

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.

* NATIONAL RESEARCH FELLOW.

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

BY EDWARD UHLER CONDON*

MUNICH, GERMANY

Communicated April 18, 1927

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

data are used to give a semi-quantitative discussion of the neutral hydrogen molecule. His values are:

Nuclear separation	1.0	1.3	1.6	1.8	2.0	2.2	2.4	2.95
Electronic energy	2.896	2.648	2.436	2.309	2.204	2.109	2.025	1.836

The unit of separation is the Bohr 1_1 orbit radius of hydrogen atom, that of energy is the ionization potential of atomic hydrogen.

In all this work the tacit assumption is made that, because of the large masses of the nuclei, the problem can be solved regarding the nuclei as fixed at a distance which is one of the parameters of the problem. When the energy of the electronic motion as a function of the distance is known, the energy of the Coulomb repulsion of the fixed nuclei is added and so the variation of the total energy of the non-rotating non-vibrating molecule with nuclear distance is found. The minimum of this curve is taken as the "equilibrium" separation of the nuclei and the value of the minimum is taken as the energy of the molecule in that electronic state. (More correctly, the small amount $1/2h\nu$ is to be added to the minimum value.) If the nuclei are no longer regarded as fixed this curve is regarded as giving the "law of force" governing the rotational and vibrational motions of the molecule. That this is the correct procedure in the classical mechanics was shown by Born and Heisenberg:⁸ that it remains correct in the quantum mechanics has not yet been definitely proved. There is no reason to believe, however, that it is not correct, and it will be used here without further justification.

When the nuclei of a hydrogen molecule ion are far apart one is dealing virtually with a free hydrogen atom and a proton. The electronic energy is then mainly that of the Coulomb interaction between the proton and the electronic charge of the atom. If the atom were not Stark-affected by the proton, this would be just equal to the nuclear repulsion and the total energy would be simply R for all values of the nuclear separation (all values are negative), where R is the Rydberg constant. But the proton induces a polarization of the H-atom and, therefore, the energy of proton-electron interaction is greater than that of proton-proton. On the other hand, when the nuclear separation is zero and the electron moves under the influence of a double central charge, the energy is that of the lowest state of ionized helium. Burrau's numerical integrations supply values of the electronic energy for intermediate electronic separations. When the nuclear repulsive energy (curve *b*, Fig. 1) is added to Burrau's values there results curve *a*, figure 2, which is Burrau's curve for H_2^+ . The equilibrium separation is 2 units (i.e., 2 times the radius of the Bohr 1_1 hydrogen orbit) and the minimum energy is $1.204 R = 16.28$ volts. The heat of dissociation is $0.204R = 2.76$ volts. Burrau checks the value with experiment by an indirect comparison with the ionization potential of H_2 as discussed later in this paper.

Turning now to the neutral molecule one expects, on the Pauli principle of assigning quantum numbers, that the two electrons will be in equivalent orbits. The starting point, therefore, for the approximate treatment of the problem is a model in which the two electrons have no mutual influence

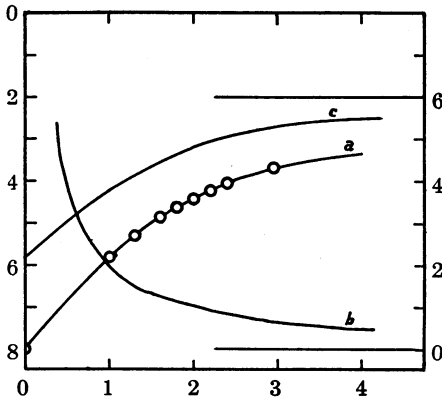


FIGURE 1

Electronic and nuclear energy in H_2 . *a*, Values for non-interacting electrons. *b*, Coulomb energy of nuclear repulsion. *c*, Approximate electronic energy curve for interacting electrons. Units: ordinates, 1 = Rydberg constant, abscissas, 1 = radius of first Bohr orbit in hydrogen atom.

and each moves as it would if alone in the ground state of H_2^+ as given by Burrau. The electronic energy of this model at each distance is evidently just twice that for H_2^+ . This curve of doubled H_2^+ values is given here as *a* of figure 1. Combined with the Coulomb proton-proton energy this yields curve *b*, figure 2, for the energy curve of the neutral H_2 molecule with uncoupled electrons. This gives an equilibrium separation of 1.075 units, i.e., a moment of inertia of 2.7×10^{-41} gr. cm.² The heat of dissociation is $1.800R = 24.36$ volts.

