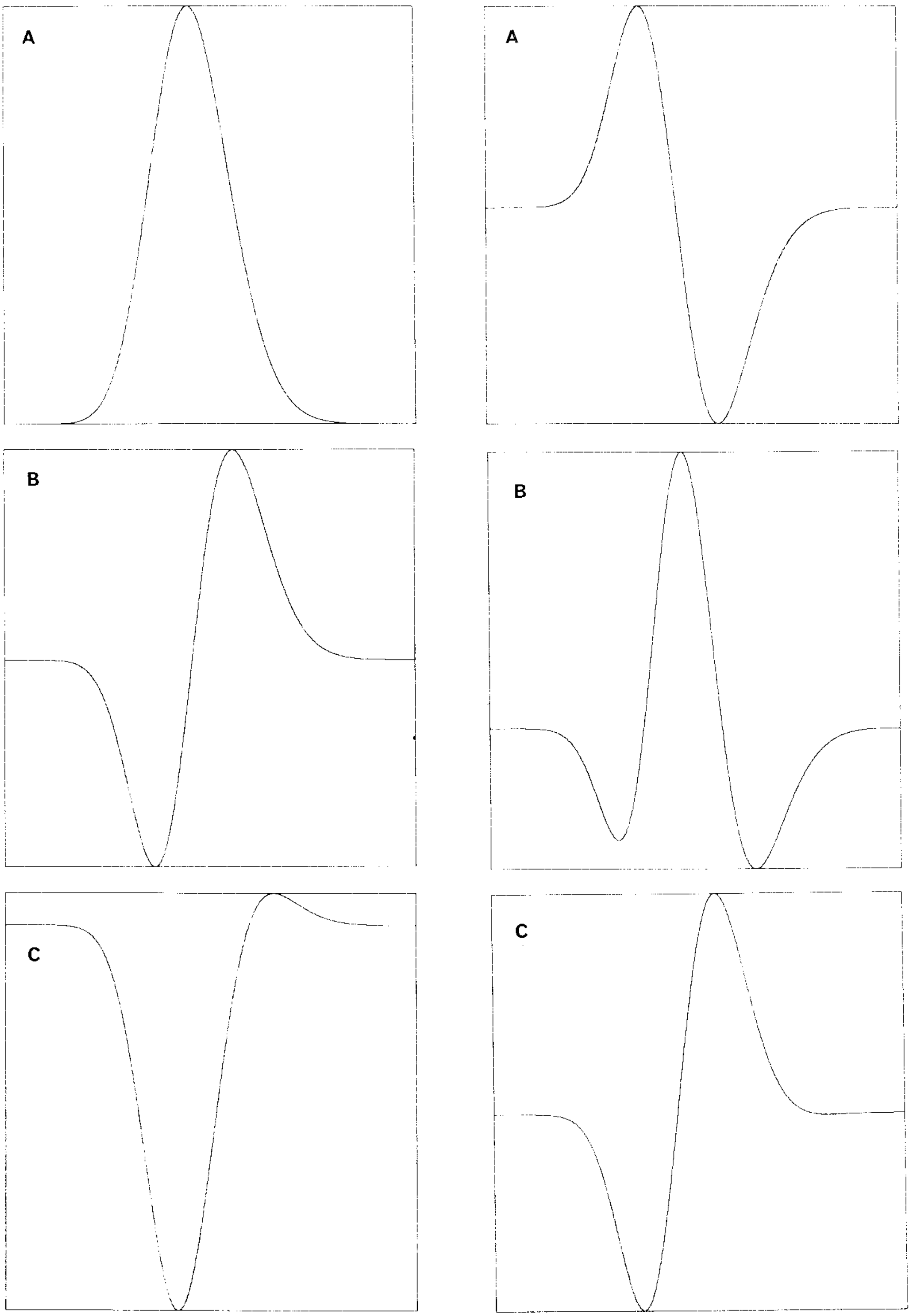


FIGURE 7.7

The forms of the zeroeth order (A), first derivative (B), and second (C) derivative wavefunctions of HF for the v = 0 state (left) and v = 2 state (right). Differentiation is with respect to the strength of an axial field.

it to be a combination of the unperturbed v = 0 and v = 2 wavefunctions. In the doubly harmonic model, the second derivative wavefunctions may be a linear combination of every state from v' - 2 to v' + 2, including v'.

In the doubly harmonic model, vibrational polarization comes about from the shift in the equilibrium bond length and in the equilibrium potential energy from applying an external field. In an exact analysis, vibrational polarization also comes from a change in the curvature or shape of the potential because of the applied field, and this happens as a result of there being either electrical or mechanical anharmonicity or both. From calculations, these features can be separated and their relative sizes examined in specific cases. Before doing that, it is useful to see the connection between the physical picture of vibrational polarization and the derivative wavefunctions. With FIGURE 7.7, one can envision how the ground state wavefunction will evolve as an axial field is slowly turned on. Starting with a very weak field, so that derivatives beyond the first may be ignored, the wavefunction is a mixture of the zeroeth order and first derivative functions. That will be a function which in form is quite like the zeroeth order wavefunction but with its point of maximum amplitude shifted to the right (to the left for the opposite orientation of the field). That shift in the point of the highest probability density goes hand-in-hand with the shift in the equilibrium due to the application of the field. The vibrational polarization brings about an on-average change in the bond length.

TABLE 7.12 lists dipole moment, dipole polarizability and dipole hyperpolarizability values for the ground and first two excited vibrational states of hydrogen fluoride using different levels of treating the vibrational motion. The most dramatic effect of vibration, relative to the equilibrium *electronic* properties is for the hyperpolarizability. In part, this is because the hyperpolarizability of HF is of relatively small magnitude around the equilibrium, yet changing quickly. However, it is not vibrational averaging that makes the most significant effect. Rather it is the vibrational polarization arising from the equilibrium shift that would occur were a field applied. This fact was first demonstrated by Bartlett [S-27, A-15]. From the values in TABLE 7.12, it is obvious that this vibrational polarization is already apparent within the doubly harmonic model. There are effects of mechanical anharmonicity and electrical anharmonicity, but they are much less important.

The mechanically harmonic results in TABLE 7.12 are more similar to the doubly harmonic results than are the electrically harmonic results. This says that in this case, the anharmonicity of the potential plays a more noticeable role in determining the state properties than does the non-linearity of the properties. This is true both for simple vibrational averages and for complete or derivative property values. Comparisons this

TABLE 7.12

Doubly harmonic, harmonic, vibrationally averaged, and complete evaluations of the vibrational state dipole moment, and axial dipole polarizability and hyperpolarizability of HF [D-21]. Values are in a.u. The dipole moment from the electronic wavefunction included correlation effects at the ACCD level, but the polarizability and hyperpolarizability are SCF level results obtained with DHF. The equilibrium values (eq) are the values of the electronic wavefunction at the equilibrium of the potential curve (0.9254 Angstroms). The mechanically harmonic values (mh) are from a harmonic potential with the same equilibrium separation and equilibrium force constant. The electrically harmonic values (eh) are obtained with a linear functional form for the electrical properties, with the slopes determined from two near equilibrium points. The doubly harmonic (dh) values use the mechanically harmonic potential and the electrically harmonic properties. The complete values, those with no harmonic assumptions, are designated with a subscript "v", and were obtained from a DNC calculation. The bracketed values are vibrational averages. If properties at a certain level are strictly identical for all vibrational states, then they are listed only for the v = 0 state.

	v = 0	*v = 1*	*v = 2*	
E_v-E_0 (cm^{-1})	0.0	3961	7757	
(expt.)	0.0	3961	7751	[G-16]
$\mu^{eq} = \mu^{dh}$	0.716			
$\mu^{mh} = <\mu>^{mh}$	0.716	0.716	0.716	
$\mu^{eh} = <\mu>^{el}$	0.725	0.744	0.764	
$\mu_v = <\mu>_v$	0.725	0.744	0.762	
μ_{expt} [G-16]	0.718	0.736		
α^{eq}	5.723			
α^{dh}	5.562			
$<\alpha>^{mh}$	5.777	5.886	5.995	
α^{mh}	5.616	5.725	5.834	
$<\alpha>^{eh}$	5.911	6.256	6.612	
α^{eh}	5.739	6.061	6.391	
$<\alpha>_v$	5.946	6.426	6.959	
α_v	6.115	6.612	7.160	
β^{eq}	9.14			
β^{dh}	0.73			

	$v = 0$	$v = 1$	$v = 2$
$<\beta>^{mh}$	9.66	10.71	11.76
β^{mh}	1.07	2.12	3.17
$<\beta>^{eh}$	10.17	11.90	13.67
β^{eh}	1.06	1.58	2.03
$<\beta>_v$	10.51	13.59	17.26
β_v	-0.47	-1.07	-1.99

detailed are not usually carried out, and it is most common to assume that the first important correction to the doubly harmonic model is, in fact, mechanical anharmonicity.

The differences in properties among low-lying vibrational state is more pronounced for the dipole polarizability than for the dipole moment, and for the hyperpolarizability than the polarizability. Further multipole moments and polarizabilities for the lowest three vibrational states of HF are given in TABLE 7.13.

TABLE 7.13

Derivative Numerov-Cooley values for vibrational state electrical properties of HF. Values are in a.u. See TABLE 7.12 for other details of the calculation.

	$v = 0$	$v = 1$	$v = 2$
M_{xx}	1.292	1.248	1.202
M_{yy}	2.202	2.214	2.225
$P_{x,xx}$	-2.595	-3.184	-3.860
$P_{x,yy}$	0.197	0.218	0.238
$P_{y,xy}$	-0.345	-0.401	-0.463
$P_{xx,xx}$	5.270	6.154	7.288
$P_{xx,yy}$	0.239	0.199	0.158
$P_{xy,xy}$	1.344	1.435	1.538
$P_{yy,yy}$	2.848	2.902	2.965
$P_{yy,zz}$	1.184	1.202	1.224
$P_{yz,yz}$	0.832	0.850	0.870

Vibrational and Rotational Motion Effects. Vibrational effects on electrical properties have been evaluated with different models for quite a number of small molecules, but rotational effects are also of interest. An expression given by Buckingham [B-36] offers one way of evaluating the vibrational-rotational state dependence of properties of a diatomic. This expression is based on a harmonic oscillator model, with a perturbing cubic potential, represented by the cubic force constant, a, and with centrifugal distortion. The property is almost electrically harmonic, having a linear and quadratic dependence on the displacement coordinate. With "ω_e" and "B_e" as the equilibrium vibrational frequency and rotational constant, Buckingham's expression is,

$$P_{\upsilon J} = P_e + (\upsilon + \tfrac{1}{2})(P''_e - 3\,a\,P'_e)\left(\frac{B_e}{\omega_e}\right) + 4\,J(J+1)\,P'_e\left(\frac{B_e}{\omega_e}\right)^2 \qquad (7\text{-}27)$$

P' is the first derivative of the property function P(x) with respect to x, evaluated at the equilibrium, and P" is the second derivative. x is chosen as a reduced displacement coordinate, $x = (r - r_e) / r_e$.

In a study of N_2, Maroulis and Bishop [M-22] used Eqn. (7-27) and evaluated the rotational term for the quadrupole and hexadecapole moments. A change form the $J = 0$ state to the $J = 1$ state, according to their values, would affect the moments by about one part in 10^6. This way of treating vibrational and rotational effects on electrical properties is easily employed. It is not complete, but since the effects are often small, it tends to be sufficient in most instances. The expression has also been given and used specifically for J=0 by Amos [A-11] to give vibrational state dependence. For the nitrogen molecule, Amos found permanent moments and dipole polarizabilities varying by 2% or less from vibrational state to vibrational state.

Analytical techniques for finding properties of individual vibrational-rotational states have not yet been developed. The one analytical technique (DNC) for vibration only relies on a numerical solution of the (one-dimensional) derivative eigenequations. Generalizing to more than one dimension, as would be necessary for treating rotation, is a serious complication. Bishop et al. [B-49] have given expressions for vibrational-rotational state dipole polarizabilities derived from a second order perturbation expression for the energy of a vibrating-rotating molecule in a uniform field. Numerical wavefunctions are employed for the zeroeth order functions, and this enables full allowance for vibration-rotation coupling or centrifugal distortion.

Calculations carried out by Bishop et al. on a manifold of vibrational-rotational states of LiH and HF led to evaluations of thermal averages and macroscopic polarizabilities.

Vibrational Transition Moments. The electrical properties of a molecule can be used to compute radiative transition moments via several schemes. A transition dipole is generally taken to be an off-diagonal element of the matrix representation of the dipole moment in the basis of molecular states. For the n and m vibrational states, the transition moment is,

$$D_{n,m} = \left\langle \Psi_n | \mu | \Psi_m \right\rangle \tag{7-28}$$

With the approximation of being electrically harmonic (eh), the transition moment reduces to a matrix element of the vibrational coordinate, r, times the slope of the dipole moment function at equilibrium. The first or constant term in the electrically harmonic form of the dipole moment function contributes nothing because of the orthogonality of the n and m states.

$$D^{eh}_{n,m} = \left\langle \Psi_n | r | \Psi_m \right\rangle \frac{d\mu}{dr}\Big|_{r_e} \tag{7-29}$$

Both expressions are easy to use for diatomics where numerical wavefunctions of the vibrational states may make for a simple calculation of the integrals.

The most approximate form of a transition moment invokes the doubly harmonic (dh) approximation. With mechanical harmonicity alone, the integrals $< \psi_n | r | \psi_m >$ are simple and non-zero only if n and m are adjacent levels. In those cases, the integrals are directly proportional to the square root of the quantum number. Thus, the doubly harmonic expression for the transition moments requires knowing only the slope of the dipole moment function at the equilibrium and the equilibrium force constant or else the vibrational frequency.

$$D^{dh}_{n,n+1} = \sqrt{n+1}\,\sqrt{2m\omega_e}\,\frac{d\mu}{dr}\Big|_{r_e} \tag{7-30}$$

This expression for transition moments is widely used in electronic structure calculations because it requires no more than the evaluation of a second derivative of the energy at the equilibrium structure. (It is a second derivative because μ is already a first derivative.)

An *ab initio* calculation [L-17] has given doubly harmonic and complete values for transition moments of HF, and has shown how these change because of the presence of perturbing fields. The field free v = 0 → 1 moment that was obtained using Eqn. (7-28) was 0.09915 Debye, while a value of 0.09898 was obtained with the doubly harmonic approximation, Eqn. (7-30). The measured value is 0.0985 [S-26]. For the $v = 0 \rightarrow 2$ overtone transition moment, the calculated value is -0.01131 Debye. The doubly harmonic value is identically zero, and the experimental value is -0.0127 Debye.

The doubly harmonic model is computationally advantageous for polyatomic systems where the equilibrium frequencies and equilibrium slopes of the dipole moment functions can be obtained by differentiation methods. (Interesting ways of achieving efficiency in calculating these quantities have been considered by Komornicki and McIver [K-10] and Yamaguchi et al. [Y-3].) One way in which a more complete treatment can be carried out in a polyatomic problem is to use a basis of normal mode functions to find the matrix representation of the dipole moment function. The dipole moment function may be restricted to be linear in the displacement coordinates (.e., electrically harmonic) or allowed to take a more general form. Then if a transformation has been found from the normal mode basis to a basis that diagonalizes an anharmonic Hamiltonian, it can be applied to the dipole moment matrix. The resulting matrix will contain the transition moments between the (anharmonic) states. The error sources will be truncation in the expansion of the potential, truncation in the functional form of the dipole, and truncation in the normal mode basis.

