QuantumMechanical Treatment of Helium Hydride MoleculeIon HeH+

J. Y. Beach

The various methods that have been employed for the separation of isotopes have been discussed by Aston.[6] The present results suggest some of the conditions under which thermionic emission can be utilized for this purpose. It is evident that when the atoms to be emitted as thermions do not have to conform to any definite lattice structure within the emitter conditions approaching ideal evaporation may be realized. Emission from fused salts show an appreciable isotope effect. In the case of metallic emitters the positive ions which have been held in interstitial solution exhibit a preferential emission of the light isotope ions while those held in replacement solution show little if any effect.

The values for the abundance ratios which have just been presented may now be employed in estimating the atomic weights of these elements by the method recently described in detail for potassium.[7] The atomic weight of 39.094 obtained for potassium remains un-changed. With 1.00027 for the conversion factor from the physical to the chemical scale and -8.2 for the packing fraction, the atomic weight of rubidium comes out to be 85.46. This value compares favorably with 85.44 accepted by the committee on atomic weights and 85.48 recently obtained by Archibald, Hooley and Phillips.[8]

In estimating the atomic weight of lithium it is necessary to apply a correction for the isotope effect of free evaporation to the abundance ratio obtained from fresh filaments. Assuming this correction is initially that for ideal evaporation the abundance ratio becomes $11.60\sqrt{7/6}=12.52$. With this corrected value for the abundance ratio and 7.0146 and 6.0146 obtained by Bainbridge[9] for the isotope masses the atomic weight comes out to be 6.939. The most recent values for the isotope masses[10] of $Li^6=7.0180$ and $Li^6=6.0167$ lead to 6.942 for the atomic weight. Both these values are in close agreement with the accepted value of 6.940.

[6] F. W. Aston, *Mass-Spectra and Isotopes* (Edward Arnold & Co., London, 1933).
[7] A. Keith Brewer, J. Am. Chem. Soc. **58**, 370 (1936).

[8] Archibald, Hooley and Phillips, J. Am. Chem. Soc. **58**, 70 (1936).
[9] K. T. Bainbridge, Phys. Rev. **44**, 56 (1933).
[10] M. L. Oliphant, Nature **137**, 396 (1936).

Quantum-Mechanical Treatment of Helium Hydride Molecule-Ion HeH+

J. Y. BEACH, *Gates Chemical Laboratory, California Institute of Technology*
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Helium hydride molecule-ion has been treated by the variation method, including ionic and polarization terms in the variation function and varying the effective nuclear charge. The equilibrium internuclear distance is found to be $1.57a_0$. Fitting a parabola to the lower part of the best potential energy curve leads to a value of 0.43 megadyne/cm for the force constant and a value of 2800 cm^{-1} for the fundamental vibration frequency. The minimum energy obtained for the system is $-5.844W_H$, which, when subtracted from the best value for the energy of the helium atom using the same type of variation function, gives a value for the dissociation energy of 2.02 ev. The doubly charged ion, HeH^{++}, is found to be unstable.

SINGLY charged helium hydride molecule-ion has been known[1] for many years from mass spectroscopic investigations of helium hydrogen mixtures. Its position with respect to that of $H^2H^2H^{1+}$ in the mass spectrograph has been used to determine accurately the mass of the deuteron.[2] Spectroscopic work has not shown the existence of this ion.

The only previous quantum-mechanical discussion of HeH+ is a variation treatment made by Glockler and Fuller.[3] They consider two problems: (1) The interaction of a proton with an excited helium atom, the wave function for the electrons being $\psi_1=ae^{-\alpha r_1}$ and $\psi_2=(b+cr_2)e^{-\beta r_2}$; and (2) the interaction of a hydrogen atom with a singly ionized helium atom, the wave functions

[1] F. W. Aston, *Isotopes*, Both editions; T. R. Hogness and E. C. Lunn, Phys. Rev. **26**, 44 (1925).
[2] K. T. Bainbridge, Phys. Rev. **44**, 57 (1933).