Naturally, such a model gives only a very rough approximation to the truth. But it is to be

observed that the above model does set a definite lower limit on the moment of inertia of the molecule. For the electronic interaction, whatever its amount, will be positive and will decrease monotonously with increasing nuclear separation, since it is the repulsive potential of interacting-like charge. It acts to increase the ordinates of curve *b*, figure 1, by decreasing amounts and, therefore, shifts the minimum of the resultant curve to larger abscissas. This seems to be an important conclusion inasmuch as *the lower limit here definitely given by quantum mechanics is greater than nine of the thirteen values obtained on various theories from specific heat data* as presented in the recent thorough review of the the subject by Van Vleck and Hutchisson.⁴

Turning now to the electronic interaction, the analysis of Hund⁵ provides the important result that the electronic term of the lowest state of a molecule changes continuously from its value for a neutral atom of equal number of electrons to its value for the dissociated atoms, according to the new quantum mechanics. Herein lies an important difference between the old and the new quantum theory which is essential to the argument of this paper. That unexcited molecules dissociate into two unexcited

atoms as a result of vibrations of infinite amplitude has been shown empirically by Birge and Sponer.⁶

The first approximation to the electron interaction in unexcited helium has been computed by Unsöld,⁷ by means of the wave mechanics, who finds $5.5 R$ for the whole atom, i.e., $1.5 R = 20.3$ volts for the ionization potential. Empirically the value is $5.818R$ for the total energy. At large distances the model goes over into two neutral hydrogen atoms. The electronic energy will, therefore, be asymptotically equal to the Coulomb interaction of an electron and a proton, for it is made up of the repulsion of the two electrons and the attraction of each proton for the electron of the other atom. Moreover, the situation is now that of the interaction of two neutral units so that polarization deformation of each atom by the other will be much smaller than in the case of H_2^+ . Inasmuch as Burrau's work shows that at a distance of 2.95 units the electronic part of the H_2^+ energy differs from the pure Coulomb by about $0.1 R$, it is safe to assume for the H_2 molecule a closer approach to Coulomb value for abscissas greater than 3 units. For intermediate points, a natural assumption is to reduce the doubled Burrau value in the ratio $5.818:8.00$ in order to secure agreement with helium. If this is done it is found that the resulting curve joins on to the Coulomb curve smoothly. Curve c of figure 1 has been drawn from the theoretical values so reduced up to the value for 2.4 and joined on to a Coulomb curve for abscissa values of 3 and greater.

The result of combining c and b of figure 1 is to give c of figure 2 as the energy curve for the hydrogen molecule. The minimum of this curve corresponds to a moment of inertia of 4.26×10^{-41} gr. cm.², and to a heat of dissociation of 4.4 volts. The latter value agrees to within 0.1 volt with the band spectrum value of Witmer and of Dieke and Hopfield.⁸ These figures should be compared with a moment of inertia of 4.91×10^{-41} gr. cm.² and $1.422 R$ heat of dissociation found by Hutchisson⁹ from a cross orbit model of H_2 on classical quantum theory.