Calculations by Swanton et al. [S-47] on the three isoelectronic pyramidal systems NH_3, H_3O^+ and CH_3^- showed that the doubly harmonic approximation for the dipole transition moments was appropriate even with the lower inversion barriers where larger departures from harmonic behavior would be expected. Further evidence of the usefulness of the doubly harmonic approximation was given in a detailed study of the water molecule by the same investigators [S-48]. Calculations were done with a number of basis sets and at the SCF and three correlated levels. An important conclusion presented in this comprehensive study was that both diffuse and tight polarization functions were essential for the accurate determination of transition intensities. This is in line with the overall basis requirements for obtaining accurate permanent moments and polarizabilities, of course.

Botschwina's calculations on HCN, HCP and C_2N_2 [B-26] included IR (vibrational dipole) intensities. Compared against experimental values, the use of correlated wavefunctions seems to have given better results than the use of SCF wavefunctions. In some cases, SCF significantly overestimated the intensities relative to correlated wavefunction values.

The dipole polarizability function can be used similar to the dipole moment function in order to compute Raman intensities and depolarization ratios. A doubly harmonic approximation may be employed, and so it is the first derivative of the dipole polarizability tensor with respect to a displacement coordinate that must be obtained. This is a third derivative of the electronic energy. Swanton et al. [S-49] have carried out calculations of this sort for water and for the water dimer. They reported that the main effect of hydrogen bonding is on the anisotropy of the polarizability tensor. They also demonstrated why there should be lower Raman scattering activity for intermolecular vibrations than for intramolecular modes.

A great deal has been learned about electrical properties from *ab initio* calculations. But this is probably only the start of what will be done. From the numerous methods developments over the last several years, there now exist high-powered theoretical techniques to obtain electrical properties, and there is solid practical understanding to set standards of reliability. It is quite likely that new uses for this information will emerge because of how comprehensive the picture of electrical properties can be. An increasingly active area is non-linear optical response where calculations of hyperpolarizabilities are essential.

Chapter Eight

MAGNETIC PROPERTIES

The electron distributions in molecules are sensitive to external magnetic fields and the magnetic fields of nuclei. How they respond and adjust to fields constitute properties such as magnetic multipole susceptibilities and hypersusceptibilities, and also chemical shifts. This can be studied by adding interaction terms to the molecular Hamiltonian in ways that are analogous to the ways used to study electrical properties. However, there are important differences because the interaction Hamiltonians for magnetic field effects are usually more complicated.

Magnetic Interactions. The comparison between magnetic and electric fields from classical magneto-electrostatics is a useful starting point for understanding magnetic interactions [A-7]. As discussed in the prior chapter, the electrical potential, V(x,y,z), may be expanded in field components, field gradient components and so on. The corresponding magnetic feature is not as simple as a scalar function and is instead a vector function, **A**(x,y,z), called the *vector potential.* There are three components, A_x, A_y, and A_z, which may change independently with position. That is,

$$\begin{aligned} A_x &= A_x(x,y,z) \\ A_y &= A_y(x,y,z) \\ A_z &= A_z(x,y,z) \end{aligned} \tag{8-1}$$

Each of these components may be expanded in a power series about some chosen origin.

The magnetic field, **B**, is the curl of **A**.

$$\mathbf{B} \equiv \nabla \times \mathbf{A} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{vmatrix} \tag{8-2}$$

In general, **B** may vary with position because **A** may depend on position. Magnetic moments and susceptibilities are derivatives with respect to **B**, not **A**. However, it is **A** that enters the interaction Hamiltonian for the electronic wavefunctions experiencing a magnetic potential. That Hamiltonian may be constructed by replacing each electron's momentum operator in the following way [A-7,S-43].

$$\mathbf{p} \longrightarrow \mathbf{p} + \frac{e}{c}\mathbf{A} \qquad (8\text{-}3)$$

The sign of the term with **A** is specific for electrons or negatively charged particles. In atomic units, the fundamental charge, e, is one, and the speed of light, c, is 137.0360. All following expressions are written with atomic units and are specific for electrons. The interaction Hamiltonian may be broken into two parts, $\hat{H}_1$ and $\hat{H}_2$.

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2 \qquad (8\text{-}4)$$

$$\hat{H}_1 = \frac{1}{2} \sum_i^{\text{electrons}} \left[\mathbf{A}(\vec{\mathbf{r}}_i) \bullet \mathbf{p}_i + \mathbf{p}_i \bullet \mathbf{A}(\vec{\mathbf{r}}_i)\right] c^{-1} \qquad (8\text{-}5)$$

$$\hat{H}_2 = \frac{1}{2} \sum_i^{\text{electrons}} \mathbf{A}(\vec{\mathbf{r}}_i) \bullet \mathbf{A}(\vec{\mathbf{r}}_i)\, c^{-2} \qquad (8\text{-}6)$$

$\hat{H}_0$ is the field-free electronic Hamiltonian. $\vec{\mathbf{r}}_i$ is the position vector of the i^{th} electron. This Hamiltonian has a term, $\hat{H}_2$, with a second order dependence on the vector potential, while in contrast, electrical interaction gives rise to no more than a first order dependence on the scalar electrical potential.

There may be several magnetic sources, such as one or more external fields, magnetic nuclei, and unpaired electron spins. Each source contributes to the total vector potential for the system in a vector sum.

$$\mathbf{A}(\mathbf{r}_i) = \sum_s^{\text{sources}} \mathbf{A}_s(\mathbf{r}_i) \qquad (8\text{-}7)$$

Consequently, the $\hat{H}_2$ Hamiltonian may contain cross-terms, e.g., $\mathbf{A}_s \bullet \mathbf{A}_t$.

A general relation needs to be established between the power series expansions of **A** and **B**. For notation purposes, a superscript will designate a derivative evaluated at the chosen origin. Thus, B_y^x means the first derivative of $B_y(x,y,z)$ with respect to x and evaluated at x=y=z=0, i.e., at the origin of the power series expansion. B_z^o means $B_z(0,0,0)$ and similarly, A_z^o means $A_z(0,0,0)$. An arbitrary vector potential may be chosen by specifying values for these parameters:

$$A_x(x,y,z) = A_x^o + x A_x^x + y A_x^y + z A_x^z + \frac{1}{2} x^2 A_x^{xx} + \ldots$$

$$A_y(x,y,z) = A_y^o + x A_y^x + y A_y^y + z A_y^z + \frac{1}{2} x^2 A_y^{xx} + \ldots \qquad (8\text{-}8)$$

$$A_z(x,y,z) = A_z^o + x A_z^x + y A_z^y + z A_z^z + \frac{1}{2} x^2 A_z^{xx} + \ldots$$

The parameters in Eqn. (8-8) are the parameters that enter the interaction Hamiltonian linearly and quadratically. Using the techniques of Chapter Five, differentiation of the Schrodinger equation may be carried out with respect to these parameters. Using Eqn. (8-2), these parameters combine to form the parameters in **B**. For example, according to Eqn. (8-2),

$$B_x(x,y,z) = \frac{\partial}{\partial y} A_z(x,y,z) - \frac{\partial}{\partial z} A_y(x,y,z) \qquad (8\text{-}9)$$

Expressed as a power series,

$$B_x(x,y,z) = B_x^o + x B_x^x + y B_x^y + z B_x^z + \frac{1}{2} x^2 B_x^{xx} + \ldots \qquad (8\text{-}10)$$

Substituting Eqn. (8-8) into Eqn. (8-9) and then equating with like terms in Eqn. (8-10) yields,

$$\begin{aligned} B_x^o &= A_z^y - A_y^z \\ B_x^x &= A_z^{xy} - A_y^{xz} \quad \text{etc.} \end{aligned} \qquad (8\text{-}11)$$

A general expression for the relation between the power series terms is,

$$B_i^\alpha = A_k^{\alpha j} - A_j^{\alpha k} \quad \text{where} \begin{pmatrix} i \\ j \\ k \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \begin{pmatrix} y \\ z \\ x \end{pmatrix}, \text{or} \begin{pmatrix} z \\ x \\ y \end{pmatrix} \qquad (8\text{-}12)$$

α means differentiation to an arbitrary order with respect to x, y, and z.

The simple relation between energy derivatives with respect to **A** and energy derivatives with respect to **B** may be obtained through chain rule differentiation. The energy, E, is a function of **A**, and the elements of **B** are functions of **A** in the simple form given by Eqn. (8-12). A transformation of variables (**A** to **B**) is implicit, and to follow the process, we will write Eqn. (8-12) in a representative way (for all cases)

$$B = x - y \qquad (8\text{-}13a)$$

and at the same time introduce another parameter/variable, C, which is the other independent variable that may be constructed from "x" and "y" (or really, A parameters).

$$C = x + y \tag{8-13b}$$

The desired energy derivatives are with respect to B, whereas the directly obtained derivatives are with respect to x and y. The chain rule may now be used.

$$\frac{\partial E}{\partial x} = \frac{\partial E}{\partial B}\frac{\partial B}{\partial x} + \frac{\partial E}{\partial C}\frac{\partial C}{\partial x} = \frac{\partial E}{\partial B} + \frac{\partial E}{\partial C} \tag{8-14a}$$

$$\frac{\partial E}{\partial y} = \frac{\partial E}{\partial B}\frac{\partial B}{\partial y} + \frac{\partial E}{\partial C}\frac{\partial C}{\partial y} = -\frac{\partial E}{\partial B} + \frac{\partial E}{\partial C} \tag{8-14b}$$

The second step in these two equations uses Eqn. (8-13) to evaluate the partial derivatives of B and C with respect to x and y. Combining terms in Eqn. (8-14) yields,

$$\frac{\partial E}{\partial B} = \frac{1}{2}\left(\frac{\partial E}{\partial x} - \frac{\partial E}{\partial y}\right) \tag{8-15}$$

For higher differentiation, one obtains,

$$\frac{\partial^n}{\partial B^n} = \left[\frac{1}{2}\left(\frac{\partial}{\partial x} - \frac{\partial}{\partial y}\right)\right]^n \tag{8-16}$$

Returning to the explicit notation used in Eqn. (8-12), a general derivative with respect to the parameters in **B** may be related to derivatives with respect to the parameters in **A**.

$$\left(\frac{\partial}{\partial B_i^{\alpha}}\right)^n \left(\frac{\partial}{\partial B_r^{\beta}}\right)^m \cdots = \left[\frac{1}{2}\left(\frac{\partial}{\partial A_k^{\alpha j}} - \frac{\partial}{\partial A_j^{\alpha k}}\right)\right]^n \left[\frac{1}{2}\left(\frac{\partial}{\partial A_t^{\beta s}} - \frac{\partial}{\partial A_s^{\beta t}}\right)\right]^m \cdots \tag{8-17}$$

This general result is the means for finding magnetic multipole susceptibilities and hypersusceptibilities.

Magnetic Properties. The first derivatives of the electronic energy with respect to the parameters of **B** associated with a uniform magnetic field, i.e., B_x^o, B_y^o and B_z^o, are the elements of the magnetic dipole arising from the electron distribution. (These are zero for closed shell or zero angular momentum systems.)

First derivatives with respect to higher order parameters in **B** would be associated with components of higher order magnetic multipoles. Second derivatives are magnetic susceptibilities, and third and higher derivatives are magnetic hypersusceptibilities. Keeping with the notational style of Chapter Seven, we will designate these derivatives as elements of various rank polytensors, **S** (for susceptibility).

$$\mathbf{S}^{(2)}_{\alpha,\beta} \equiv \frac{\partial^2 E}{\partial B_\alpha \partial B_\beta}\Big|_{\mathbf{B}=0} \tag{8-18}$$

$$\mathbf{S}^{(3)}_{\alpha,\beta,\gamma} \equiv \frac{\partial^3 E}{\partial B_\alpha \partial B_\beta \partial B_\gamma}\Big|_{\mathbf{B}=0} \qquad \text{etc.} \tag{8-19}$$

The superscript on **S** indicates the rank of the polytensor. α, β, and γ are collective indices for the parameters for an arbitrary **B**, such as those in Eqn. (8-10). The ordering of these elements can be taken to be the following.

$$B^o_x,\ B^o_y,\ B^o_z,\ B^x_x,\ B^y_x,\ B^z_x,\ B^x_y,\ B^y_y,\ B^z_y,\ B^x_z,\ B^y_z,\ B^z_z,$$

$$B^{xx}_x,\ B^{xy}_x,\ B^{xz}_x,\ B^{yx}_x,\ B^{yy}_x,\ B^{yz}_x,\ B^{zx}_x,\ B^{zy}_x,\ B^{zz}_x,\ B^{xx}_y,\ \ldots$$

This is an anticanonical ordering for subscripts or for superscripts as used for the electrical moment polytensors. In this ordering scheme, the superscript changes most rapidly, going through all possibilities associated with a particular electric moment order, and then the subscript is changed. The susceptibility polytensors are symmetric. The order of the superscripts in the B parameters may be freely permuted, but the subscripts on these parameters may not be exchanged with the superscripts. It is important to realize that in general, $B^y_x \neq B^x_y$.

A chemical shielding tensor represents the change in the molecular energy from the interactions connected with both an external field and magnetic nuclei. As such, a formal definition might be that the chemical shielding is a second derivative of the energy, comparable to a susceptibility.

$$\sigma_{\alpha,\beta} = \frac{\partial^2 E}{\partial B_\alpha \partial b_\beta}\Big|_{\mathbf{B}=0,\mathbf{b}=0} \tag{8-20}$$

where **b** is the field associated with a nuclear magnetic moment (dipole). The vector potential arising from an intrinsic magnetic dipole moment **m** is,

$$\mathbf{A}(\mathbf{r}) = \mathbf{m} \times \mathbf{r} / r^3 \tag{8-21}$$

where **r** is the position vector originating at the location of the point dipole **m**, and so,

$$\mathbf{b}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r}) = \nabla \times \mathbf{m} \times \mathbf{r} / r^3 \tag{8-22}$$

One may think of the three components of **m** as parameters. Thus, differentiation of the energy with respect to the parameters in a power series expansion of **b** implies differentiation with respect to **m** via the relation of Eqn. (8-22). Another definition of the chemical shielding tensor is in terms of derivatives with respect to the components of **m**, and one has,

$$\sigma_{\alpha,\beta} = \frac{\partial^2 E}{\partial B_\alpha \partial m_\beta}\bigg|_{\mathbf{B}=0,\mathbf{m}=0} \tag{8-23}$$

The process to work out the derivative expression is to sum the vector potentials from **B** and **m** as in Eqn. (8-7) and then form $\hat{H}_1$ and $\hat{H}_2$, as in Eqns. (8-5) and (8-6), in terms of the **A** parameters of each. Derivatives obtained with respect to these **A** parameters would be combined to yield the derivatives in Eqn. (8-23). Explicit expressions where this has been done for chemical shielding tensors are available [F-7].

Phenomenologically, the chemical shielding tensor is introduced as a tensor that alters the field at a magnetic nucleus in a proportional way with respect to any externally applied field.

$$\mathbf{B} = (1 - \sigma)\, \mathbf{B}^{ext} \tag{8-24}$$

Thus, the total field experienced at a nucleus is dimished or augmented by an amount proportional to σ and to the external field. This phenomenological definition must assume that σ is independent of **m** and **B** and that the energy of interaction is $-\mathbf{m}\bullet\sigma\bullet\mathbf{B}$, with no higher dependence on **m** or **B**. There is no formal argument that the interaction energy is strictly truncated at this simple dependence, though the fields usually encountered are weak enough to insure the high quality of this truncation approximation. Any higher dependence on **m** and **B** that may happen to be identified would correspond to higher order derivatives of the energy. Even as magnets for generating external fields become more powerful, it remains that **m**, the nuclear dipole field, is small and not adjustable. Truncating the interaction energy to a linear dependence on **m** is not at all drastic, and typically the $\hat{H}_2$ term arising from nuclear dipole fields is neglected entirely because it is very small [S-43].