[3] G. Glockler and D. L. Fuller, J. Chem. Phys. **1**, 886 (1933).

for the electrons being $\psi_1 = ae^{-\alpha r_{a1}}$ and $\psi_2 = be^{-\beta r_2}$. When in the first case α and β are put equal to 2 and 0.7, respectively, the interaction is repulsive at all distances. The functions ψ_1 and ψ_2 are the $1s$ and $2s$ hydrogen-like wave functions, the helium atom being approximately in the first excited state. In case two α and β are put equal to 2 and 1, the resulting potential energy curve has a minimum of 8.1 ev at $1.3a_0$. In this calculation the unsymmetrical Sugiura-type integral was neglected. As pointed out by Glockler and Fuller, including this integral will raise the energy by an undetermined amount.

The above calculation is not evidence for the existence of HeH$^+$. The dissociation energy, 8.1 ev, obtained by making the above approximation, is with respect to the dissociation products hydrogen atom and helium ion, while the difference in the ionization potentials of hydrogen and helium is 10.9 ev. Under these conditions the molecule would be unstable with respect to dissociation into a helium atom and a hydrogen ion. To prove the stability of the molecule it is necessary to show that for some intermediate internuclear distance the energy of the molecule is less than the energy of the helium atom.

The variational integral

$$W = \int \Psi^* H \Psi d\tau / \int \Psi^* \Psi d\tau$$

gives an upper limit for the energy of a system. Ψ is an approximate wave function. H is the Hamiltonian operator and in this case is

$$H = -\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{h^2}{8\pi^2 m}\nabla_2^2 - \frac{2e^2}{r_{a1}} - \frac{2e^2}{r_{a2}}$$
$$-\frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{r_{12}} + \frac{2e^2}{R}. \quad (1)$$

When a variation function of the form $\Psi = \sum_{n=1}^{m} c_n \psi_n$ is used, the condition that W be a minimum with respect to the constants c_n is that the determinantal equation $|H_{ij} - \Delta_{ij}W| = 0$ (Eq. (1)) be satisfied,[4] where $H_{ij} = \int \psi_i H \psi_j d\tau$ and $\Delta_{ij} = \int \psi_i \psi_j d\tau$. The approximate energy for the ground state

will be the lowest root of this equation. The constants, c_n, are obtained by solving the set of linear equations $\sum_{j=1}^{m} c_j(H_{ij} - \Delta_{ij}W)$, $i = 1, 2, \cdots m$. Most of the integrals required in evaluating H_{ij} and Δ_{ij} were used by Rosen[5] and Weinbaum[6] in discussing the hydrogen molecule. Dr. Weinbaum has not published his integrals but kindly placed them at my disposal. The integrals used in this calculation, not tabulated by Rosen,[5] are given in the appendix.

The variation functions used here are composed of the following functions:

$$a(1) = (Z^3/\pi a_0^3)^{\frac{1}{2}} e^{-Zr_{a1}/a_0},$$
$$b(1) = (Z^3/\pi a_0^3)^{\frac{1}{2}} e^{-Zr_{b1}/a_0}, \quad (2)$$
$$a'(1) = (Z^5/\pi a_0^5)^{\frac{1}{2}} r_{a1} \cos \theta_{a1} e^{-Zr_{a1}/a_0}$$

and the same functions for electron (2). Each function is normalized to unity. $a(1)$ is the ground state wave function for a hydrogenic atom of nuclear charge Z, and satisfies the equation

$$\left(-\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{Ze^2}{r_{a1}}\right)a(1) = -Z^2 W_H a(1)$$

where $W_H = (e^2/2a_0)$. $a'(1)$ is a first excited wave function for a hydrogenic atom of nuclear charge $2Z$ and satisfies the equation

$$\left(-\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{2Ze^2}{r_{a1}}\right)a'(1) = -Z^2 W_H a'(1).$$

This form of $a'(1)$ was used by Rosen[5] in introducing polarization into the hydrogen molecule calculation. It is very convenient as it leaves the exponents in $a(1)$ and $a'(1)$ identical making the calculation of integrals much simpler. In the present calculation the same effective nuclear charge, Z, is used in each term of the variation functions. This is done to eliminate the necessity of calculating the unsymmetrical Sugiura integral and other integrals. This procedure was adopted by Pauling[7] in treating the helium molecule-ion He$_2^+$.

