

709. *A New Solution of the Wave Equation for H^- .*

By B. F. GRAY and H. O. PRITCHARD.

A method of obtaining the exact solution of the wave equation for H^- from the known exact solution for H_2^+ is examined and shown to be satisfactory; the analysis shows that there exists only one state of the negative hydrogen ion which is stable with respect to a normal hydrogen atom.

INSPECTION of the wave equations for H^- and H_2^+ , denoted in subscripts by A and B respectively, after separation of the translational motion, reveals that they are of the same form, differing only by an exchange of the masses of the electron and the proton, m and M respectively. If the lowest eigenvalue of the equation for H_2^+ is

$$E_B = E(M, m)$$

then it follows that

$$E_A = E(m, M)$$

with a similar relation holding for the eigenfunctions. This of course is only true for the exact eigenvalues and eigenfunctions, the difference $|E_A - \tilde{E}(m, M)|$ giving us a (very sensitive) test of the accuracy of an approximation $\tilde{E}(M, m)$ to E_B . This correspondence would, in principle, allow us to obtain E_B from E_A , but we cannot do this in practice because E_A has only been obtained directly by use of the variation principle.

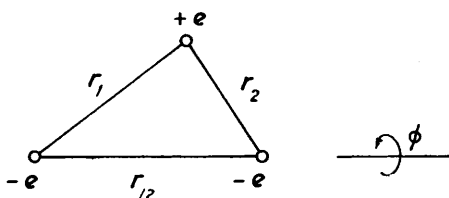
The wave equations of H^- and H_2^+ have not hitherto been identified purely because of

the choice of the origin of the co-ordinates. If for H^- we take a co-ordinate system (see Fig. 1) with

$$\xi = \frac{r_1 + r_2}{r_{12}}, \quad \eta = \frac{r_1 - r_2}{r_{12}}, \quad \text{and } \phi$$

as our variables, then the wave equation is identical with that for H_2^+ with nuclear motion, except for the interchange of m and M . It is now permissible (the principle of covariance) to consider the electrons in H^- as moving in the field of a rapidly moving proton, *i.e.*, the "inverse" of the Born-Oppenheimer approximation for H_2^+ . The reason is that the "electronic energy" of H_2^+ is an energy of motion of the electron *relative* to the two nuclei, and if this motion is rapid, it is equally permissible to speak of the motion of the two protons as rapid, relative to the electron. Whichever origin we choose, the energy of the relative motion must be invariant. Furthermore, it is convenient to separate off the energy of a hydrogen atom, corrected for nuclear motion; this energy is proportional to $[(1/m) + (1/M)]^{-1}$ and is clearly invariant under the mass transformation. Hence the bond dissociation energy of H_2^+ must transform into the ionisation potential of H^- and we can deal directly with these quantities.

FIG. 1.



Intuitively, the application of the principle of covariance means that we can picture the H^- ion as a proton about which is distributed a Morse-type oscillator, *i.e.*, the two electrons are vibrating with respect to each other and their motion relative to the nucleus is superimposed upon this vibration. They are, of course, also rotating relatively to an axis fixed in space, but the contribution to the effective potential from centrifugal effects is zero for the lowest energy level ($j = 0$) and is so great for $j = 1$ (owing to the small moment of inertia) that the system would ionise (the analogue of dissociation of molecules by rotation). Hence we need consider only the ground rotational levels of any electron vibrational states.

Curve A of Fig. 2 shows the total energy of H_2^+ (taken from the exact solution of the static wave equation by Bates, Ledsham, and Stewart¹), referred to the (invariant) energy of a hydrogen atom as zero. This is now to be interpreted as representing the vibration with respect to each other of the two electrons in H^- . Assuming that this is a Morse curve, we can deduce the relevant constants (*i.e.*, D the minimum energy and a the anharmonicity constant) from a knowledge of three equally spaced points in the neighbourhood of the minimum.² The important quantity, which determines both the number of allowed energy levels and their energies,³ is

$$k = [2\pi\sqrt{(M'D)}]/\hbar a$$

where M' is the mass of the vibrating particles (if they are both equal). For curve A we find that $k_2 = 20.32$ whence $k_A = k_B/\sqrt{1836} \approx 0.47$, and since for a Morse oscillator the number of allowed energy levels is the largest integer less than $(k + \frac{1}{2})$ this means that at

¹ Bates, Ledsham, and Stewart, *Phil. Trans.*, 1953, *A*, **246**, 215.

² Rosen, *Phys. Review*, 1931, **38**, 2099.

³ Condon and Morse, "Quantum Mechanics," McGraw-Hill, New York, 1929, pp. 71-72.

this level of approximation H^- is not stable. (As a corollary, in the fixed-nucleus approximation, the equilibrium internuclear separation in H_2^+ is precisely $2a_0$, since this is the most probable interelectronic separation for this model of H^- .)