In molecules possessing unpaired electrons, the phenomenological dipolar electron spin-nuclear spin hyperfine coupling interaction is,

$$\hat{H}_{SI} = \vec{\mathbf{S}} \bullet \mathbf{T} \bullet \vec{\mathbf{I}} \tag{8-25}$$

where $\vec{S}$ is the electron spin vector and $\vec{I}$ is the nuclear spin vector. The intrinsic magnetic dipole moments are proportional to the spin vectors, and the proportionality constants are collected in the tensor **T**. The elements of the tensor operator **T** for magnetic dipole-dipole interaction is [B-45],

$$T_{\alpha\beta} \quad = \quad g_e g_n \mu_B \mu_n \frac{3\alpha\beta - r^2 \delta_{\alpha\beta}}{r^5} \quad \text{where } \alpha,\beta = \{x,y,z\} \qquad (8\text{-}26)$$

where r is the magnitude of the position vector relative to the nuclear center with moment **m**. The constants are the electron and nuclear g-factors and the electronic and nuclear magnetons. The form of **T** is that arising from the classical interaction of two *point* dipoles, while treating the nucleus as being non-vanishing in size brings in the *contact interaction.* The spin Hamiltonian may include that interaction as well [B-45]. The Hamiltonian in Eqn. (8-25) is a spin-Hamiltonian. In terms of the electronic Hamiltonians we have been considering, this interaction may enter as an $\hat{H}_2$ term as in Eqn. (8-6). It involves the cross term of the contributions to the vector potential arising from the intrinsic magnetic moments. In this way of thinking, it may be possible to regard **T** as a second derivative property. However, it is more common to work in the spin-Hamiltonian picture and just use the expectation value of the elements of **T** over the electronic wavefunction.

Dipole-dipole interaction is a fundamental term in the Hamiltonian for systems with intrinsic spins. For two magnetic nuclei, the dipole-dipole interaction may be unimportant because of the large distance between the centers in a molecule. The spins of magnetic nuclei may be coupled, of course, via the electrons and this gives rise to the usual NMR spin-spin couplings [A-7,F-1]. To analyze these couplings from first principles, $\hat{H}_2$ must include the the interaction between the magnetic nuclei and the electrons, and this must include the contact interaction.

Construction of One-electron Operators. The perturbing operators in Eqns. (8-5) and (8-6), or for the specific field in Eqn. (8-21), or the tensor operator of Eqn. (8-26) are one-electron operators. The first step in applying derivative techniques for the analytical evaluation of magnetic properties is the construction of matrix representations of appropriate operators in the chosen atomic orbital basis. Should expectation values for properties suffice, they are just traces of the products of these matrix operators with the one-electron density matrix. For uniform and dipolar fields, evaluating the integrals over basis functions of the operators is relatively straightforward, and computational means have been in existence for this purpose throughout most of the history of quantum chemistry. For more general situations, perhaps anticipating exotic magnetic probing of molecules in the future, Augspurger

[A-17] has completed implementation of a scheme for evaluation of the one-electron integrals over atomic basis functions of the general form,

$$\int \phi_a(x,y,z) \left\{ x^i y^j z^k \left(\frac{\partial}{\partial x}\right)^s \left(\frac{\partial}{\partial y}\right)^t \left(\frac{\partial}{\partial z}\right)^u \frac{1}{r^p} x^f y^g z^h \right\} \phi_b(x,y,z)\, dx\, dy\, dz$$

where f, g, h, i, j, and k may be zero or any positive integers and p may one or zero. The atomic basis functions may be Cartesian gaussians of any type, s, p, d, f, etc.

For operators where p = 0, the integral separates into integrals over x, y, and z. The representative form of these integrals is

$$\int_{-\infty}^{\infty} x^N e^{-\alpha_a (x - x_a)^2} e^{-\alpha_b (x - x_b)^2} dx \qquad (8\text{-}27)$$

That is, the x, y, z dependence of the Cartesian gaussians and the x, y, z, dependence of the operator can be collected together. This dependence will multiply a product of two simple gaussians. Should the operator or the basis functions be specified relative to different centers, then some combination of integrals of the form of Eqn. (8-27) but with lower values of N will be needed, as in,

$$\int (x - x_o)^3 f(x)\, dx = \int x^3 f(x)\, dx - 3x_o \int x^2 f(x)\, dx + 3\, x_o^2 \int x\, f(x)\, dx - x_o^3 \int f(x)\, dx$$

There are standard means for evaluating integrals of the type of Eqn. (8-27), and so all that is necessary is an open-ended procedure to combine integrals with suitable binomial coefficients [A-17].

When p = 1, separability is lost; however, this problem is overcome by using a Fourier transform as is standard in the evaluation of electron-nuclear attraction integrals [T-9]. The substitution for 1/r is,

$$\frac{1}{r} = \frac{1}{2\pi^2} \int_{-\infty}^{\infty} \frac{d\vec{k}}{|\mathbf{k}|^2} e^{i\vec{k}\cdot\vec{r}} \qquad (8\text{-}28)$$

The Fourier transform of the derivative of 1/r is

$$\left(\frac{\partial}{\partial x}\right)^r \left(\frac{\partial}{\partial y}\right)^s \left(\frac{\partial}{\partial z}\right)^t \frac{1}{r} = \frac{1}{2\pi^2} \int_{-\infty}^{\infty} \frac{d\vec{k}}{|\mathbf{k}|^2} k_x^r k_y^s k_z^t e^{i\vec{k}\cdot\vec{r}} \qquad (8\text{-}29)$$

The exponential involving **r** can be separated,

$$e^{i\vec{k}\cdot\vec{r}} = e^{ik_x x} e^{ik_y y} e^{ik_z z} \tag{8-30}$$

and then the desired quantity involves separate integration over x, y, and z and then over $\vec{\mathbf{k}}$. The generalization to all types of operators and all Cartesian basis functions is accomplished through logic in the combining of the intermediate pieces that is not specialized or restricted [A-17].

Evaluation of Derivatives. The operator $\hat{H}_1$ in Eqn. (8-5) is pure imaginary and is anti-Hermitian, while $\hat{H}_2$ is real and Hermitian [S-42]. In the derivative Schrodinger equations for the magnetic parameters, all the operators and wavefunctions will be either pure imaginary or real. To see this, consider the first and second derivative expressions for an arbitrary **A** parameter, "a".

$$\left(\hat{H}_o - E_o\right)\Psi_o^a = -\left(\hat{H}_o^a - E_o^a\right)\Psi_o \tag{8-31}$$

Integration with Ψ_o^* applied on the left means that E_o^a is the expectation value of $\hat{H}_o^a$, one part of the pure imaginary operator $\hat{H}_1$. With Ψ_o real, the expectation value of the pure imaginary operator is either imaginary or zero. Thus, the right hand side of Eqn. (8-31) is a purely imaginary function, and so Ψ_o^a on the left hand side must also be. The second derivative expression may be examined likewise.

$$\left(\hat{H}_o - E_o\right)\Psi_o^{aa} = -\left(\hat{H}_o^{aa} - E_o^{aa}\right)\Psi_o - 2\left(\hat{H}_o^a - E_o^a\right)\Psi_o^a \tag{8-32}$$

The right hand side terms are real, and so Ψ_o^{aa} must be real.

Each derivative equation can be multiplied by some power of *i* so as to make the equation purely real. This makes it convenient to use real terms for each derivative order of an operator, matrix, or wavefunction scaled by the appropriate power of *i*., as in the series $X_o, iX_1, -X_2, -iX_3, X_4, iX_5, \ldots$ for some quantity X. Each X_j is real. In a procedure such as derivative Hartree-Fock (DHF) (see Chapter Five), the scaling by $(i)^n$ may be carried implicitly. The calculated derivative energies and wavefunctions may be multiplied by the appropriate power of *i* at the end of a calculation. That power, of course, is just the order of differentiation. To see this, consider the following power series expansions.

$$H = \sum_{n=o}^{\infty} \frac{(a)^n}{n!} H_o^{a^n} = \sum_{n=o}^{\infty} \frac{(ia)^n}{n!} \tilde{H}_o^{a^n} \tag{8-33a}$$

$$E = \sum_{n=o}^{\infty} \frac{(a)^n}{n!} E_o^{a^n} = \sum_{n=o}^{\infty} \frac{(ia)^n}{n!} \tilde{E}_o^{a^n} \tag{8-33b}$$

$$\Psi = \sum_{n=0}^{\infty} \frac{(a)^n}{n!} \Psi_o^{a^n} = \sum_{n=0}^{\infty} \frac{(i\,a)^n}{n!} \tilde{\Psi}_o^{a^n} \qquad (8\text{-}33c)$$

Substitution in Eqn. (8-32) yields an expression of identical form after multiplying the equation by -1:

$$(\tilde{H}_o - \tilde{E}_o)\, i^2\, \tilde{\Psi}_o^{aa} = -i^2 (\tilde{H}_o^{aa} - \tilde{E}_o^{aa})\, \Psi_o - 2\,(i\,\tilde{H}_o^{a} - i\,\tilde{E}_o^{a})\, i\, \tilde{\Psi}_o^{a}$$

$\tilde{E}$ values may be directly computed and then multiplied by a power of *i* to yield the true derivatives of the energy.

Gauge Dependence. A vector **Y** for which $\nabla \times \mathbf{Y} = 0$ may be added to the vector potential **A** without changing the magnetic field **B**. Any such change in the vector potential must leave the true magnetic field response properties unaffected. This arbitrariness in the vector potential is an arbitrariness in the choice of the *gauge*. A *gauge transformation* is any specific change in **A** that leaves **B** unchanged. The freedom to choose the gauge is somewhat, though not entirely, like the freedom to specify the zeroeth term of the scalar electrical potential, V_0. The choice of V_0 does not alter the permanent electrical moments or polarizabilities, and one should expect to see like invariance in magnetic properties with respect to the choice of the gauge. Working in the *Coulomb gauge* means that $\nabla \cdot \mathbf{A} = 0$.

Because of the basis set truncation in an *ab initio* calculation with conventional orbital functions, magnetic properties are not strictly invariant to the choice of the guage. This is particularly problematic for small basis sets where sharply differing values are obtained upon varying the choice of the gauge. Ditchfield [D-19,37] established the use of orbitals that were dependent on **A** in such a way that the final results were independent of the choice of the gauge. These have been designated as *gauge invariant atomic orbitals* (GIAO), though it is not the atomic orbitals that are invariant but the magnetic properties. (Ditchfield has pointed out that "gauge-dependent" is a better way of describing these orbitals [D-38].) GIAO's are constructed from conventional, atom-centered basis functions by choosing a coordinate system origin for the species under study and incorporating an origin dependent function. Let $\mathbf{R}_\alpha$ be the position vector from that origin to the α-nucleus. For a uniform magnetic field, **B**, a GIAO, $\phi(\mathbf{r})$, at the center α is defined using some conventional Gaussian function centered on the α nucleus, $\chi(\mathbf{r})$:

$$\phi(\mathbf{r}) \equiv \chi(\mathbf{r})\, e^{-i\, \mathbf{B} \times \mathbf{R}_\alpha \cdot \mathbf{r}/2} \qquad (8\text{-}34)$$

The GIAO's have a complex exponential dependence on the part of the vector potential arising from the external uniform magnetic field, and one may substitute

$$\mathbf{A}_{\text{ext}} = \frac{1}{2}\, \mathbf{B} \times \mathbf{R}_{\alpha} \tag{8-35}$$

for the direct product in Eqn. (8-34). The form of the GIAO's leads to one- and two-electron integrals that are dependent of the external magnetic field.

The one-electron *current density* associated with a wavefunction Ψ is defined [S-43] as

$$\mathrm{j}(\mathbf{r}) = \frac{1}{2i}\left(\Psi^{*}\nabla\Psi - \Psi\nabla\Psi^{*}\right) - \mathbf{A}\Psi^{*}\Psi / c \tag{8-36}$$

and should be gauge invariant and conserved. Epstein [E-3] has shown that use of GIAO's does not insure current conservation because the GIAO wavefunction is not invariant to a gauge transformation. The gauge invariance is termed an "enforced" invariance because the gauge dependence of the GIAO's amounts to changing the basis to follow a gauge change, "or equivalently, by always returning to the original gauge to do the calculation" [E-3]. The GIAO's may be thought of as providing basis set flexibility that would be found only in larger conventional sets. The usefulness of GIAO's is something mainly demonstrated by calculational results.

Schindler and Kutzelnigg [S-42] have significantly generalized the use of gauge dependent orbitals for the calculation of NMR parameters. Instead of a common origin for $\mathbf{R}_{\alpha}$ in Eqn. (8-34), they use the centroid of charge of each different occupied orbital, applying the same type of exponential involving the vector potential, but to the molecular orbitals. While additional terms must be computed with this approach, only conventional two-electron integrals involving the original basis functions are required.

Magnetic Susceptibilities and Shielding. There have been a sizable number of calculations of magnetic properties of molecules, though such calculations are not as extensive as calculations of electrical properties. Some of the first were those of Ditchfield using GIAO's, and a survey of early results obtained with 4-31G bases is given in TABLE 8.1. In direct comparisons of GIAO and field-independent basis results, Ditchfield found that the GIAO procedure yielded more uniform ^{13}C and proton shifts and better agreement with experiment [D-19]. Among the worst cases was the proton shielding for HCN relative to methane. The field-independent basis gave -26.3 ppm, the GIAO basis gave -3.79 ppm, and the measured value was -2.83 ppm. A recent comparison of GIAO values versus conventional bases, again at the

TABLE 8.1

Calculated and experimental ^{13}C chemical shifts reported by Ditchfield [D-39]. The shifts are in ppm relative to methane. The calculations were at the 4-31G/SCF level using GIAO's.

Molecule	*Calculation*	*Experiment*
CH_3F	-65.4	-77.5
CH_2F_2	-98.3	-111.3
CHF_3	-115.5	-118.7
CF_4	-126.2	-123.9
HCCH	-75.2	-76.0
C_2H_4	-130.8	-125.6
C_2H_6	-7.4	-8.0
H_2CO	-199.6	-197.0
CH_3OH	-45.5	-51.4
CH_3NH_2	-26.5	-30.4

TABLE 8.2

Magnetic shielding constants (in ppm) calculated by Fukui et al. [F-7] with a 4-31G and larger bases at the SCF level. (Experimental values are those quoted in their report.) For H_3O^+ and OH^-, the shielding is relative to H_2O.

		Oxygen shielding	*Proton shielding*
H_2O	Experiment	334	30.2
	4-31G (gauge center O)	266	26.4
	4-31G (gauge center H)	282	87.1
	4-31G GIAO	327	32.4
	DZP GIAO	327	31.2
H_3O^+	Experiment	-9	-14.5
	DZP GIAO	-27.6	-9.0
OH^-	Experiment		-1.8
	DZP GIAO	-8.5	7.9

4-31G/SCF level, has been reported by Fukui et al. [F-7]. As shown in TABLE 8.2, the gauge invariant values are in much better agreement with experimental values than the results with the small conventional basis. It is also interesting that enlarging the basis to include polarization functions had a very small effect on the shielding constants. With this study and calculations on a series of diatomics, Fukui et al. [F-8] have argued that small basis GIAO results are superior to calculations lacking gauge invariance, even those with larger bases.

Lazzeretti et al. [L-22] calculated the magnetic susceptibility of water, methane and ammonia with conventional or field-independent bases. The contributions were partitioned into diamagnetic and paramagnetic parts, and the former were found to be the more insensitive to the basis set size. A summary of their results is given in TABLE 8.3. In a further study of these three molecules, Lazzeretti and Zanasi [L-23] argued in favor of the use of large basis sets instead of GIAO's, in part, because gauge dependence of the basis does not insure current conservation [E-3]. Their computed shielding values are given in TABLE 8.4. The QZP basis (designated as basis "IV" by the authors) was a flexible (11s 7p 2d / 6s 5p 1d) contracted set for carbon, nitrogen and oxygen. For both shielding tensor and susceptibilities, the results with this size of a basis are in fairly good agreement with measured values. In a more detailed basis set study of water, Lazzeretti and Zanasi [L-24] used a triply polarized basis and found diminishment of the gauge sensitivity and very good agreement with measured values. Similar calculations have been reported for second row hydrides [L-25] and for benzene [L-26].