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[4] See for example Pauling and Wilson, *Introduction to Quantum Mechanics*.

[5] N. Rosen, Phys. Rev. **38**, 2099 (1931).
[6] S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).
[7] Linus Pauling, J. Chem. Phys. **1**, 56 (1933).

It is evident that the stable state of the molecule is a singlet state so we shall require the variation function to be symmetric in the spatial coordinates of the two electrons (and anti-symmetric in the spin coordinates). In the following paragraphs we shall calculate the energy of the systems for several such variation functions. It will be found possible, by taking a linear combination of the lowest lying states for simple wave functions, to obtain a calculated value of the energy of the molecule that is lower than the experimental value for the helium atom.

1. NORMAL HELIUM ATOM AND PROTON

The most stable state for the system for a single wave function of the types we are considering, Eq. (2), is the state helium atom and proton. It will therefore be necessary, if the lowest value of the energy is desired, to include this state in the calculation. Taking as the electronic wave function of the system $\Psi = a(1)a(2)$, Eq. (1) for the energy becomes

$$W = \int \Psi^* H \Psi d\tau$$

$$= \left\{ 2Z^2 - 2Z \left[\frac{27}{8} - 2e^{-2\rho} \left(1 + \frac{1}{\rho} \right) \right] \right\} W_H,$$

where $\rho = ZR/a_0$. This interaction is repulsive at all distances and is shown by curve C, Fig. 1 for the case that $Z = 27/16$. When ρ equals infinity this expression becomes the familiar expression for the energy of a helium atom for hydrogen-like wave functions with variable effective nuclear charge, $W = (2Z^2 - 27Z/4)W_H$. This energy is a minimum when $Z = 27/16$ then $W = -5.695 W_H$. The experimental value and the value calculated by Hylleraas[8] for the helium atom is $-5.807 W_H$.

2. HYDROGEN ATOM AND HELIUM ION

The symmetric variation function,

$$\Psi = a(1)b(2) + a(2)b(1),$$

corresponds to an electron pair bond between the two atoms. The energy, is shown by curve B
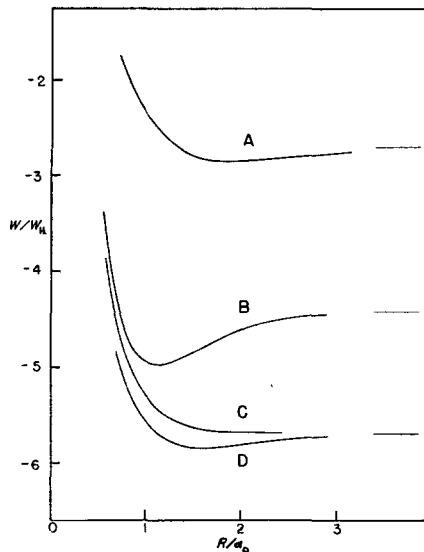
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[8] E. A. Hylleraas, Zeits. f. Physik 65, 209 (1930).

