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¹ *Nature*, 119, 558 (1927).

² This hypothesis was suggested to the author in conversation with Dr. F. Zwicky.

³ Sommerfeld, "Atombau," 4th ed., p. 222.

COUPLING OF ELECTRONIC AND NUCLEAR MOTIONS IN DIATOMIC MOLECULES

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While for many important problems the quantum mechanical coupling between the motion of the nuclei and of the electrons in a diatomic molecule may be ignored, there are others in which this coupling is the main factor. Among the various phenomena which are conditioned by this coupling and which have recently attracted attention the following may be mentioned:

1. The mechanism of the dissociation of molecules by light absorption. This question has been discussed by Franck who, with his co-workers, is also doing important experimental work in this field.¹

2. The mechanism of dissociation of molecules as a primary consequence of excitation by electron collision. The ideas of Franck on (1) have here been applied by Birge and Spomer² to a discussion of the experimental results of Hogness and Lunn.

3. The relative transition probabilities for the various vibrational transitions associated with a single electron transition in the emission or absorption of light by a molecule; i.e., the problem of intensity distribution in electronic band systems. This question has been treated recently by the writer.³

4. The mechanism of the process whereby molecules may be excited to vibration levels by electron collision without simultaneous electronic excitation. That this process actually occurs is proved by the recent experiments of Harries, carried out in Franck's laboratory.⁴

All of these phenomena permit of being understood in terms of the new quantum mechanics, at least in a qualitative way, as it is the purpose of this note to show.

The complete quantum-mechanical problem of a diatomic molecule, from the Schrödinger point of view, calls for the solution of a partial differential equation in $3N + 6$ independent variables, if N is the number of electrons in the molecule. The problem is distinguished from the prob-

lem of a complicated atom, by the presence of two particles of large mass, instead of one. The usual theory of the diatomic molecule, however, replaces the actual model of two nuclei and N electrons affecting each other with Coulomb forces by one which consists simply of two masses affecting each other by a more or less arbitrary potential energy law. This effective potential energy is supposed to result from the average of the reactions of the rapidly moving electrons on the nuclei together with the mutual Coulomb repulsion of the nuclei.

The known success of this simpler model in explaining the energy levels, in general, and the infra-red transition probabilities, makes it natural to suppose that the heavy masses of the nuclei bring about a partial or approximate separation of variables in the Schrödinger equation. The three coördinates which correspond to the motion of the center of gravity of the system in space are readily separated out. Similarly, if rotation is neglected, the system is described by the nuclear separation, R , and the electronic coördinates, denoted in the aggregate by X . The assumption of partial separation of variables here made requires the two following results:

(a) The energy-levels (eigenwert parameter) are the sum of a function depending only on the electronic quantum numbers, denoted in the aggregate by e , and a function of both the electronic quantum numbers and a vibrational quantum number, n .

(b) The amplitude function, ψ , is the product of two factors, one of which depends on all of the quantum numbers and only the nuclear separation, R , while the other depends only on the electronic quantum numbers and the electronic and nuclear coördinates. That is, one has

$$E = E_1(e) + E_2(e, n)$$

$$\psi(e, n, X, R) = \psi_1(e, X, R) \cdot \psi_2(e, n, R).$$

This assumption, of course, needs justification in terms of the theory of the Schrödinger equation. An attempt to do this is being made. But, making the assumption, the four coupling phenomena already listed come within a single picture.

Numbers 1 and 3 are simpler than 2 and 4 for radiative transitions are simpler than those involving electron collisions. For the purpose of computing such transition probabilities one has to consider the matrix component of the electric moment of the molecule with regard to the initial and final state. This matrix component, referring to the initial state e', n' and the final state e'', n'' , is given by

$$M(e'e''n'n'') = \int \int M(X, R) \psi(e'n'XR) \psi(e''n''XR) dXdR$$

in which $M(X, R)$ is equal to the electric moment of the molecule in the configuration X, R . The integration is over all values of the coördinates.

For the purpose of comparing various vibration transitions associated with the same electronic transition, one may perform the integration over the electronic coordinates. One obtains thereby an effective electric moment function, $m(R)$, for computing the different vibration transitions. The complete matrix component is then the integral of this moment function over the product of the two vibrational factors of the amplitude function.

The vibrational factor in this formula may safely be identified with the amplitude function obtained from the simple anharmonic oscillator treatment of the molecule problem. These amplitude functions have the essential characteristic that they approach a zero value asymptotically, but rapidly, outside of the region of the corresponding classical motion. Inside this region they oscillate, having as many zeros as the order of the quantum state. *Herein lies the quantum mechanical justification of the picture used by Franck* in discussing the dissociation of molecules by light absorption, and which has found application in the theory of transition probabilities in electronic band systems.

The Franck picture is that the favored transitions are those for which the classical vibrational motions cover over-lapping regions of the nuclear separation coordinate. Clearly this comes out of the quantum mechanical treatment by the property of the Schrödinger amplitude function of having its largest values at the coordinate values covered by the classical motion. Hence the larger values of the matrix components are, in general, those for which both amplitude function factors in the integrand have large values for the same values of the independent variable; i.e., those of over-lapping classical motion. The quantum-mechanical formula differs in two respects from the earlier treatment. One is that transitions of small probability corresponding to non-over-lapping classical vibration motions are made possible by the fact that the Schrödinger amplitude functions have values outside the range of the classical motion. Also, since the amplitude function oscillates within the range of the classical motion there is the possibility of a kind of interference in the transition probabilities, reducing the value associated with a transition which corresponds to over-lapping classical motions. This may be the explanation of the irregular alternations of intensity in the Wood's resonance spectrum of iodine, already discussed by Lenz in terms of the old correspondence principle for intensities.