It seems clear at this point that there is a similarity in basis set requirements for second derivative magnetic properties to that for electrical polarizabilities. Both require significant flexibility in valence and polarization sets. This is not surprising because a conventional valence basis is usually not capable of adequately describing the electronic readjustment that occurs in response to fields. It is interesting that introducing gauge dependence into a modest basis makes it possible to achieve good quality results. This field dependence amounts to a special kind of flexibility to respond to magnetic fields, for the currents induced by external fields to be described. In the case of electrical polarizabilities, making the basis functions field-dependent introduces the flexibility for the center of the functions to be displaced from the atomic center because of a field. In this way, even an s-basis function can be polarized, and thus, a small basis proves useful. At the same time, it is encouraging that conventional, field-independent bases are not unmanageable at the size required for accurate results. The use of large, but field-independent bases may provide better flexibility in that basis sets can be systematically enlarged and properties tested for convergence.

TABLE 8.3

Calculated magnetic susceptibilities of first row hydrides (in ppm a.u.) [L-22].

Molecule	*Basis*	*Component*	*Diamagnetic*	*Paramagnetic*	*Total*
H_2O	MBS	xx	-166.18	8.25	-157.93
		yy	-183.20	15.59	-167.61
		zz	-198.26	15.30	-182.96
	DZ	xx	-157.74	7.54	-150.20
		yy	-170.56	12.19	-158.37
		zz	-185.05	14.58	-170.47
	QZP	xx	-163.09	6.83	-156.26
		yy	-171.46	12.70	-158.76
		zz	-183.53	24.23	-159.30
	Expt. [a]	xx		8.16	
		yy		15.73	
		zz		26.66	
NH_3	MBS	xx	-246.61	16.58	-230.03
		zz	-275.67	15.30	-260.37
	DZ	xx	-229.62	16.95	-212.67
		zz	-254.04	21.73	-232.31
	QZP	xx	-229.93	28.05	-201.88
		zz	-247.49	56.65	-190.84
	Expt.[b]	xx		33.57	
		zz		64.64	
CH_4	MBS	ave.	-354.93	20.69	-344.24
	DZ	ave.	-334.72	35.54	-299.18
	QZP	ave.	-317.42	94.54	-222.88
	Expt. [c]	ave.	-299.3	104.3	-195

[a] Values deduced [A-18] from measured rotational magnetic moments [K-15]. [b] [E-4]

[c] [A-19:20]

TABLE 8.4

Calculated magnetic shielding tensor components for the heavy nuclei in water, ammonia and methane (in ppm) [L-23]. The origin in each calculation was the molecular center of mass.

Molecule	*Basis*	*Component*	*Diamagnetic*	*Paramagnetic*	*Total*
H_2O	MBS	xx	419.04	-199.17	219.87
		yy	416.40	-378.23	38.17
		zz	414.91	-339.64	75.27
	DZ	xx	416.39	-146.61	269.78
		yy	416.05	-246.23	169.82
		zz	415.33	-214.92	200.41
	QZP	xx	414.19	-55.91	358.28
		yy	415.82	-116.63	299.19
		zz	415.78	-122.53	293.25
		ave.	415.26	-98.36	316.90
	Expt. [a]	ave.			334
NH_3	MBS	xx	353.84	-244.71	109.13
		zz	351.53	-195.64	155.89
	DZ	xx	353.71	-153.97	199.74
		zz	353.89	-129.97	223.92
	QZP	xx	352.51	-77.26	275.25
		zz	355.56	-115.37	239.99
		ave.	353.46	-89.96	263.50
	Expt.[b]	xx		-76	
		zz		-117	
		ave.		-89.7	
CH_4	MBS	ave.	292.93	-133.96	158.97
	DZ	ave.	295.70	-78.75	216.95
	QZP	ave.	296.30	-100.34	195.96
	Expt. [a]	ave.			196

[a] [A-21] [b] [K-16]

The properties discussed so far are equilibrium properties, or properties appropriate for fixed geometries of the molecules. Just as for electrical properties (see Chapter Seven) vibration and rotation may affect or contribute to the intrinsic molecular properties. This is of particular importance when making critical comparisons with experimental values. Ditchfield has carried out calculations on three diatomics to find the vibrational and rotational state dependencies of the magnetic shielding tensors [D-40]. The shielding tensors were computed for various separation distances and the derivatives of the tensor elements with respect to the reduced stretching coordinate, s, were computed. These were combined with vibrational averages of the stretching coordinate to yield approximate property values for the manifold of vibrational-rotational states.

$$\sigma_{\upsilon J} = \sigma_e + \sigma_e^{s} \langle s \rangle_{\upsilon J} + \frac{1}{2} \sigma_e^{ss} \langle s^2 \rangle_{\upsilon J} + \cdots \qquad (8\text{-}37)$$

The superscripts on σ designate the order of differentiation with respect to s, each derivative being evaluated at the equilibrium. With vibration-rotation state values, thermal averages were obtained to find the temperature dependence of the shielding. TABLE 8.5 gives certain of the results that were obtained. The changes from state to state are small, but the thermal averages show an improved kind of agreement with experiment [D-40].

The effect of hydrogen bonding on NMR parameters is of interest in order to understand NMR solution spectra. *Ab initio* studies that have been carried out have

TABLE 8.5

Calculated vibrational-rotational state (vJ) shielding tensor components (in ppm) [D-40].

v	J	H_2		HF (at H)		HF (at F)	
		σ_{xx}	σ_{yy}	σ_{xx}	σ_{yy}	σ_{xx}	σ_{yy}
0	0	25.69	27.33	21.07	43.43	379.82	482.10
0	1	25.67	27.31	21.07	43.41	379.68	482.10
0	2	25.63	27.26	21.06	43.38	379.41	482.10
1	0	25.07	26.61	20.82	41.89	344.36	482.07
1	1	25.05	26.59	20.81	41.87	344.19	482.07
1	2	25.00	26.54	20.80	41.84	343.87	482.07

been on hydrogen bonded dimers, for the most part. Ditchfield and coworkers have calculated shielding tensors for a number of dimers containing water and other -OH molecules [D-41:42,R-13:14]. A selection of their results in TABLE 8.6 shows that the shifts in the isotropic shielding are typically a few ppm. The anisotropies, however, show more significant changes. This corresponds to an observation that shielding along the axis of the hydrogen bond is generally increased while shielding in the two orthogonal directions is diminished. The result is greater anisotropy. A sizable portion of these changes in shielding were found to be brought about by the change in currents at the proton center from hydrogen bonding. A connection with hydrogen bonding mechanisms was also suggested [D-41:42], though the 4-31G basis sets used may be too small to confidently associate shielding changes with charge transfer, polarization, etc.

Chemical shifts are often used to deduce structural information, and for hydrogen bonded systems, Berglund and Vaughan [B-46] established a correlation between separation distance and chemical shifts through measurements on a series of solids. This led to the calculations of Rohlfing et al. [R-13:14] which explored the dependence of monomer orientation in the magnetic shielding of several hydrogen bonded dimers. An important correlation between the separation distance and the *isotropic* shielding was found.

TABLE 8.6

Calculated magnetic shielding for water complexes (in ppm) [D-41:42]. Shieldings are for the proton in the XOH species.

Complex	σ_{iso} [a]	$\Delta\sigma$ [a]	$\delta(\sigma_{iso})$ [a]	$\delta(\Delta\sigma)$ [a]
$HOH\text{-}OH_2$	29.76	30.34	-2.95	12.03
$CH_3OH\text{-}OH_2$	28.6	32.7	-4.3	15.6
$NH_2OH\text{-}OH_2$	25.4	27.4	-4.4	12.1
$HOOH\text{-}OH_2$	23.1	24.4	-4.7	11.9
$FOH\text{-}OH_2$	19.2	17.6	-4.9	6.4

[a] $\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$; $\Delta\sigma = \sigma_{11} - (\sigma_{22} + \sigma_{33})/2$ where σ_{11}, σ_{22} and σ_{33} are the principal values of σ with σ_{11} the largest. δ refers to the difference between values for the complex and the isolated monomer.

Calculations by Tossell and Lazzeretti [T-10] correctly gave the trend in shielding of ^{31}P in the series PF_3, PO_4^{3-}, PF_4, PF_5 and PF_6^-. Conventional or guageless bases were employed, (6s5p2d) set for phosphorus and a (4s3p1d) set for fluorine. Though the trend among the series was well predicted, the isotropic phosphorus shieldings tended to be overestimated by around 20%. Values for the anisotropy in the shielding tensors were in agreement with available experimental values to about 10%. A similar study [T-11] of the ^{29}Si series of molecules, SiF_4, SiF_5^-, SiF_6^{2-}, and SiO_4^{4-}, gave particularly promising results. The correlation between silicon chemical shift and bond length in SiF_4 and SiO_4^{4-} was found only to be weak. Thus, observed variations in ^{29}Si NMR spectra of silicate solids and solutions [G-17,S-44:45] and significant correlations with Si-O distance implies an indirect relationship. The calculations also seemed to give an accurate determination of the shielding anisotropy upon distorting the otherwise tetrahedral SiO_4^{4-}. The calculations, in this case, provide the means for understanding the correlations between spectra and structure and are likely to extend the capability of deducing structure from NMR spectra.

Large, gauge-independent basis set calculations of Weller et al. [W-8] yielded shielding values nearly independent of the gauge origin. The calculations were on Al^{3+} with CO. Attachment of the cation on one side of CO yielded a sizable shift for the carbon shielding, opposite to the shift for attachment on the opposite side. Energetics for the two structures were comparable. Weller at al. suggested that because of these results, the experimentally observed ^{13}C NMR shifts in decationated zeolites imply that the site for attachment of Al^{3+} and CO is at the oxygen atom.

Spin-spin coupling. Evaluation of spin-spin coupling tensors poses a challenging computational problem. As mentioned earlier, the coupling arises primarily through interaction of the two nuclear magnetic moments with the electronic environment. With two magnetic nuclei, there are two interaction terms in the electronic Hamiltonian, one for each magnetic source (nuclei). Of course, these terms are independent of external fields. Derivatives may be calculated with respect to the magnetic moment components of the nuclei, and these are the elements of the spin-spin coupling tensor, **J**. Calculations by Lazzeretti and coworkers [L-27:28] have shown the expected [S-43] major importance of the Fermi contact portion of the interaction Hamiltonians in the isotropic spin-spin coupling for a few small molecules and ions. Anisotropy in the coupling tensors was reported to depend very much on the Fermi contact-spin dipolar contributions.

A very high level theoretical examination of spin-spin coupling has been reported by Sekino and Bartlett [S-46]. They evaluated that part of the spin-spin coupling developing through Fermi contact, applying it first to the HD molecule as a

TABLE 8.7

Calculated Fermi-contact nuclear spin-spin coupling constants for the HD molecule (in Hz) [S-46].

Level of Treatment	*Basis Set:* (9s)	(8s2p/5s2p)	(10s5p1d)	(12s5p1d)
SCF	54.97	54.55	51.74	52.50
MBPT(2)	41.53	40.90	37.18	37.63
MBPT(3)	38.34	38.43	35.59	36.02
MBPT(4)	38.32	38.82	36.28	36.71
Full CI	41.13	41.56	38.96	39.45
From expt.[a]				40.95

[a] The Fermi-contact term was estimated from a measured coupling constant.

critical test. Very large basis sets were employed and the results, obtained via numerical differentiation, are shown in TABLE 8.7. The inclusion of correlation effects is seen to be more significant than extension of the inclusion of polarization functions. Shown in TABLE 8.8 are the results obtained for the HF molecule. Correlation is quite

TABLE 8.8

Calculated Fermi-contact nuclear spin-spin coupling constants for $H^{19}F$ (in Hz) [S-46].

Level of Treatment	*Basis Set:* DZ	F(6s4p2d); H(3s1p)	F(7s4p2d); H(5s2p)
SCF	170.68	436.79	453.39
MBPT(2)	127.43	283.85	279.69
MBPT(3)	130.17	288.95	289.38
MBPT(4) (SDTQ)	141.09	302.81	305.55
CCSD	145.67	320.69	325.36
From expt.[a]			343

[a] The Fermi-contact term was estimated from a measured coupling constant.

TABLE 8.9

Coupling constants (in Hz) for singly and multiply bonded small molecules [L-29].

Molecule		MCSCF	CI[a]	Total[b]	Expt.[c]
J(CH):					
H_2CCH_2		193.0	-46.6	146.6	156.4
H_2CO		209.9	-42.5	166.2	172.0
HCCH		291.7	-56.7	231.4	248.7
HCN		299.0	-60.8	234.4	275.0
J(HH) IN A CH_2 GROUP:					
H_2CCH_2		-15.8	11.3	-2.7	2.3
H_2CNH		1.9	6.5	7.6	
H_2CO		28.9	1.2	32.0	40
J(HH) OVER THREE BONDS:					
H_2CCH_2	*cis*	20.2	-9.3	10.9	11.4
	trans	27.9	-11.3	18.1	19.1
HCCH		17.7	-11.7	9.1	9.6

[a] Incremental effect.

[b] The total includes orbital contributions evaluated by analytical differentiation (e.g., CPHF). These were very small in all cases.

[c] See [L-29] for various sources of experimental values.

important in this system. There is an apparent over-valuing of correlation effects at the second order MBPT level. In this larger system, polarization functions have a much more important role than in HD. Correlation calculations were also carried out for ethylene using a DZP basis and rather nice agreement with experiment was obtained for the H-H, C-C and H-C coupling constants.

An interesting set of calculations of spin-spin coupling constants by Laaksonen [L-29] separated dynamical and non-dynamical correlation effects and compared coupling over one through three bonds. The calculational approach was to explicitly include the Fermi contact in the one-electron part of the Hamiltonian and obtain the second derivative of the energy with respect to the magnetic moments on two coupled nuclei by means of finite differences. The finite difference scheme was carried out with a spin-unrestricted MCSCF wavefunction and then with a subsequent CI that used the MCSCF wavefunction as the reference. Calculations were done with a double-zeta basis, though a number of tests with near triple-zeta bases gave very similar results. Certain of the spin-spin coupling constants reported in this work are given in TABLE 8.9; the agreement with measured values is quite good overall. The importance of dynamical correlation is seen to be significant in these calculations.

It is clear that *ab initio* calculations can provide useful understanding and prediction of molecular magnetic properties. Magnetic properties tend to be the most treacherous to compute, however, and there have been less of these calculations than calculations of other properties. This situation is likely to change as modern theoretical techniques and new computing hardware make it possible to study magnetic properties of more complicated systems. The calculations will serve as tools for elucidating structure in concert with NMR spectra, and not just as confirmation of the underlying chemical physics.

Chapter Nine

LOCAL APPROACHES AND NEW FRONTIERS

It is fitting to conclude this volume with a section that attempts to look ahead and to anticipate the developments that will be important in future calculations of molecular structures and properties. For at least two decades, *ab initio* electronic structure theory has been a computing-intensive area of scientific research, and it is sure to continue that way. It is not surprising, then, that many developments in theoretical methods have tended to go hand-in-hand with computer hardware developments. For instance, whether to save certain intermediate values in a large-scale electron correlation calculation is an issue that reappears whenever there are changes in the cost, availability and speed of memory relative to external (disk) storage. Differences in architectures (e.g., scalar, parallel, concurrent) require adaptation as well, and sometimes new approaches arise from the rethinking of basic steps. However, the overall trend is clearly toward methods with built-in adaptability to different architectures and different hardware configurations. Thus, even as there may be important developments that couple with computing technology advances in the years immediately ahead, the long-term issues for computing structures and properties concern the basic, machine-independent elements of theoretical approaches and how they scale with problem size.