To obtain a positive electron affinity it is necessary to go to the next stage of approximation in H_2^+ , *i.e.*, to include adiabatic coupling terms between the electronic and the nuclear motions. These have already been evaluated at some internuclear separations by Dalgarno and McCarroll⁴ who found them to be repulsive below $2a_0$ but attractive at greater distances (but negligible at all separations, affecting only the fifth significant figure in the bond dissociation energy—this directly contradicted Wu and Bhatia⁵ who found them to affect higher places, being repulsive for distances greater than $2a_0$). If we take Dalgarno and McCarroll's corrections which, although they are negligible for H_2^+ itself,

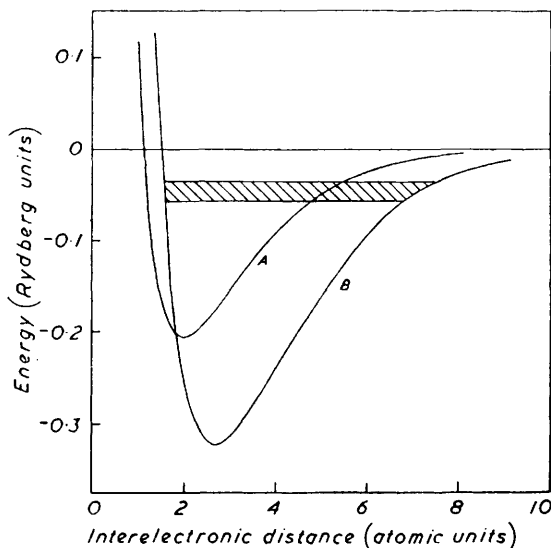


FIG. 2.
The shaded region represents the uncertainty in the zero-point energy arising from the assumption that curve B is a true Morse curve over the whole oscillation.

become multiplied by 1836 under the mass transformation, we obtain curve B of Fig. 2 for the variation of energy with interelectronic separation. This is a reasonable Morse curve, since fitting various sets of points gives values in the range $a = 1.030 \pm 0.065 a_0^{-1}$ and $D = 0.3290 \pm 0.0075$ Rydberg. These mean values lead to a value for k_A of 0.788, thus establishing that there is almost certainly only one level of H^- stable with respect to a normal hydrogen atom (other states of H_2^+ lie very much higher in the energy spectrum although adiabatic coupling terms may be larger⁴). The energy of a Morse oscillator is

$$E = -D(k - n - \frac{1}{2})^2/k^2$$

where n , the quantum number of the vibration, can range from zero to the largest integer less than $(k - \frac{1}{2})$. Substituting the value of k found for curve B in this expression leads to an electron affinity of 0.044 Rydberg, *i.e.*, a total energy of -1.044 ± 0.012 Rydberg, compared with the best variation calculation of -1.0554 Rydberg.

In order to obtain the energy limit of the adiabatic approximation, it would be necessary to calculate the coupling corrections at more internuclear separations than are at present available⁴ and to solve the wave equation numerically by using curve B for the potential energy, in order to avoid the assumption that it is a Morse curve. However, it is unlikely that the correct energy will be approached unless non-diagonal elements are considered in the coupling between nuclear and electronic motions. Nevertheless, we are dealing

⁴ Dalgarno and McCarroll, *Proc. Roy. Soc.*, 1956, A, **237**, 383.

⁵ Wu and Bhatia, *J. Chem. Phys.*, 1956, **24**, 48.

here with a process which converges to the correct eigenvalue (this has not yet been shown to be so for the Hylleraas method, particularly in the case of H^-); we hope to undertake this programme soon and at the same time to study the helium atom (*i.e.*, by solving the H_2^+ problem with a doubly-charged electron) for which there are many more stable levels, in order to establish the exact correspondence between the various states under the mass transformation, *i.e.*, the correspondence between electronic, vibrational, and rotational excitation for the molecule on the one hand, and electronic excitation and spin and orbital angular momentum for the atom on the other.

The energy value obtained in the present calculation proves beyond doubt that Dalgarno and McCarroll's corrections are correct; those of Wu and Bhatia would give an energy corresponding to an even more unstable system than is obtained without using the corrections. The calculation also re-emphasises the fact that it is only the total energy of the system which is meaningful and that the nature of the individual energy terms depends on how the problem is tackled. In our calculation, the individual terms are coulombic, kinetic, adiabatic coupling, and zero-point vibration energies, whereas in the standard treatments one has coulombic, kinetic, exchange, and correlation-energy terms; furthermore, the inclusion of coupling between nuclear and electronic motions increases the most probable interelectron distance from $2a_0$ to $2.69a_0$, an effect which is associated with a "screening constant" in orbital treatments.

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THE UNIVERSITY, MANCHESTER.

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