FIG. 1. Potential energy curves. A, $\Psi = a(1)a'(2) + a'(1)a(2)$; B, $\Psi = a(1)b(2) + b(1)a(2)$; C, $\Psi = a(1)a(2)$; D, $\Psi = a(1)a(2) + k_1(a(1)b(2) + b(1)a(2)) + k_2(a(1)a'(2) + a'(1)a(2))$.

in Fig. 1 for the case that $Z = 27/16 = 1.69$. This energy can be minimized with respect to Z for each value of ρ. When this is done a value of W only 0.04 percent lower than that for $Z = 27/16$ is obtained, the effective charge then being equal to 1.72. When ρ equals infinity the energy becomes $W = (2Z^2 - 6Z)W_H$ which is a minimum when $Z = 3/2$ and $W = -4.5 W_H$. The correct value for the sum of the energies of a hydrogen atom and a helium ion is $-5 W_H$. This discrepancy is due to the fact that we have taken the same effective charge on the two atoms.

This calculation is the same as that made by Glockler and Fuller except that here the same effective nuclear charge is used on both atoms and consequently all the integrals can be calculated. This curve indicates the existence of a metastable attractive state for HeH+.

3. EXCITED HELIUM ATOM AND PROTON

The variation function

$$\Psi = a(1)a'(2) + a'(1)a(2),$$

in conjunction with $a(1)a(2)$, will be used to represent a polarized helium atom. The potential energy corresponding to the variation function $a'(1)a(2) + a(1)a'(2)$ alone is shown by curve A in Fig. 1 for the case that $Z = 27/16$. This curve

is higher than that for the corresponding triplet state, $a'(1)a(2)-a(1)a'(2)$, but the triplet state does not combine with the more important singlet states, nondiagonal matrix elements being equal to zero, so cannot be used. When the energy for the singlet state is minimized with respect to the effective nuclear charge, the energy curve is lowered by about $0.35W_H$, the corresponding value of the effective nuclear charge at the minimum being 1.26.

4. COMBINATION OF §§1 AND 3

Using $\Psi=a(1)a(2)+k(a'(1)a(2)+a(1)a'(2))$ as a variation function, the energy appears as a root of a quadratic secular equation, Eq. (1). The result of solving the equation is shown by curve B in Fig. 2 for the case that the effective nuclear charge is 27/16. It is not possible to minimize easily with respect to the effective nuclear charge so the quadratic is merely solved for several values of the effective charge. It is found that the energy is worse for any value of the effective charge much different than 27/16. The minimum energy for this curve is $W=-5.750$ at $R=1.60a_0$. The normalized

FIG. 2. Potential energy curves. A, $\Psi=a(1)a(2)$; B, $\Psi=a(1)a(2)+k(a(1)a'(2)+a'(1)a(2))$; C, $\Psi=a(1)a(2)+k(a(1)b(2)+b(1)a(2))$; D, $\Psi=a(1)a(2)+k_1(a(1)b(2)+a(2)b(1))+k_2(a(1)a'(2)+a'(1)a(2))$. The dashed line represents the experimental value for the energy of the normal helium atom.

function is

$$\Psi=0.99a(1)a(2)+0.13(a(1)a(2)+a(1)a'(2)).$$

The best value of the energy of the system at R equals infinity for this type of variation function is $-5.695W_H$, giving for the dissociation energy of the molecule $0.055W_H$ or 0.74 ev. The stabilization resulting from the use of this variation function can be attributed to a polarization of the helium atom.

5. COMBINATION OF §§1 AND 2

The energy corresponding to the variation function $\Psi=a(1)a(2)+k(a(1)b(2)+b(1)a(2))$ is shown in curve C in Fig. 2 for the case that $Z=27/16$. The normalized function is $0.97a(1)a(2)+0.24(a(1)b(2)+b(1)a(2))$. It is not easy to minimize with respect to the effective charge so again the quadratic secular equation is solved for several values of the effective charge, the calculated energy being much higher when the effective charge is much different than 27/16. The lowest value obtained is $W=-5.805$ at $R=1.60a_0$, which, when subtracted from the value $-5.695W_H$ for the helium atom, gives a dissociation energy of $0.110W_H$ or 1.49 ev. The form of the variation function suggests that this is due to the partial formation of a covalent bond.