The growth in the cost of a calculation to determine a molecular structure using conventional *ab initio* techniques is at least quartic with problem size. More precisely, an *ab initio* calculation at some particular basis set level of quality will require a number of basis functions, N, that is largely proportional to the molecular size. There will be on the order of N^4 two-electron integrals over the basis functions. Since even for the simplest wavefunction, all are used in the calculation, this number dictates the minimum size-dependence of the computational costs. With the inclusion of electron correlation effects, the scaling may be fifth order (e.g., N^5) and higher. This is a substantial growth rate for computing costs, and obtaining properties and various energy derivatives exacerbates the computing difficulties for large molecules. It is worthwhile to notice that an overnight improvement in computing speed/power of one million times -- enough to generate headlines most everywhere -- would only lead to a ten-fold increase in the molecule size capability for a high quality calculation with a conventional treatment of electron correlation. A less dramatic but more realistic hundred-fold improvement, though nice, would not be sufficient to open up large-scale problems of molecular clustering or non-linear optical properties of polymers to high level calculation. Knowing that $\sqrt[6]{100} = 2.15$ means that such a significant hardware improvement would yield a comparatively paltry two-fold increase in molecular size capability.

Because of the rapid scaling of computing costs with problem size, a number of special ideas have been developed, and others are emerging, that manage to exploit chemical knowledge in ingenious ways for the sake of computational advantage. These ideas accomplish, or may accomplish, serious reduction in computing demands by blending chemical and physical insight with high-powered computing algorithms. Basically, the intellectual task is to focus computing effort on those elements of a problem that pertain to the chemical questions being asked. This requires the understanding of electronic structure that has come about through detailed, high-level *ab initio* calculations over many years in order that accuracy not be sacrificed. And it requires understanding computational algorithms at the level of individual operations in order to really achieve a savings. Developments of this sort have been made and are being made. A few will be discussed here.

There are, of course, approaches to electronic structure that exist or that spring up from outside the practice of conventional *ab initio* technology. Though not considered here, many of these may prove important even in future developments of *ab initio* technology. Likewise, many features of *ab initio* technology tend to get borrowed and used as such other approaches evolve. An example would be basis sets being introduced as an intermediate representation in a *non*-basis set scheme. It seems that any approach labelled as distinctly different from *ab initio* approaches will, in the end, pull *ab initio* technology closer to it rather than displace it. There is so very much understanding and computational finesse in *ab initio* methods any ideas of real worth can and will be assimilated. The following topics, though, are primarily mainstream *ab initio* ideas for enhancing problem size capability.

Effective Core Potentials. *Ab initio* calculations were originally *all-electron* (AE) calculations where all of the electrons were treated on an equal footing. With heavier elements, it becomes more and more the case that core electrons affect the valence electronic structure independent of the chemical environment. To a good extent, the energetic separation between core and valence electrons plus the differences in their spatial distributions means that the core electrons do not participate in bonding. For these reasons, semi-empirical procedures such as Huckel theory can ignore core electrons from the start, absorbing their effect into the parameters. In an *ab initio* treatment, the valence electrons must "see" the core as a true electron distribution in order to obtain a realistic description. However, one may still take advantage of the fact that the core does not need to adjust to new chemical environments by modeling the core's effect on the valence as a one-electron potential, an *effective core potential* (ECP). Since calculational costs grow sharply with the number of basis functions, there is substantial savings from eliminating core basis functions by the use of an ECP. In a rough sense, this makes the cost of *ab initio* calculations independent of the rows in the periodic table for the atoms involved. ECP's are a good illustration of how physical and chemical insight, in this case that chemistry is dictated by valence electrons, can be used to improve calculational capability.

Melius and Goddard [M-26] introduced ECP's for *ab initio* quantum chemical calculations about fifteen years ago. There are several considerations in finding effective potentials (see, for instance, [M-26,K-17]), and the approach of Melius and Goddard was to choose potentials so as to best reproduce shapes and energies of *ab initio* valence orbitals. The end product, however the ECP is determined, is that an ECP calculation requires adding a one-electron potential to the Hamiltonian and deleting the core electrons that the potential represents. It is particularly workable to construct this potential in terms of Gaussian functions since this makes evaluation of integrals of the potential over atomic basis functions straightforward: The same integration techniques as used for conventional Hamiltonian one-electron integrals may be employed. The usual form for these potentials is a linear combination of Gaussians multiplied by angular momentum projection operators.

$$u_k(r) = r^{n_k} e^{-\varsigma_k r^2} \qquad (9\text{-}1)$$

The $u_k(r)$ Gaussian functions are contracted into potentials associated with a given l orbital angular momentum.

$$V_l(r) = \sum_k d_{kl}\, u_k(r) \qquad (9\text{-}2)$$

With L being one greater than maximum angular quantum number of the core electrons, the effective potential is,

$$V^{ECP}(r) = V_L(r) + \sum_{l=0}^{L-1} \{V_l(r) - V_L(r)\} \sum_{m=-l}^{l} |\, lm \rangle \langle\, lm\,| \qquad (9\text{-}3)$$

The set of parameters that specify a particular ECP are $\{ d_{kl} \}$ and $\{ \varsigma_k \}$. The use of ECP's has led to *ab initio* calculations on transition metal clusters of considerable size and to a very large number of applications studies in general.

Generally Contracted Bases. The idea of using special contractions of primitive functions to achieve concise representations has been exploited since Gaussian basis sets, now the most commonly used in electronic structure, were first tried. In particular, where a single or primitive Gaussian function is at its worst relative to a Slater function, several Gaussians combined together will be a better basis function. For core regions, it is standard practice to contract Gaussians for this reason. At the same time, some of the justifications for replacing the core with a pseudopotential apply to using relatively less functions per electron in the core than in the valence region. Split valence bases (see Chapter Three) are of this type.

The typical contracted Gaussian basis is assembled in segments, where a given primitive function is used in for only one basis function. The contraction coefficients are often obtained by optimization of atomic orbital wavefunctions (i.e., at the SCF level). With typically little contraction of valence functions, flexibility is maintained for the atom-optimized functions to represent the bonding etc. in a molecule. Of course, this means that high quality bases may need to be large, and calculational studies discussed in the last three chapters show this to be the case.

A generally contracted basis allows a given primitive function to be used in all the atom's basis functions. There is some computational overhead in using a general contraction because in the evaluation of the two-electron integrals the contraction leads to a process that is somewhat of a partial integrals transformation. Almlof and Taylor [A-22] have recently described considerable success in using generalized contractions. They use an extensively vectorized algorithm [A-23] so that the transformation due to contraction is not a significant computational expense. Because, as they point out, use of SCF orbitals for contraction coefficients yields bases not especially suitable for correlation calculations, they take contraction coefficients from the natural orbitals of atomic CI calculations. As shown by a few examples in TABLE 9.1, very good recovery of correlation effects is accomplished with this contraction scheme. Furthermore, general contraction of this sort or others yields bases less likely to display basis set superposition error. Collins and Gallup have explored the relation of BSSE to basis contraction at a very detailed level and with similar conclusions [C-25].

Electronic Structure in Local Spaces. Local space treatments are a very important new frontier for electronic structure methods. They hold great promise for the extension of electronic structure technology to massive problems. There are many types of local approaches, and certain of them will be considered in detail here. Again, the underlying idea is to focus computational effort on the regions of most chemical interest. The challenge is to make sure that the interface between the local region of interest and the surrounding medium is treated realistically.

TABLE 9.1

SCF and correlation energies (in a.u.) with natural orbital contracted bases [A-22].

Species	*Primitives*	*Contraction*	*SCF Energy*	*Correlation*
Ne	(9s 5p)	none	-128.528 221	-0.137 193
		[5s 4p]	-128.528 219	-0.137 063
		[4s 3p]	-128.528 123	-0.134 861
		[3s 2p]	-128.526 723	-0.127 406
N_2	(13s 8p 6d)	none	-108.986 307	-0.338 118
		[6s 5p 4d]	-108.985 913	-0.337 304
		[5s 4p 3d]	-108.984 833	-0.335 395
		[4s 3p 2d]	-108.983 483	-0.329 330

The interesting part of many chemical problems is a local feature, such as a binding site on a solid surface or an intramolecular hydrogen bond in a protein. Sometimes large problems of this sort can be scaled down to a manageable size by carrying out the desired calculations for a fragment of the complete system, where the fragment includes the local region of interest. It is meant to be a small molecule version of the real problem. The obvious difficulty in trimming down an extended molecular system for the sake of computation is that convergence of the desired property with respect to the size of the trimmed-down fragment may be slow, or worse, it may be erratic. This means that it is hard to know if the results for the fragment calculation are true to the entire system.

The alternative to pruning molecules calls for a *local space* approach where there is not only complete wavefunction adjustability in the local region but also flexibility for electronic charge to be transferred self-consistently into or out of the local region and for the local region to polarize or be polarized by the surrounding medium. A type of electronic structure problem to keep in mind as an example is following the energy of a system of two molecular subunits approaching each other and interacting at specific sites on each. Those specific sites comprise the local region of interest or the region where the greatest change in electronic structure is likely to be found. At large separation where there is no interaction at all, the wavefunction for the entire system, or *supersystem*, may be correctly constructed from wavefunctions obtained for the isolated subunits or fragments.

At the SCF level, it might seem that only a few of the supersystem orbitals would need to change as the subunits were brought closer together. Restricting the wavefunction to changes in only a few orbitals, though, would accomplish little computational savings unless they were strictly localized to a small number of basis functions. That would be an additional constraint, one that would not let charge density flow into or out of the local region even though the interaction might properly lead to that.

The local space approach (LSA) of Kirtman [K-6:7] allows for adjustment in the wavefunction for a local set of basis functions and then exploits the idempotency of the one-electron density in order to insure that electronic charge may be self-consistently transferred to and from the embedded local region. This reduces the computational cost to that of a local fragment but without imposing unwarranted constraints or inflexibility on the supersystem. The LSA has been formulated for Hartree-Fock wavefunctions and for certain correlated wavefunctions, such as the separated electron pair model [K-11] and CISD and CCD [K-12]. For the CI and coupled cluster formulations, the matrix-orientation of self-consistent electron pair (SCEP) theory [M-7:8] is ideally suited. In SCEP, the correlated wavefunctions are represented by pair coefficient matrices which play a similar role to the first order density matrix in LSA-SCF.

Saebo and Pulay [P-20,S-34:36] have developed a very powerful and effective "local CI" method also using the matrix orientation of SCEP. It identifies *local domains* of atomic orbitals (basis functions) to correlate the electron pairs. It has been implemented for CI, ACCD and MBPT through fourth order. It is suited to treatment of the entire system's correlation.

Polymatrix Approach for SCF and Local Space SCF. Kirtman has completely formulated the LSA for SCF wavefunctions [K-6:7]. However, an alternate development is introduced here to explain the LSA because of formal and computational features of its organization. The idea is a *polymatrix* approach with symbolic analogs to conventional density matrix treatments. As will be discussed, this is a essentially super-generalization of old density matrix methods.

THE SHELL REPRESENTATION. A polymatrix in this discussion is a matrix whose elements may be matrices themselves. A polymatrix may be thought of in *symbolic form* or *explicit form.* Symbolic form means each element is a single value or a single variable as in a conventional matrix. It is mentioned here mainly for understanding the polymatrix concept; otherwise, it is useful only for a few simple logic steps. Explicit form, which is the focus of the whole construction, means that the elements of a polymatrix are matrices, specifically matrices whose row and column dimension is the number of basis functions.

The use of matrices in quantum mechanical problems implies a basis representation of operators. In conventional SCF, any one-electron operator matrix, such as the Fock operator, may be expressed in the basis of atomic basis functions or else in the basis of molecular orbitals, a transformation from the atomic function basis. The basis for a Hamiltonian CI matrix is simply the chosen set of electron configurations, or N-electron functions. For the polymatrix approach, though, the basis is somewhat more abstract. It is the set of orbital *shells* for the wavefunction. A shell is a subset of the orbitals of a system for which the appropriate Fock operator for finding the orbitals is the same for all the orbitals in the subset and has the same type of contribution from each orbital in the subset. In the SCF treatment of a closed-shell wavefunction, there are two shells, the occupied set and the empty or virtual set. In this case, though the same Fock operator is appropriate for all the orbitals, the occupied orbitals "contribute" to the Fock operator, all in the same way, but the virtuals do not. Another example is the following open-shell, single-determinant wavefunction, $\Psi = 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma\alpha\, 5\sigma\alpha$. Here, there are three shells, the doubly occupied orbitals 1σ, 2σ, 3σ, the half-filled orbitals 4σ, 5σ, and the empty or virtual orbitals. The rows and columns of a polymatrix are labelled by the shells for the problem.

Kirtman has formulated SCF for closed-shell wavefunctions [K-6:7] where all the polymatrices will be 2 x 2's. The polymatrix organization introduced here is intended to provide immediate generalization to open-shell SCF problems and to MCSCF. Indeed, it is applicable to SCF and MCSCF without the local space approximation, and it then is a reorganization of McWeeny's density matrix approach [M-17].

SHELL DENSITY MATRICES. The usual definition of a one-electron density matrix can be used for all shells of a system. Let {i,j,k,...} designate the different shells and let C be the matrix of orbital expansion coefficients in terms of the basis functions. Then a shell density is

$$[\mathbf{R}_i]_{\alpha\beta} \equiv \sum_{s}^{s\in\{i\}} C^*_{s\alpha} C_{s\beta} \tag{9-4}$$

The sum is over the orbitals, s, in the i^{th} shell and α and β label atomic basis functions. These matrices are orthogonal and idempotent:

$$\mathbf{R}_i \mathbf{S} \mathbf{R}_j = \delta_{ij} \mathbf{R}_i \tag{9-5}$$

where **S** is the matrix of basis function overlap integrals. Eqn. (9-5) may be thought of as an orthonormality relation in an abstract space where the directions are the shell densities. Indeed, this is the space of the polymatrix formulation, and though saying that rows and columns of a polymatrix are labelled by shells, it is more precise to say they are labelled by shell densities. The density matrices loosely take the role of basis functions or unit vectors in this space.

The non-orthogonality of the basis functions complicates expressions by introducing the overlap matrix. This can be avoided formally by redefining the density matrices of Eqn. (9-4):

$$\mathbf{R}'_i \equiv \mathbf{S}^{\frac{1}{2}}\,\mathbf{R}_i\,\mathbf{S}^{\frac{1}{2}} \qquad (9\text{-}6)$$

In all following expressions, these modified densities will be used and designated without primes.

In three-dimensional Cartesian space, a vector may be specified by unit vectors in the x, y, and z directions.

$$\vec{\mathbf{v}} = x\hat{i} + y\hat{j} + z\hat{k} = (x\ y\ z)\begin{pmatrix}\hat{i}\\ \hat{j}\\ \hat{k}\end{pmatrix} \qquad (9\text{-}7)$$

Likewise, a column array of the shell densities, $\mathbf{R}_i$, may be used to express an arbitrary "vector" in the shell density space. This is a *polyvector.*

*S*YMBOLIC AND *E*XPLICIT *F*ORMS. A unit vector in the "direction" of the second shell density in explicit form is

$$\vec{\mathbf{v}} = \begin{pmatrix}\mathbf{0}\\ \mathbf{R}_2\\ \mathbf{0}\\ \mathbf{0}\\ \cdots\end{pmatrix} \qquad (9\text{-}8)$$

where **0** is a matrix over the atomic basis functions with all elements zero. A symbolic form for this vector, useful for seeing the overall logic, is

$$\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ \cdots \end{pmatrix}$$

This vector has simple values of one and zero for its elements. The symbolic polymatrix representation of a shell density is also trivial. It is a matrix of zeroes except for the diagonal element corresponding to the given shell; the value of that diagonal element is one.