To illustrate the semi-quantitative numerical behavior of the new quantum mechanical formula, two cases have been worked out roughly. For the purpose, $m(R)$ was regarded simply as a constant and the vibrational amplitude functions were taken to be the Hermitian polynomial harmonic oscillator solutions.⁵ The harmonic oscillator solutions depend on the initial and final electronic state through the vibration frequencies

and centers of oscillation associated with the two states. The relative transition probabilities are measured by the product of the square of the matrix component and the fourth power of the quantum frequency involved, in accordance with the classical dipole radiation formula.

Thus, applied to the $n' = 0$ progression of the Schumann-Runge bands of oxygen, one obtains for the relative intensity of the bands corresponding to various final state vibration quantum numbers, n'' :

$n'' =$	0	1	2	3	4	5	6		
	8.4×10^{-6}	9×10^{-5}	5×10^{-4}	1.6×10^{-3}	6.6×10^{-3}	0.008	0.019		
					7	...	13	15	17
					0.03	...	0.88	1.00	1.13

Experimentally, Runge measured on his plates only the bands $n'' = 11$ to $n'' = 17$, as being the strongest. This is in good semi-quantitative agreement with the foregoing calculations.

On the other hand, S_2N offers a band system characterized by a very slight change in moment of inertia and frequency of vibration between the two electronic states.⁶ Correspondingly, zero change in the vibration quantum number is the most probable. This comes out of the matrix formula since, had there been no change in moment of inertia or natural frequency, the two amplitude functions in the formula would have been members of the same normal-orthogonal set of functions, so that only the zero vibration change would be allowed. When this is "almost" the case, the functions are "almost orthogonal" thus favoring the zero change in vibrational quantum number.

Turning now to the coupling processes 2 and 4, one may interpret these in essentially the same way as a consequence of Born's quantum mechanical analysis of the problem of the collision of a charged particle with an atomic or molecular system.⁷ A free electron colliding with a molecule interacts with each of the electrons and the nuclei in the molecule according to the Coulomb law. If this energy of interaction be developed in negative powers of the distance of the electron from the center of gravity of the molecule, the development begins with an inverse cube term representing the interaction between the free electron and the dipole moment of the atom. The higher powers of the development correspond to the interaction with the quadrupole and higher moments of the electric charge of the molecule. When these are neglected, Born's analysis shows the probabilities of excitation of a molecule by electron impact are proportional to the square of the matrix component of the electric moment of the molecule in regard to the initial and final states in question. This, however, is the same quantity as that which measures the probabilities of transition associated with light emission and absorption. Therefore, to the order of approximation which replaces the

electron interaction with the molecule by that between the electron and equivalent dipole, one has that vibration transitions associated with electronic excitation of the molecule will be the same whether the process is radiative or a result of a collision. This is the justification of the argument of Birge and Sponer in discussing the experiments of Hogness and Lunn.

Using this same analysis of the collision problem, it is clear that the action of a colliding electron on a molecule in exciting vibration transitions without electron excitation, the fourth type of coupling in the list, is a consequence of the non-vanishing of the same matrix components as those which measure the probability of vibration transitions in infra-red, vibration-rotation bands. The correlation is, however, not a sharp one, for in the collision process the electric moments of higher order of the molecule may be active.

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¹ Franck, *Trans. Faraday Soc.*, 1925; Dymond, E. G., *Zeits. Phys.*, 34, 553 (1925); Kuhn, H., *Zeits. Phys.*, 39, 77 (1926).

² Birge and Sponer, *Phys. Rev.*, 28, 259 (1926).

³ Condon, E., *Ibid.*, 28, 1182 (1926).

⁴ Harries, W., Preliminary report at meeting of the Deutschen Physikalischen Gesellschaft, Hamburg, Feb. 6, 1927.

⁵ Schrödinger, *Ann. Phys.*, 79, 514 (1926).

⁶ Compare treatment and discussion in *Phys. Rev.*, 28, 1182 (1926).

⁷ Born, *Zeits. Phys.*, 38, 803 (1926).

WAVE MECHANICS AND THE NORMAL STATE OF THE HYDROGEN MOLECULE

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The problem of the motion of a particle attracted by two fixed centers of force according to the Coulomb force law can be treated by classical mechanics and has been used in quantum theory by Pauli and Niessen for a theory of the hydrogen molecule ion.¹ In the quantum mechanics, where the energy levels are determined as the "eigenwerte" of Schrödinger's equation, the variables are separable and the boundary value problem is easily set up. But thus far a satisfactory treatment of the differential equations involved is lacking. Burrau² has recently carried out a numerical integration of the problem for the lowest energy level of an electron moving under the influence of two fixed centers of Coulomb attraction as a function of the distance apart of these centers. In this paper, Burrau's