6. COMBINATION OF §§1, 2 AND 3

The best variation function used is of the form $\Psi=a(1)a(2)+k_1(a'(1)a(2)+a(1)a'(2))+k_2(a(1)b(2)+b(1)a(2))$. On the basis of calculations 5 and 6, in which it was found that the best value of the effective charge was not far from 27/16, calculations were made only for the case that $Z=27/16$. The energy appears as a root of a cubic secular equation and is shown by curve D, Fig. 2 and by curve D, Fig. 1. The normalized function is $\Psi=0.97a(1)a(2)+0.10(a'(1)a(2)+a(1)a'(2))+0.20(a(1)b(2)+b(1)a(2))$. The lowest energy obtained is $-5.844W_H$ at $R=1.57a_0$. This, when subtracted from the helium atom value of $-5.695W_H$, gives a value for the dissociation energy of $0.149W_H$ or 2.02 ev. This dissociation energy is obtained by using the energy of the helium atom calculated from a variation function of the same type as the one used for the undissociated molecule. This pro-
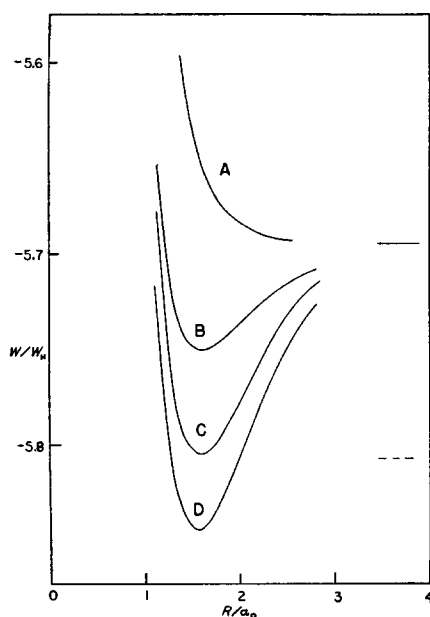
cedure assumes that the error in the energy is the same at the equilibrium distance and at infinity. A lower limit for the dissociation energy is obtained by subtracting the minimum energy for the molecule from the experimental value, $-5.807W_H$, for the helium atom. The result is $0.037W_H$ or 0.50 ev. This positive result proves conclusively that the molecule is stable. The value 2.02 ev, however, is probably much closer to the actual value of the dissociation energy.

Fitting a parabola to the bottom part of the curve leads to a value for the force constant of 0.43 megadyne/cm and a fundamental vibration frequency of 2800 cm^{-1}.

THE MOLECULE-ION HeH^{++}

Doubly charged helium hydride molecule-ion was treated by the same type of variation function, $\Psi = a(1) + k_1 b(1) + k_2 a'(1)$. The resulting potential energy curve shows no minimum and differs only slightly from $-4W_H + e^2/R$. The one electron bond between the two atoms is not sufficiently strong to overcome the Coulomb repulsion. Another molecule in which there is Coulomb repulsion between the atoms, the helium molecule ion, He$_2^{++}$, has been treated by Pauling[7] including ionic terms in the variation

function. In this case the electron pair bond formed is strong enough to overcome the Coulomb repulsion of the two atoms, there being a minimum in the potential energy curve. The instability of HeH^{++} is due to the lack of degeneracy of the two states He$^+$H$^+$ and He^{++}H.

DISCUSSION

From a comparison of curves B and C, Fig. 2, it is seen that the introduction of polarization into the variation function is about half as effective in stabilizing the molecule as the introduction of the covalent bond. It is therefore qualitatively correct to say that two-thirds of the stabilization is due to the formation of a covalent bond and one-third is due to polarization of the helium atom. The strength of the bond, 2.02 ev, is surprisingly great in view of the small coefficients of the covalent bond term and the polarization term, 0.20 and 0.10, in the variation function given in section 6. It is roughly half as strong as the bond in the hydrogen molecule, 4.10 ev, calculated[6] from the same type of variation function.

I wish to thank Professor Linus Pauling for making many valuable suggestions during the preparation of this paper.