THE IDEMPOTENT DENSITY POLYMATRIX. Any shell's density polymatrix, which will be designated $\mathbf{T}^{(i)}$ for the i^{th} shell, is idempotent. Multiplication of the $\mathbf{T}^{(i)}$ of a shell by that of another shell yields a zero matrix. This is true both in the symbolic and explicit forms.

A correction or adjustment to a shell density, such as that from one iteration in solving for the self-consistent field, must preserve the idempotency of each shell's density. Let **T** be the density polymatrix of some shell and let τ be a correction polymatrix. Idempotency requires

$$(\mathbf{T} + \tau)^2 = \mathbf{T} + \tau \qquad (9\text{-}9)$$

In terms of individual elements, this is,

$$\sum_{k}^{\text{shells}} (\mathbf{T} + \tau)_{ik} (\mathbf{T} + \tau)_{kj} - (\mathbf{T} + \tau)_{ij} = 0 \qquad (9\text{-}10)$$

Eqn. (9-10) represents N^2 equations for a problem with N shells, though only $N(N+1)/2$ equations are unique because of the symmetry of **T**.

Certain expressions hold in symbolic form as well as in explicit form. The only general way in which each form is equally valid is if the explicit forms relate to the symbolic forms by a contraction as in the following example for a two-shell case.

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \Rightarrow \begin{pmatrix} a\mathbf{1} & b\mathbf{1} \\ c\mathbf{1} & d\mathbf{1} \end{pmatrix} \equiv \begin{pmatrix} a\ 0\ 0 \ldots & b\ 0\ 0 \ldots \\ 0\ a\ 0 \ldots & 0\ b\ 0 \ldots \\ 0\ 0\ a \ldots & 0\ 0\ b \ldots \\ \ldots & \\ c\ 0\ 0 \ldots & d\ 0\ 0 \ldots \\ 0\ c\ 0 \ldots & 0\ d\ 0 \ldots \\ \ldots & \end{pmatrix} \qquad (9\text{-}11)$$

Density matrix expressions in the explicit form can be in any orbital representation (e.g., basic functions or molecular orbitals). An example of operations is the two-shell version of Eqn. (9-10), which yields the following three equations.

$$\begin{aligned} (\mathbf{T}+\tau)_{11}\,(\mathbf{T}+\tau)_{11} + (\mathbf{T}+\tau)_{12}\,(\mathbf{T}+\tau)_{21} - (\mathbf{T}+\tau)_{11} &= 0 \\ (\mathbf{T}+\tau)_{11}\,(\mathbf{T}+\tau)_{12} + (\mathbf{T}+\tau)_{12}\,(\mathbf{T}+\tau)_{22} - (\mathbf{T}+\tau)_{12} &= 0 \\ (\mathbf{T}+\tau)_{21}\,(\mathbf{T}+\tau)_{12} + (\mathbf{T}+\tau)_{22}\,(\mathbf{T}+\tau)_{22} - (\mathbf{T}+\tau)_{22} &= 0 \end{aligned} \qquad (9\text{-}12)$$

Stated in symbolic form with **T** being the density for shell one, $\mathbf{T} = \left(\begin{smallmatrix} 1 & 0 \\ 0 & 0 \end{smallmatrix}\right)$,

$$\begin{aligned} \tau_{11}\tau_{11} + \tau_{12}\tau_{21} + \tau_{11} &= 0 \\ \tau_{11}\tau_{12} + \tau_{12}\tau_{22} &= 0 \\ \tau_{22}\tau_{22} + \tau_{21}\tau_{12} - \tau_{22} &= 0 \end{aligned} \qquad (9\text{-}13)$$

Eqn. (9-13) is really just a change of representations, and the three equations are equivalent to Eqn. (9-12). It is useful to transform explicit τ_{ij} elements from an orbital representation to a basis function representation, or from a symbolic representation (of the orbital representation). The "unit vectors" in the space of the shell density provide the transformation of the τ polymatrix elements to the basis of atomic functions.

$$\tilde{\tau}_{ij} = \mathbf{R}_i\,\tau_{ij}\,\mathbf{R}_j \qquad (9\text{-}14)$$

Using these matrices (i.e., substituting $\tau_{ij} \Rightarrow \tilde{\tau}_{ij}$) in the first expression of Eqn. (9-13) yields,

$$\mathbf{R}_1\,\tau_{11}\,\mathbf{R}_1\,\mathbf{R}_1\,\tau_{11}\,\mathbf{R}_1 + \mathbf{R}_1\,\tau_{12}\,\mathbf{R}_2\,\mathbf{R}_2\,\tau_{21}\,\mathbf{R}_1 + \mathbf{R}_1\,\tau_{11}\,\mathbf{R}_1 = 0 \qquad (9\text{-}15)$$

The idempotency of each shell **R** (Eqn. (9-5) using the matrices of Eqn. (9-6)) simplifies Eqn. (9-15) somewhat. Then the following condition must hold if Eqn. (9-15) is to be satisfied for any $\mathbf{R}_1$.

$$\tau_{11}\mathbf{R}_1\tau_{11} + \tau_{12}\mathbf{R}_2\tau_{21} + \tau_{11} = 0 \tag{9-16}$$

Similarly, two other expressions result.

$$\tau_{11}\mathbf{R}_1\tau_{12} + \tau_{12}\mathbf{R}_2\tau_{22} = 0 \tag{9-17}$$

$$\tau_{22}\mathbf{R}_2\tau_{22} + \tau_{21}\mathbf{R}_1\tau_{12} - \tau_{22} = 0 \tag{9-18}$$

Eqns. (9-16,17,18) are standard expressions that give the restrictions on how the density may change (via τ) while preserving idempotency.

FREE ADJUSTMENT OF THE DENSITY. The correction to the density, τ, must satisfy the conditions just derived. This is an inconvenient correction because it is not freely adjustable. McWeeny has provided a way of using a freely adjustable matrix to correct the density [M-17], and it may be set up in the generalized polymatrix approach. First, though, recall that the SCF energy is invariant to a unitary mixing of orbitals of any one shell. Thus, the adjustments of interest are those that connect (or mix) the densities of different shells.

Z is the designation used here for a freely adjustable element of a special polymatrix, **V**. **V** forms the correction to a shell density **T**, and so Z must be an off-diagonal element. For a closed-shell wavefunction (two shell case),

$$\mathbf{V} = \begin{pmatrix} 0 & 0 \\ Z & 0 \end{pmatrix} \tag{9-19a}$$

For the most general type of adjustment, Z will be a matrix other than a constant times **1**. For more than two shells, **V** may be formed as

$$\mathbf{V} = \begin{pmatrix} 0 & 0 & 0 & \dots \\ Z_{21} & 0 & 0 & \dots \\ Z_{31} & 0 & 0 & \dots \\ Z_{41} & 0 & 0 & \dots \end{pmatrix} \tag{9-19b}$$

The adjusted density, $(\mathbf{T} + \tau)$, in terms of **V** is

$$\mathbf{T} + \tau = (\mathbf{T} + \mathbf{V})\ \mathbf{G}\ (\mathbf{T} + \mathbf{V})^{\dagger} \qquad (9\text{-}20)$$

where **G** is a matrix chosen to insure idempotency of the corrected density. **Z** may be freely chosen because the idempotency is imposed "after the fact."

The idempotency condition for finding **G** is derived by multiplying the corrected density of Eqn. (9-20) times itself and setting the result equal to itself. This is shown in the following expression where an intermediate product has been placed in brackets.

$$(\mathbf{T} + \mathbf{V}) \left[\mathbf{G}\ (\mathbf{T} + \mathbf{V})^{\dagger}\ (\mathbf{T} + \mathbf{V})\ \mathbf{G} \right] (\mathbf{T} + \mathbf{V})^{\dagger} = (\mathbf{T} + \mathbf{V})\ \mathbf{G}\ (\mathbf{T} + \mathbf{V})^{\dagger} \qquad (9\text{-}21)$$

The polymatrix product in brackets on the left hand side of Eqn. (9-21) must equal **G**. The simple structure of **T** and **V** leads to a simple product, and using the two-shell case as an example, the following is obtained.

$$\left[(\mathbf{T} + \mathbf{V})^{\dagger}\ (\mathbf{T} + \mathbf{V}) \right] = \begin{pmatrix} \mathbf{X} & 0 \\ 0 & 0 \end{pmatrix} \qquad (9\text{-}22)$$

Using this in Eqn. (9-21) and equating the bracketed term with **G**, gives the following equations for elements of **G**.

$$\begin{aligned} \mathbf{G}_{11}\,\mathbf{X}\,\mathbf{G}_{11} &= \mathbf{G}_{11} & \qquad \mathbf{G}_{11}\,\mathbf{X}\,\mathbf{G}_{12} &= \mathbf{G}_{12} \\ \mathbf{G}_{21}\,\mathbf{X}\,\mathbf{G}_{11} &= \mathbf{G}_{21} & \qquad \mathbf{G}_{21}\,\mathbf{X}\,\mathbf{G}_{12} &= \mathbf{G}_{22} \end{aligned} \qquad (9\text{-}23)$$

$\mathbf{G}_{11}$ must be the inverse of **X**, while $\mathbf{G}_{12}$ and $\mathbf{G}_{21}$ are not determinable or are arbitrary. $\mathbf{G}_{22}$ is given by $\mathbf{G}_{12}$ and $\mathbf{G}_{21}$. The simplest choice is to let the arbitrary elements be zero, and that will be assumed here.

Rewriting the first expression in Eqn. (9-23) in the basis of shell densities (as in Eqn. (9-4)) and substituting the actual product of matrices from Eqn. (9-22) for **X** gives,

$$\begin{aligned} &\tilde{\mathbf{G}}_{11}\,(\tilde{\mathbf{T}}_{11}\tilde{\mathbf{T}}_{11} + \tilde{\mathbf{Z}}^{\dagger}\tilde{\mathbf{Z}})\,\tilde{\mathbf{G}}_{11} = \tilde{\mathbf{G}}_{11} \quad \text{or,} \\ &\mathbf{R}_1\mathbf{G}_{11}\mathbf{R}_1(\mathbf{R}_1 + \mathbf{R}_1\mathbf{Z}^{\dagger}\mathbf{R}_2\mathbf{R}_2\mathbf{Z}\mathbf{R}_1\mathbf{B})\,\mathbf{R}_1\mathbf{G}_{11}\mathbf{R}_1 = \mathbf{R}_1\mathbf{G}_{11}\mathbf{R}_1 \end{aligned} \qquad (9\text{-}24)$$

Using the idempotency of the **R** matrices allows for a simplification of Eqn. (9-24).

$$\mathbf{R}_1\mathbf{G}_{11}\mathbf{R}_1(\mathbf{1} + \mathbf{Z}^{\dagger}\mathbf{R}_2\mathbf{Z}\mathbf{R}_1)\,\mathbf{R}_1\mathbf{G}_{11}\mathbf{R}_1 = \mathbf{R}_1\mathbf{G}_{11}\mathbf{R}_1 \qquad (9\text{-}25)$$

From this,

$$\tilde{\mathbf{G}}_{11} = \mathbf{R}_1\mathbf{G}_{11}\mathbf{R}_1 = \left(1 + \mathbf{Z}^{\dagger}\mathbf{R}_2\mathbf{Z}\mathbf{R}_1\right)^{-1} \equiv \mathbf{X}^{-1} \qquad (9\text{-}26)$$

The correction to the density associated with the freely adjustable matrix **Z** is now determined.

$$\tilde{\tau} = \begin{pmatrix} \tilde{\mathbf{X}}^{-1} - \mathbf{R}_1 & \tilde{\mathbf{X}}^{-1}\tilde{\mathbf{Z}}^{\dagger} \\ \tilde{\mathbf{Z}}\tilde{\mathbf{X}}^{-1} & \tilde{\mathbf{Z}}\tilde{\mathbf{X}}^{-1}\tilde{\mathbf{Z}}^{\dagger} \end{pmatrix} \qquad (9\text{-}27)$$

Eqn. (9-27) is a general result for the full basis function space using the two shell example case. From any freely chosen **Z**, a correction to the density, τ, can be found which preserves idempotency.

LOCAL SPACE APPROXIMATION. The local space approximation is invoked by restricting the otherwise freely adjustable matrix **Z** to have non-zero elements where both the row and column labels correspond to atomic basis functions contained in a subset of the entire basis called the local space set, {L}. The local space set would be basis functions on the atoms in the local region of interest. It could be enlarged to test or insure convergence with respect to the size of {L}. Notice that even though **Z** is restricted within the LSA, there is still freedom for charge to move into or out of the local region. This comes about because the entire density may change upon correction via **Z**. This freedom may be thought of as a freedom to mix in an overall way the "unit vector" densities of the shells, apart from the freedom (only available within the local space) to redo the "directions" of those (shell density) unit vectors.

Computational savings is achieved, in part, by contracting matrices that may have non-zero elements only in the local space block. Take **A** to be a matrix with N rows and columns, where N is the number of basis functions for the entire system, and with only accidental zero-valued elements. Take **a** to be a matrix which is identically zero outside of some block with n rows and columns, where n < N. It is not necessary that the ordering of rows and columns is such that there is a concise n-by-n block in **a**; a dispersed arrangement of the n^2 elements is just as workable. Multiplication of these two matrices will require less than the normal N^3 operations because of the structure of **a**.

$$\mathbf{B}_{ij} = \sum_{k}^{N} \mathbf{A}_{ik}\,\mathbf{a}_{kj} \quad \text{but} \quad \mathbf{B}_{ij'} = \sum_{k'}^{n} \mathbf{A}_{ik'}\,\mathbf{a}_{k'j'} \qquad (9\text{-}28)$$

Taking the primed indices to refer to the functions in {L}, the second summation is an n^2N operation. Matrix transformations are of two types. **aBc** = **d** is an $(n^2N + n^3)$

process. **AbC** = **D** is an ($n^2N + nN^2$) process. The entire sequence of conventional matrix operations required in an SCF iteration will be reduced in computational steps by at least n/N [K-13].

Hartree-Fock Equations and Solutions for the Wavefunction. If **h** is the conventional Fock operator expressed in the atomic orbital basis, standard density matrix approaches for a closed shell system [M-3] show that the energy is minimized when the following condition has been satisfied.

$$\mathbf{R}_1\,\mathbf{h}\,\mathbf{R}_2 + \mathbf{R}_2\,\mathbf{h}\,\mathbf{R}_1 = 0 \qquad (9\text{-}29)$$

This can be generalized for multiple shells (with properly constructed Fock operators) and cast into the polymatrix form.

$$\tilde{\mathbf{h}} = \begin{pmatrix} \mathbf{R}_1 \\ \mathbf{R}_2 \\ \cdots \end{pmatrix} \mathbf{h} \begin{pmatrix} \mathbf{R}_1 & \mathbf{R}_2 \cdots \end{pmatrix} = \begin{pmatrix} \mathbf{R}_1\mathbf{h}\mathbf{R}_1 & \mathbf{R}_1\mathbf{h}\mathbf{R}_2 & \cdots \\ \mathbf{R}_2\mathbf{h}\mathbf{R}_1 & \mathbf{R}_2\mathbf{h}\mathbf{R}_2 & \cdots \\ & \cdots & \end{pmatrix} \qquad (9\text{-}30)$$

The condition for having minimized the energy is that $\tilde{\mathbf{h}}$ is block-diagonal, or that the off-diagonal blocks between shells are zero. To solve for the densities that correspond to the SCF wavefunctions, **Z** is chosen according to the size of the off-diagonal elements of $\tilde{\mathbf{h}}$. The process is carried out iteratively. The iterative cycle comes full circle when the τ matrices are found from **Z** and a new $\tilde{\mathbf{h}}$ is constructed.