Another interesting consequence follows from the relation of the H_2

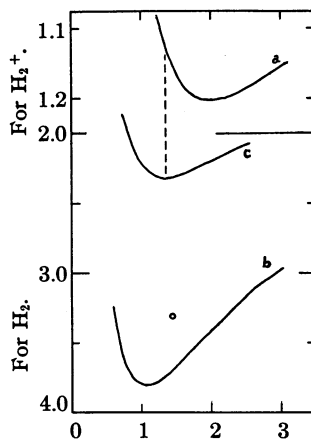


FIGURE 2
Resultant energy curves in H_2^+ and H_2 . *a*, Burrau's curve for H_2^+ . *b*, Curve for H_2 for non-interacting electrons. *c*, Approximate curve for H_2 with interacting electrons. The small circle in the crook of curve *b*, represents the equilibrium position and energy on Hutchisson's classical crossed-orbit model of H_2 . Units: same as figure 1 (note different scales of ordinates for H_2 and H_2^+).

energy curve to that of H_2^+ . According to a principle put forward by Franck, changes involving the electrons in a molecule will affect the nuclei mainly indirectly through the change in molecular binding.¹⁰ According to this view, the most probable event in an electron collision experiment by means of which an electron is removed from H_2 , is the removal of an electron while the nuclei are at a distance of 1.350 units. This requires an amount of energy given by the difference between 2.325 R and the ordinate of the H_2^+ curve at 1.350, namely 1.125 R . This is the theoretical apparent ionization potential and amounts to 1.2 R or 16.2 volts in good agreement with the mean experimental value 16.1 given by Franck and Jordan.¹¹ On the other hand, the true energy of the process $H_2 \rightarrow H_2^+ + e^-$, where H_2^+ is in the lowest state, is the difference between the ordinates of the minima of the H_2 and H_2^+ curves, i.e., 1.12 $R = 15.2$ volts, comparing favorably with value of Witmer and of Dieke and Hopfield from the ultra-violet band spectrum of H_2 .

The theoretical value of the frequency of vibration, depending on the curvature of the curve at its minimum, is naturally more uncertain. Calculation shows that the curve gives a frequency of vibration of 5300 $cm.^{-1}$, about 20% higher than the value 4360 $cm.^{-1}$ from experiment.⁸ As for the moment of inertia, while it is larger than most of the values from specific heat theories, it is in accord with the larger values which have been found by Richardson and Tanaka¹² from analysis of the hydrogen bands.

In conclusion it seems proper to emphasize that Burrau's calculation of H_2^+ and the extension here to H_2 constitute the first quantum-theoretic quantitative discussion of the binding of atoms into molecules by electrons—the valence forces of chemistry. The quantitative success of the new quantum mechanics in the face of the classical theory's failure must serve to lend strong support to the new methods.

* NATIONAL RESEARCH FELLOW.

¹ For a review of the status of the H_2^+ and H_2 problems prior to the new quantum mechanics see Van Vleck, *Quantum Principles and Line Spectra*, p. 88. Also discussion by Kemble in last chapter of National Research Council Report on "Molecular Spectra in Gases."

² Burrau, *Danske Vidensk. Selskab. Math.-fys. Meddel.*, **7**, 14, Copenhagen (1927).

³ Born and Heisenberg, *Ann. Physik*, **74**, 1 (1924).

⁴ Van Vleck and Hutchisson, *Physic. Rev.*, **28**, 1022 (1926).

⁵ Hund, *Zs. Physik*, **40**, 742 (1927).

⁶ Birge and Sponer, *Physic. Rev.*, **28**, 259 (1926).

⁷ Unsöld, *Ann. Physik*, **82**, 355 (1927).

⁸ Witmer, *Physic. Rev.*, **28**, 1223 (1926); Dieke and Hopfield, *Zs. Physik*, **40**, 299 (1926).

⁹ Hutchisson, *Physic. Rev.*, **29**, 270 (1927).

¹⁰ Franck, *Trans. Far. Soc.*, **21**, part 3 (1925). See also discussion by Birge, p. 248 of National Research Council Report on "Molecular Spectra in Gases," and quantum mechanical treatment by Condon, these PROCEEDINGS, **13**, 462 (1927).

¹¹ Franck and Jordan, *Anregung der Quantensprünge durch Stösse*.

¹² Richardson and Tanaka, *Proc. Roy. Soc.*, **106A**, 663 (1924).