APPENDIX

The simpler integrals are omitted. The integrals, $M_{001, 0}$ and $M_{010, 0}$, are evaluated by the use of the Neumann expansion in confocal elliptic coordinates. The functions $H(m, n, \rho)$ and $S(m, n, \rho)$ are defined by Rosen.[5]

$$M_{000, 0} = \int \frac{a^2(1)a(2)b(2)}{r_{12}} dv_1 dv_2 = \frac{Z}{a_0} \left\{ e^{-\rho}\left(\frac{5}{16\rho} + \frac{1}{8} + \rho\right) - e^{-3\rho}\left(\frac{5}{16\rho} + \frac{1}{8}\right) \right\}$$

$$M_{001, 0} = \int \frac{a^2(1)a'(2)b(2)}{r_{12}} dv_1 dv_2 = \frac{\rho}{2} M_{000, 0} + \frac{Z}{a_0}\frac{\rho^6}{480} [A\{-225H(5, 4, \rho) + 135H(5, 2, \rho) + 195H(3, 4, \rho) - 117H(3, 2, \rho)$$

$$+ 225S(3, 5, \rho) - 60S(1, 5, \rho) + 225S(4, 4, \rho) - 120S(2, 4, \rho) - 195S(3, 3, \rho) + 72S(1, 3, \rho) - 135S(4, 2, \rho)$$

$$+ 72S(2, 2, \rho)\} + B\{375H(5, 4, \rho) - 225H(5, 2, \rho) - 195H(1, 4, \rho) + 117H(1, 2, \rho) - 375S(3, 5, \rho) + 100S(1, 5, \rho)$$

$$- 375S(4, 4, \rho) - 125S(2, 4, \rho) + 120S(0, 4, \rho) + 225S(4, 2, \rho) + 75S(2, 2, \rho) - 72S(0, 2, \rho) + 195S(3, 1, \rho)$$

$$- 72S(1, 1, \rho)\} + C\{-375H(3, 4, \rho) + 225H(1, 4, \rho) + 225H(3, 2, \rho) - 135H(1, 2, \rho) + 375S(2, 4, \rho) - 100S(0, 4, \rho)$$

$$+ 375S(3, 3, \rho) - 225S(3, 1, \rho) - 100S(1, 3, \rho) - 225S(2, 2, \rho) + 60S(0, 2, \rho) + 60S(1, 1, \rho)\}]$$

$$M_{010, 0} = \int \frac{a(1)a'(1)a(2)b(2)}{r_{12}} dv_1 dv_2 = \frac{\rho}{2} M_{000, 0} + \frac{Z}{a_0}\frac{\rho^6}{96} [A\{9H(5, 2, \rho) - 3H(5, 0, \rho) + 9H(3, 2, \rho) - 3H(3, 0, \rho) - 9S(4, 2, \rho)$$

$$+ 3S(4, 0, \rho) - 9S(1, 5, \rho) + 3S(2, 0, \rho)\} + B\{-27H(5, 2, \rho) + 9H(5, 0, \rho) - 9H(1, 2, \rho) + 3H(1, 0, \rho)$$

$$+ 27S(4, 2, \rho) - 9S(4, 0, \rho) + 9S(2, 2, \rho) - 3S(2, 0, \rho) + 27S(1, 5, \rho) - 3S(1, 1, \rho)\} + C\{27H(3, 2, \rho) - 9H(3, 0, \rho)$$

$$- 9H(1, 2, \rho) + 3H(1, 0, \rho) - 27S(2, 2, \rho) + 9S(2, 0, \rho) - 27S(1, 3, \rho) + 9S(1, 1, \rho)\}],$$

where
$$A = \int_{-1}^{+1} xe^{-\rho x}dx, \quad B = \int_{-1}^{+1} x^3 e^{-\rho x}dx, \quad \text{and} \quad C = \int_{-1}^{+1} x^5 e^{-\rho x}dx.$$