It is important to point out that the logic and generalized derivation is carried out with polymatrices, but that calculations require only matrices of conventional size or less. The dimensions are either the number of basis functions of the entire system (N) or the number of functions in the local space (n). It is true that extra matrix transformations are required to carry out an SCF calculation with this form of density matrix process, but the process is the key to exploiting the small size of a local space. The extra several steps are balanced against a significant cost reduction of at least n/N.

Construction of Operators within the LSA. A crucial computational aspect of *ab initio* LSA calculations is the construction of the Fock operator and the processing of the two-electron integrals. Because of how the density may change within the LSA, the complete set of two-electron integrals are not required to construct and update the Fock matrix on each iteration [K-13].

Kirtman has invented an effective procedure for processing the two-electron integrals when updating the Fock operator from one iteration to the next [K-13]. This procedure will be explained as if it were applied without the LSA. As discussed thereafter, the procedure becomes computationally effective when the size of the local space is about one fourth or less of the size of the complete space.

The two-electron integrals enter $\tilde{\mathbf{h}}$ for a closed shell case in the following way.

$$\left[\tilde{\mathbf{h}}_{ij}\right]_{\alpha\beta} \leftarrow \left[\tilde{\mathbf{g}}_{ij}^{k}\right]_{\alpha\beta} \tag{9-31}$$

$$\equiv \sum_{\mu}\left[\mathbf{R}_{i}\right]_{\alpha\mu}\left(\sum_{\gamma\delta}\left[\mathbf{R}_{k}\right]_{\gamma\delta}\left\{2(\gamma\delta|\mu\nu)-(\gamma\mu|\delta\upsilon)\right\}\right)\sum_{\nu}\left[\mathbf{R}_{j}\right]_{\nu\beta}$$

(γ and δ would be within the local space set of functions for an LSA treatment.) For other than a closed shell wavefunction, the two-electron integrals would enter with Coulomb and exchange parts, but different factors. For the closed shell case, $\mathbf{R}_k$ in Eqn. (9-31) is the density of the occupied orbital space. In general, though, i, j, and k may refer to three different shell densities.

A modified two-electron integral may be defined as,

$$(\gamma\delta \,||\, \mu\nu) \;=\; 2(\gamma\delta|\mu\nu) \;-\; (\gamma\mu|\delta\nu) \tag{9-32}$$

and then, the order of summations in Eqn. (9-31) is changed to give the following.

$$\left[\tilde{\mathbf{g}}_{ij}^{k}\right]_{\alpha\beta} = \sum_{\gamma\delta}\left[\mathbf{R}_{k}\right]_{\gamma\delta}\sum_{\mu\nu}\left[\mathbf{R}_{i}\right]_{\alpha\mu}\left[\mathbf{R}_{j}\right]_{\nu\beta}(\gamma\delta \,||\, \mu\nu) \tag{9-33}$$

(α, β, γ, and δ are within the local space set of functions for an LSA treatment.) The right-most summation in Eqn. (9-33) implies a half-integrals transformation, a step which can be easily carried out by conventional algorithms. The cost of this step is important and will be considered shortly, but it is important to realize that it is a step which is not repeated. In the polymatrix organization, the vector of shell densities on any given iteration may be related to the initial vector of shell densities by means of a polymatrix transformation, **C**.

$$\vec{\mathbf{R}}^{(n)} = \mathbf{C}\,\vec{\mathbf{R}}^{(o)} \tag{9-34}$$

Identifying the value represented by the last summation in Eqn. (9-33) as $\left[\mathbf{P}_{ij}^{\alpha\beta}\right]_{\gamma\delta}$, that is, as an element of a polymatrix **P** labelled by the α and β basis functions, then, the product $\mathbf{C}^{\dagger}\,\mathbf{P}^{\alpha\beta}\,\mathbf{C}$ contains the values of that summation at the nth iteration, if **P** had been constructed from the initial shell densities contained in $\vec{\mathbf{R}}^{(o)}$. Such transformed polymatrices will be designated $\mathbf{P}^{\alpha\beta\,(n)}$.

The desired elements for construction of $\tilde{\mathbf{h}}$ are obtained by carrying out the first summation in Eqn. (9-33) and then summing over the shell densities (i.e., summing over "k"). This process is a trace of polymatrix product and may be carried out efficiently, and on vector computers at high speed. The overall process is cumbersome and not suited to working in the entire space or in a space nearly as large. The advantage within the LSA is that the intermediate evaluations outlined here are carried out only within the local space. The summations in the above equations are summations only over basis functions in the local space. The computational steps may be analyzed in terms of three integers:

N - the number of basis functions in the entire space

L - the number of basis functions in the local space

S - the number of shells

The construction of the original **P** polymatrices, using quarter-integral transform techniques, will require on the order of L^3N^2 operations. Their transformation from iteration to iteration is an $L^2(LS)^3$ process. The polymatrix product traces will require SL^4 operations. This overall process exchanges dependence on N for dependence on L, a smaller number, but at a price. That price is making a fourth order process become fifth order. The trade-off is likely to be beneficial because L will generally be small. Most likely, L will be a smaller and smaller fraction of N as N and the molecule size increase.

DIFFERENTIATION. An important goal of local space developments is the ability to calculate local properties such as bond polarizabilities or bond susceptibilities, or to examine changes in total molecule properties for structural changes in local regions. To accomplish this, we can apply the derivative concepts of Chapter Five. With appropriate parameters built into the Hamiltonian, formal differentiation of Eqn. (9-29) must be carried out and the resulting equations solved for derivatives of the densities. Since the derivative Hartree-Fock (DHF) method [D-18,29] already utilizes density matrices in certain key steps, it is ideally suited for extension to local space treatments [K-13].

Local Space Correlated Wavefunctions. In the LSA approach to CI and coupled cluster wavefunctions by Kirtman and Dykstra [K-12], the expansion coefficients of the double substitution correlating configurations are contained in a density-like pair function. The representation of this function, developed for the SCEP approach [M-7:8], is in terms of the atomic basis functions via a matrix $\mathbf{C}_P$. The P subscript designates a particular pair of orbitals that have been substituted. If the coefficient of the P→ab substituted configuration is C_P^{ab}, then,

$$\mathbf{C}_P = \Sigma_{ab} \, C_P^{ab} \left[|a\rangle\langle b| + |b\rangle\langle a| \right] / \sqrt{2 + 2\delta_{ab}} \tag{9-35}$$

The rows and columns of each $\mathbf{C}_P$ matrix are labelled by the atomic basis functions. Initial choices for these matrices may be taken from calculated wavefunctions of constituent fragments. Then, in an iterative improvement process, a correction is made to each $\mathbf{C}_P$. That correction is restricted to the local space functions, but projected to preserve orthogonality between the correlating part of the wavefunction and the reference configuration. This is equivalent to the formation of $\tilde{\mathbf{h}}$ from $\mathbf{h}$ in Eqn. (9-30), except that only one diagonal element (matrix) of the resulting polymatrix is actually required. A like transformation of the two-electron integrals shrinks the computational effort to find the required matrix elements, the ones that yield the iterative improvements to the $\mathbf{C}_P$ matrices.

The local method developed by Saebo and Pulay [P-20,S-34:36] is a powerful method for intermediate and large molecules. As in the procedure mentioned in the last paragraph, the amplitudes of configurations for different electron pairs are allowed to change only with respect to certain atomic basis functions. A difference is that instead of a local space for the entire problem, there are local domains, or subsets of atomic basis functions, for each pair of electrons. This means that the procedure is well-suited to treatment of correlation throughout the molecule without an initial or fragment wavefunction. Meyer and Frommhold have used a similar idea for the purpose of avoiding basis set superposition errors [M-25].

A second way in which Saebo and Pulay achieve efficiency in their local approach is through the localization of the SCF or reference configuration orbitals. This diminishes the correlation of pairs of electron in spatially distant orbitals, the "weak pairs". The cost of a correlation calculation is at least linear in the number of pairs, and so, neglecting weak pairs yields a direct savings. With weak pairs properly chosen, their neglect makes little difference in total electronic energies and relative energies [S-36]. Forner has also worked with localized orbitals for the reference wavefunction in MP2 and CCD treatments, finding excellent results even for small molecules [F-6].

Another valuable method for correlation in large molecular systems is the local approach of Stollhoff and Fulde [S-37]. The correlating space is kept manageable by a judicious subselection at essentially the atomic orbital basis level. This appears to be a powerful scheme that recovers nearly all the correlation energy of a corresponding full space approach. Undoubtedly, there will continue to be hybridization of local space concepts as the optimum process evolves. It is already apparent that local approaches can be formulated so that computing effort is scaled down substantially from a full space problem, but the reliability is not sacrificed.

Weakly Interacting Molecules in Assemblies. Exploiting underlying chemical and physical understanding for computational advantage in *ab initio* based approaches is showing considerable promise for the specialized area of molecular assemblies and clusters. Potential energy surfaces and forces for collections of tens and hundreds of molecules and atoms are essential ingredients in molecular dynamics simulations. Typically, these are modelled or empirical surfaces, often expressed in analytical form. Were conventional *ab initio* calculations to be carried out for such problems, the geometrical degrees of freedom in large assemblies would make for an enormous number of points needed to characterize or represent the interaction surface. Thus, finding such surfaces or surface information with the reliability of contemporary electronic structure approaches, but without their cost, is an important frontier for computational chemistry.

At this time, *ab initio* electronic structure technology is being employed in special, indirect ways to develop potentials for weakly interacting assemblies. Full *ab initio* treatment, even if only at the SCF level, seems practical only for benchmarking results or for very high quality studies of very small complexes. Local space approaches will eventually prove quite useful, but their application will necessarily focus on local features. The specialized schemes for weakly bonded assemblies, at least those discussed here, are indirect. They use values of the properties of the constituent molecules and atoms, obtained from *ab initio* calculations on the isolated constituents, to construct the weak interaction surfaces. The *ab initio* information about the constituents may include their shape and size, as determined by the electron distribution, and their intrinsic electrical properties, such as dipole moments and polarizabilities.

CONSTRUCTION OF INTERACTION SURFACES FROM ELECTRICAL PROPERTIES. Two molecules or atoms may interact electrically through their charge fields. This interaction is partly classical because it does not involve intermolecular quantum features. It is not entirely classical since the charge distributions of the interacting constituents are quantum mechanically developed. It is not a complete description of an interaction potential because of the neglect of penetration of charge clouds and intermolecular quantum effects. These effects include dispersion, which is generally attractive, and exchange, which is sharply repulsive for the approach of two molecules or atoms.

Electrical interaction analysis usually assumes no penetration of charge densities among the constituents because it represents the charge densities as idealized electrical points in space (e.g., the dipolar field arises from an idealized *point* dipole). Because of what it neglects, it alone can not generate a proper potential surface for all degrees of freedom. However, there is growing evidence that it can yield certain slices through the potential surface that are true to the actual surface and that the overall defects may be removed by incorporating very simple types of extra potential terms. The advantage is the vast reduction of computing effort that comes from neglecting intermolecular quantum effects. For equivalent interacting constituent species, electrical analysis will be almost trivial for a pair, and will grow as n^2 for an assembly of n species. An *ab initio* electronic structure calculation could easily start off 10^5 times more expensive for a pair, and then will grow as n^4, and maybe worse.

As discussed in Chapter Seven, *ab initio* electronic structure technology can give permanent electrical multipole moments, multipole polarizabilities, hyperpolarizabilities and so on. These are the properties required to construct an electrically-based potential surface. Outside a molecular or atomic charge distribution, the electrical (not interaction) potential V(x,y,z) is equivalent to that arising from the molecule's point multipoles placed at the geometrical point corresponding to the multipole expansion center. Following Applequist [A-8:10], one may define polytensors that relate the potential to the moments. If **r**=(x,y,z) is the vector from that center to some point in space, the following rank one polytensor is used to find the electrical potential, V.

$$\mathbf{T}^{(1)} \equiv \left(\frac{1}{|\mathbf{r}|},\ -\nabla\frac{1}{|\mathbf{r}|},\ \nabla^2\frac{1}{|\mathbf{r}|},\ -\nabla^3\frac{1}{|\mathbf{r}|},\ \ldots \right) \qquad (9\text{-}36)$$

Explicitly, the first individual elements are,

$$\mathbf{T}_0 = \frac{1}{|\mathbf{r}|}$$

$$\mathbf{T}_1 = -\frac{\partial}{\partial x}\frac{1}{|\mathbf{r}|} = \frac{x}{|\mathbf{r}|^3}$$

$$\mathbf{T}_2 = -\frac{\partial}{\partial y}\frac{1}{|\mathbf{r}|} = \frac{y}{|\mathbf{r}|^3}$$

$$\mathbf{T}_3 = -\frac{\partial}{\partial z}\frac{1}{|\mathbf{r}|} = \frac{z}{|\mathbf{r}|^3}$$

$$\mathbf{T}_4 = \frac{\partial^2}{\partial x^2}\frac{1}{|\mathbf{r}|} = -\frac{1}{|\mathbf{r}|^3} + \frac{3x^2}{|\mathbf{r}|^5}$$

$$\mathbf{T}_5 = \frac{\partial^2}{\partial x \partial y}\frac{1}{|\mathbf{r}|} = \frac{3xy}{|\mathbf{r}|^5}$$

$$\mathbf{T}_6 = \frac{\partial^2}{\partial x \partial z}\frac{1}{|\mathbf{r}|} = \frac{3xz}{|\mathbf{r}|^5}$$

$$\mathbf{T}_7 = \mathbf{T}_5$$

. . .

$$\mathbf{T}_{13} = 15\frac{x^3}{|\mathbf{r}|^7} - \frac{9x}{|\mathbf{r}|^5}$$

and so on. The superscript "(1)" for this **T**-tensor is implied by the one index on each element. A simple dot product of rank one polytensors,

$$V(x,y,z) = \mathbf{T}^{(1)} \bullet \mathbf{M} \qquad (9\text{-}37)$$

is the electrical potential function in terms of the polytensor of moments **M** (see Chapter Seven).

The function V(x,y,z) can be expanded into components (field, field gradient, etc.) and then represented by a rank one polytensor, as done generally in Chapter Seven. For the potential of Eqn. (9-37), the polytensor, **V**, is a product of a second rank **T**-tensor and **M**.

$$\mathbf{V} = \mathbf{T}^{(2)}\,\mathbf{M} \qquad (9\text{-}38)$$

The elements of $\mathbf{T}^{(2)}$ are also found in $\mathbf{T}^{(1)}$, and so, $\mathbf{T}^{(2)}$ may be set up using $\mathbf{T}^{(1)}$.

$$\mathbf{T}^{(2)} = \begin{pmatrix} T_0 & T_1 & T_2 & T_3 & T_4 & \cdots \\ -T_1 & -T_4 & -T_5 & -T_6 & -T_{13} & \cdots \\ -T_2 & -T_7 & -T_8 & -T_9 & -T_{22} & \cdots \\ -T_3 & -T_{10} & -T_{11} & -T_{12} & -T_{31} & \cdots \\ T_4 & T_{13} & T_{14} & T_{15} & T_{40} & \cdots \\ \cdots & & & & & \\ -T_{13} & \cdots & & & & \end{pmatrix} \qquad (9\text{-}39)$$

The pattern for the arrangement of the values into $\mathbf{T}^{(2)}$ is easily followed. The interaction energy of the charge fields of constituents A and B is,

$$E_{int} = \mathbf{M}^{(A)\dagger} \mathbf{T}^{(2)} \mathbf{M}^{(B)} \qquad (9\text{-}40)$$

Through the elements of $\mathbf{T}^{(2)}$, a moment of one type on A may interact with a moment of another type on B. This is merely because the fields arising from point multipoles are not uniform, do not have uniform gradients, and so on. A point dipole on A does interact with a point quadrupole on B, for instance.

The energy of polarization is non-linear in the external potential. In terms of polytensors, the polarization energy of molecule A occurring via the polarizabilities of A and due to the field of molecule B is,

$$E_{int}^{(1)} = \frac{1}{2} \mathbf{V}^{(\text{due to B})}(\text{at A})\ \mathbf{P}^{(2)}(\text{A})\ \mathbf{V}^{(\text{due to B})}(\text{at A}) \qquad (9\text{-}41)$$

$\mathbf{P}^{(2)}$ is the square polytensor of polarizabilities that includes the dipole, the dipole-quadrupole, the quadrupole polarizability, and so on (see FIGURE 7.3). If there are several interacting molecules, then **V**(at A) is obtained as a vector sum:

$$\mathbf{V}(\text{at A}) = \sum_{B \neq A} \mathbf{V}^{(\text{due to B})}(\text{at A}) \qquad (9\text{-}42)$$

Using this total potential in Eqn. (9-41) leads to interaction terms that depend on more than two constituent species.

Hyperpolarizabilities are third rank polytensors. Their role in the interaction energy is obtained from multiplication by **V** three times, a contraction over the three tensor indices. The second hyperpolarizability terms in the interaction energy have a fourth order dependence on **V**.

The classical polarization of a particular molecular charge distribution, because of the fields of nearby molecules, means that the electrical potential it generates (as in Eqn. (9-37)) is changed from that due to its permanent moments. The polarization means that moments are induced. The composite potential of nearby molecules induces moments via the polarizabilities.

$$\mathbf{M}_{\mathrm{ind}}^{(A)} = \mathbf{P}^{(2)}(A)\,\mathbf{V}(\mathrm{at}\ A) \qquad (9\text{-}43)$$

The composite potential also induces moments via the hyperpolarizabilities with a quadratic dependence. Likewise it induces polarizabilities via the hyperpolarizabilities, and so on.

$$\mathbf{P}_{\mathrm{ind}}^{(2)}(A) = \mathbf{P}^{(3)}(A)\,\mathbf{V}(\mathrm{at}\ A) \qquad (9\text{-}44)$$

There arises, then, a set of coupled equations for the mutual polarization of two or more molecules. Considering this in the iterative manner in which the equations are often solved, the permanent moment field of molecule A induces moments (and polarizabilities) on molecule B. The field of the permanent and induced moments of molecule B polarize molecule A. The polarization of molecule A means that molecule B sees a different field, and so on. Direct matrix solution of the coupled equations is easy if only polarizabilities are included in the analysis. However, if hyperpolarizabilities are included, the equations are non-linear and iterative solution, at least, is one straightforward way of solving the equations [D-33].

The multipole expansion (permanent moments and polarization) can be continued to arbitrarily high order with new computational procedures [D-33]. It is a truncated expansion in practice, though, and subject to certain formal limitations. First, quantum mechanical charge distributions of the molecules extend, at least with small density, well away from the center of a molecule, and so it is an approximation that the charge distributions of two weakly interacting species are not penetrating or overlapping. Second, there is no assurance usually that the separation between two molecules in a region of interest is large enough for the multipole expansion to be convergent. Some tests do show a declining contribution of higher moments in small molecule dimers [D-34]. For larger molecules, the central multipole expansion will not be appropriate at short range because of sizable higher moment effects. An excellent solution is to represent the molecule by low order multipoles distributed throughout the geometrical space of the molecules as Stone has done [S-38:40].

However carried out, it is clear that the classical, electrical part of the interaction between two or more molecules or atoms can be extensively evaluated. For this to be useful in the calculation of structures and dynamics of weak clusters, this interaction must parallel the true potential surface. Or else, it must be simple to account for the differences where it does not. This is currently an active area of investigation, but there is already some basis for expecting electrical treatments to have such utility. That basis is the nature of the electronic structure change in a monomer upon complexation or hydrogen bonding to another monomer. In a calculation on the hydrogen fluoride dimer [D-35], a comparison was made between a quantum mechanical and a classical treatment of the electrical properties of the complex. Derivative Hartree-Fock theory [D-18,29] was used with a large basis set to find the quantum mechanical dipole moment, dipole polarizability and hyperpolarizability as a function of the separation distance. A classical calculation using the isolated monomer electrical properties was carried out in a corresponding way to obtain the induced contributions to the dipole, dipole polarizability and hyperpolarizability in the absence of intermolecular quantum effects. The classical analysis called for using the second and third dipole hyperpolarizabilities in order to obtain the induced hyperpolarizability. The dipole hyperpolarizability tensor was found to be quite sensitive to hydrogen bond formation, and as shown in FIGURE 9.1, the classical and quantum treatments gave similar results as the monomers were brought together. It is unlikely that this agreement would be found if it were not that the primary change in a molecule's electronic structure upon weak interaction is polarization of charge. Given that, classical electrical analysis should reveal a key share of the interaction potential energy surface.

Further evidence that polarization is the primary electronic structure change due to weak bonding may be taken from the high level *ab initio* calculations of electric field gradients at quadrupolar nuclei reported by Cummins, Bacskay and Hush [C-19:23]. In some systems, they were able to associate 80% of the change in the field gradient, or nuclear quadrupole coupling, with electrical polarization. In several cases, they have been able to account for measured quadrupole coupling in solids and gas phase complexes by modelling the surrounding medium as an electrical influence, arising from distributed charges. This is different from a classical interaction analysis since the electric field gradients at the nuclei of a molecule require full accounting of the *intra*molecular quantum features.

Probably one hundred binary complexes have already been the subject of calculational study using electrical analysis of one sort or another (for example, [B-42:43,C-24,L-19]). These studies strongly indicate that suitably extensive electrical analysis can account for orientational aspects of the structures of small complexes. Some cases are obvious: The NN-HF complex is linear with the strongest electrical

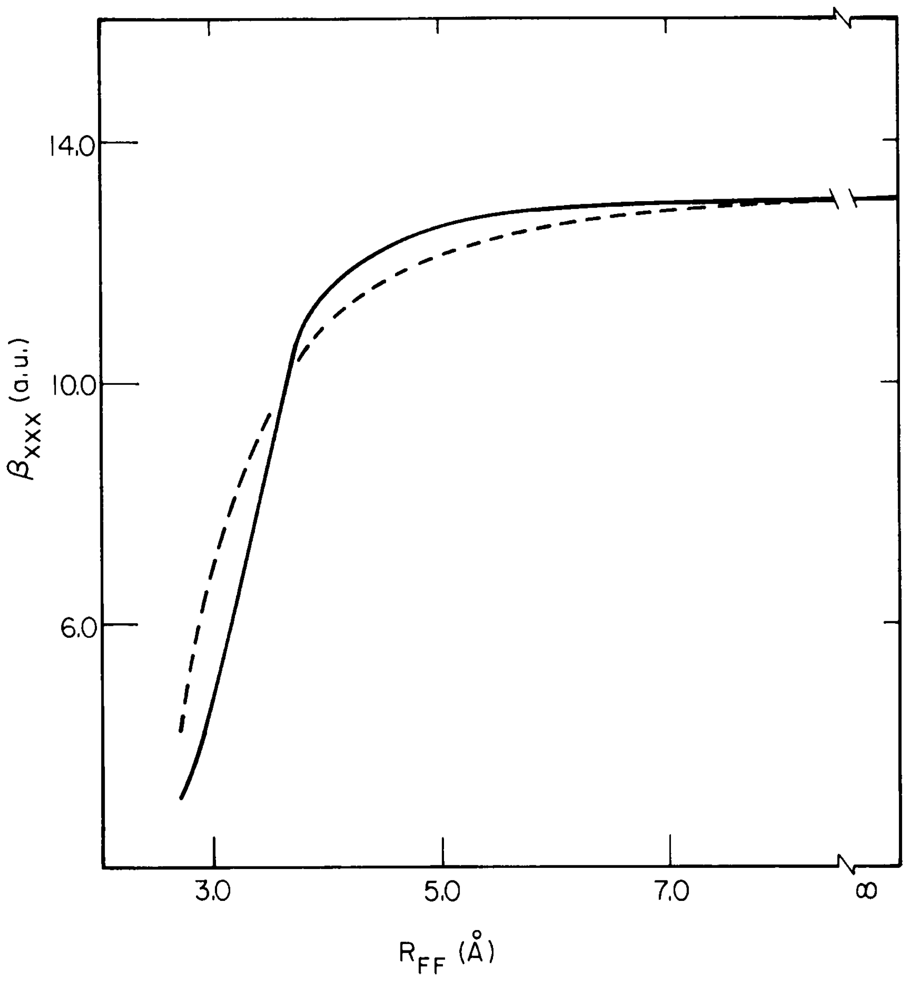


FIGURE 9.1

The axial dipole hyperpolarizability element, β_{xxx}, of the HF-dimer as a function of the fluorine-fluorine separation distance [D-35]. The x-axis is defined by the line connecting the fluorine centers. The solid line is an *ab initio*, quantum mechanical result from DHF calculations. The broken line is obtained from a classical analysis using the electrical properties of the isolated monomers.

term being that of the dipole of HF with the quadrupole of nitrogen. It is not surprising that the isoelectronic acetylene-HF complex is T-shaped (the H-end of HF points into the C-C bond) since the quadrupole of acetylene is opposite that of nitrogen. Another example is the $(HF)_2$ where the juxtaposition of dipole-dipole forces favoring a linear structure, dipole-quadrupole forces favoring a 90° structure, and quadrupole-quadrupole forces favoring a T-shape leads to the bent structure of this complex.

An interesting study that reveals much about the electrical part of weak interaction potentials is the study by Kolenbrander et al. [K-14] on the cyclic trimer $(HF)_3$. Electrical potential surfaces were generated for the independent treatment of in-plane torsions of the monomers and out-of-plane torsions. Each of the two types of surfaces were in terms of three monomer orientation angles. A large basis of product functions using free-rotor functions for each angular degree of freedom was employed. Following integration over the electrical potential surface, the Hamiltonian matrix in the product function basis was constructed and then diagonalized to yield a manifold of torsional vibrational state energies.

Spectroscopic study of $(HF)_3$ carried out by Kolenbrander in concert with the theoretical analysis yielded frequencies for two overtone transitions, each within 32 cm^{-1} of values calculated from the electrical surface. However, the two transition frequencies, as measured or as calculated, were also within 32 cm^{-1} of each other, thereby precluding an immediate assignment. Results of this study are shown in TABLE 9.2. The assignment of one of the bands to an out-of-plane transition and the other to an in-plane transition was made by calculating the deuterium substitution effect on the transition frequency and measuring it. Single or double deuterium substitution separates the frequencies. The assignment was confirmed by another calculation and another experiment. This time, the electrically determined dipole moment surface was computed and vibrational transition moments were calculated using the vibrational state wavefunctions. One of the bands was found to be about two orders of magnitude stronger than the other, and indeed, this was subsequently observed [K-14].

An interesting aspect of the theoretical work on $(HF)_3$ was the effect of polarization. The primary surfaces were generated using the dipole, quadrupole and octupole moments of HF, and incorporating polarization via the dipole polarizability and hyperpolarizability and with the dipole-quadrupole and quadrupole-quadrupole polarizability. As a test, the entire analysis was repeated for the in-plane states using only the permanent moments. The neglect of polarization in electrical analysis usually yields a small refinement in predicted equilibrium orientation angles, so one might expect little difference in the vibrational frequencies calculated with an unpolarized surface. As the results in TABLE 9.2 show, polarization had a noticeable effect on the vibrational sate energies. It changed the transition energy for the overtone band by over 100 cm^{-1}. The direction of the change was toward higher frequency, implying a flatter surface in the absence of polarization. This means that polarization effects preferentially stabilize the near equilibrium regions of the surface in this complex. Polarization is necessarily a cooperative or non-pairwise effect, and so the success of these calculations is strong support for the idea that cooperative effects arise from electrical polarization.

TABLE 9.2

Torsional vibrational frequencies of $(HF)_3$ (in cm^{-1}) from [K-14] except for neon matrix values.

	Calculated Transition Frequencies		*Experimental Frequencies*	
	Permanent Moment Surface	*Polarized Surface*	*Ne Matrix [A-16]*	*IR-IR Double Resonance*
IN-PLANE				
A' ($\nu_{A'}=1,\nu_{E'}=0$)	703	801		
E'($\nu_{A'}=0,\nu_{E'}=1$)	429	491	477	
E'($\nu_{A'}=0,\nu_{E'}=2$)	826	955		941
OUT-OF-PLANE				
A"($\nu_{A''}=1,\nu_{E''}=0$)		568	590	
E"($\nu_{A''}=0,\nu_{E''}=1$)		376		
E"($\nu_{A''}=1,\nu_{E''}=1$)		923		955

Electrical interaction energies for structures at equilibrium are often found to be comparable to the experimentally deduced stabilities or to calculated *ab initio* values. A few examples of stabilities of weak complexes are given in TABLE 9.3. The comparison between electrical and overall stabilities is insufficient to argue that electrical interaction determines the true surface: As Coulson's early analysis [C-13] revealed, there are stabilizing and destabilizing effects in a hydrogen bond and they are almost in balance. Mathematically, if the quantities x, y and z sum to yield a value c, it can not be said that x is larger in size than y and z on the basis of x alone being equal to c. On the other hand, it may mean that approximating $(y + z)$ may be easier than approximating y and z alone.

Where electrical analysis proves suitable for mapping out segments or slices of the potential energy surface, it must be that other effects, even if sizable, are in balance with each other throughout the region of interest. In the radial dependence of a weak potential, the electrical interaction is likely to be inappropriate close-in. It neglects the penetration of charge distributions and the exchange repulsion that gives rise to a strongly repulsive potential. Therefore, the challenge is to see if nature has provided an easy way to augment the electrical energies so as to properly generate *global* potential energy surfaces for weak assemblies. In other words, can simple potentials, perhaps empirical ones, be devised to augment electrical potentials and

TABLE 9.3

Stabilities of weakly bound complexes (in cm^{-1}).

Complex	*Electrical*	*Ab Initio*	*Experimental*
H_2-HF	342 [B-6]	306 [B-6]	
N_2-HF	572 [D-32]	795 [B-44]	618 [S-41]
HF-HF	1700 [D-32]	1600 [L-20]	
HCN-HF	2490 [D-32]	2307 [B-44]	2180 [L-21]
$(HF)_3$	5460 [D-36]	4900 [L-20]	

thereby give a true picture of the surface even where non-electrical contributors do not remain in balance?

Buckingham and Fowler [B-42] have used infinitely-hard walls to augment permanent moment potentials. Soft-edge, hard-walls may provide potentials that are accurate over more regions, such as partly up the inside edge of the surface. Potentials essentially of the "exponential-6" form, meaning an exponentially repulsive term in R plus an attractive R^{-6} term where R measures the separation distance, have been used as atom-based augmenting potentials [D-32]. In these potentials, the attractive term softens the onset of the exponential potential and may be thought of as arising from otherwise neglected quantum features such as dispersion. A test of the legitimacy of these types of potentials is whether the parameters in them are transferable from complex to complex. If an atom in a particular molecule must have a different van der Waals radius or a different repulsive parameter depending on what the molecule is complexed with, then the argument may be made that the augmenting potential is merely a correction and has no predictive power. So far, it appears promising how the parameters in the augmenting potentials may be used transferably [D-32], but much more tests, including comparison with entirely *ab initio* surfaces are needed.

Concluding Remarks. *Ab initio* electronic structure theory is now a well-established tool for direct computation of molecular structural parameters and molecular properties. Small molecule tests, where the most detailed calculations can be performed, have provided the proof that accurate predictions are possible from computation. There is now a calculational technology that is quite widespread. Thinking that quantum chemistry can serve only to explain or account for an observation has finally evolved into thinking of quantum chemical methods as serious tools for chemical investigation. The developments will continue, and the power of the tools will be enhanced. The forward-looking schemes mentioned in this chapter are just some of the ways in which physical and chemical insight are taken together with the experience of carrying out calculations in formulating new approaches.

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