The Normal State of the Helium Molecule Ion, He2 +

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The Normal State of the Helium Molecule Ion, He₂⁺

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A variation function constructed of hydrogen-like $1s$ functions with different values of the effective nuclear charges for He: and He.⁺ is used in the treatment of the normal state of the helium molecule-ion. The treatment leads to the values $D_e = 2.22$ e.v. and $r_e = 1.097$A for the dissociation energy and the internuclear distance, in good agreement with the experimental values.

THE normal state of the helium molecule-ion, He₂⁺, was treated by Pauling[1] who used a simple wave function constructed of hydrogen-like $1s$ functions $\psi = Z^{3/2}\pi^{1/2}e^{-\xi/2}$ with $\xi = 2Zr_A$ and a similar expression in r_B for φ. The energy expression was minimized with respect to the effective nuclear charge Z and good agreement with the experimental values was obtained. In this treatment the same effective nuclear charges were assumed for the helium atom and the helium ion, the same function being used in calculating energies at small distances and at infinity. Though this does not provide a very good approximation at infinity we might expect the errors to be about the same as at $r = r_e$ and as a matter of fact the dissociation energy, being the difference of the energy values at infinity and at r_e, came out in a very good agreement with the experimental value.

It should be expected that a much closer approximation to the wave function would result from the use of different effective nuclear charges for the helium atom and the helium ion, in which case we would have at infinity a correct wave function for He⁺ and a reasonably good approximation (the screening-constant type) for He, and we might consider the approximation at $r = r_e$ to be quite good also. In any case the repetition of the calculation with different effective nuclear charges for the atom and for the ion will provide us with some basis of judgment as to the reliability of such a treatment.

For this purpose two antisymmetric functions ψ_I and ψ_{II} can be constructed by Slater's method which would be represented by the following scheme:

	ψ	φ	ξ	η
I	$\pm$			$+$
II		$\pm$	$+$	

[1] Linus Pauling, J. Chem. Phys. **1**, 56 (1933).

where ψ and φ refer to the helium atom and ξ and η to the helium ion, with the effective nuclear charges Z for the atom and $Z' = \epsilon Z$ for the ion, ϵ thus representing the ratio of the effective nuclear charge of the ion to that of the atom.

The wave equation for a hydrogen-like atom, in a system of units with unit of length $a_0 = 0.52845$A. unit of charge e and unit of energy $e^2/a_0 = 27.06$ volt electrons, is

$$\nabla^2\psi + 2(W - V)\psi = 0, \tag{1}$$

which can be rewritten as

$$-\tfrac{1}{2}\nabla^2\psi + V\psi = W\psi, \tag{1a}$$

where $W = -Z^2/2$. The general wave equation may be written as

$$H\psi = W\psi, \tag{2}$$

with

$$H = -\tfrac{1}{2}\nabla^2 + V \quad \text{and} \quad V = \Sigma\Sigma(Z_iZ_j/r_{ij}), \tag{3}$$

the Hamiltonian function for the case of the helium-molecule-ion being

$$H = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - 2/r_{A1} - 2/r_{A2}$$
$$- 2/r_{A3} - 2/r_{B1} - 2/r_{B2} - 2/r_{B3}$$
$$+ 1/r_{12} + 1/r_{13} + 1/r_{23} + 4/r_{AB}. \tag{4}$$

The variational integral

$$E = \int\psi^*H\psi d\tau / \int\psi^*\psi d\tau$$

for our wave function takes the form

$$E = \int H(\psi_I - \psi_{II})^2 d\tau / \int (\psi_I - \psi_{II})^2 d\tau$$
$$= H_{I\,I} - H_{I\,II}/d_{I\,I} - d_{I\,II} \tag{5}$$

where

$$H_{I\,I} = (\psi_1\psi_2\eta_3|H|\psi_1\psi_2\eta_3) - (\psi_1\psi_2\eta_3|H|\eta_1\psi_2\psi_3) \tag{6}$$

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and

$$H_{I\,II} = (\psi_1\psi_2\eta_3|H|\varphi_1\varphi_2\xi_3) - (\psi_1\psi_2\eta_3|H|\xi_1\varphi_2\varphi_3). \quad (6a)$$

The different integrals occurring in subsequent calculations will be indicated by letters I or F ($I = ZF$) with subscripts. Letters s and t will be used for integrals of the type $\int \psi\varphi d\tau$. A table of all integrals used will be found in the appendix.

Leaving out for the present the term $4/r_{AB}$ in the Hamiltonian we can set up the following expressions:

$$\int \xi_1 H_1 \xi_1 d\tau_1 = \epsilon^2 Z^2/2 - 2\epsilon Z(1 + F_{1\epsilon}) = A$$

$$\int \xi_1 H_1 \eta_1 d\tau_1 = \epsilon^2 Z^2(F_{2\epsilon} - s_\epsilon/2) - 4\epsilon Z F_{2\epsilon} = B$$

$$\int \psi_1 H_1 \psi_1 d\tau_1 = Z^2/2 - 2Z(1 + F_1) = C$$

$$\int \psi_1 H_1 \varphi_1 d\tau_1 = Z^2(F_2 - s/2) - 4Z F_2 = D$$

$$\int \psi_1 H_1 \xi_1 d\tau_1 = -\epsilon^2 Z^2 t_0/2 + \epsilon Z^2 F_7$$
$$\qquad\qquad - 2Z(F_7 + F_8) = E$$

$$\int \xi_1 H_1 \psi_1 d\tau_1 = -Z^2 t_0/2 + Z^2 F_7 \qquad\qquad (7)$$
$$\qquad\qquad - 2Z(F_7 + F_8) = E'$$

$$\int \varphi_1 H_1 \xi_1 d\tau_1 = -\epsilon^2 Z^2 t_0/2 + \epsilon Z^2 F_9$$
$$\qquad\qquad - 2Z(F_9 + F_{10}) = K$$

$$\int \xi_1 H_1 \varphi_1 d\tau_1 = -Z^2 t/2 + Z^2 F_{10}$$
$$\qquad\qquad - 2Z(F_9 + F_{10}) = K'.$$

Then, in terms of A and B, we have

$$H_{I\,I} = A + (2 - t^2)C - t(K + K') + \tfrac{5}{8}Z$$
$$\qquad\qquad + 2Z F_{11} - 2Zt F_{12} + Z F_{13}$$
$$H_{I\,II} = s^2 B + (2ss_\epsilon - t_0^2)D - st_0(E + E') + Zs_\epsilon F_6 \qquad (8)$$
$$\qquad\qquad + 2Zs F_{14} - 2Zt_0 F_{15} - Zs F_{16}$$

$$d_{I\,I} = 1 - t^2$$

$$d_{I\,II} = s^2 s_\epsilon - s t_0^2.$$

Now we can write the energy integral, including

TABLE I.

	E	D_e(e.v.)	$r_e(A)$	Z	Z'
This paper	−4.930	2.22	1.097	1.734	2.029
Pauling	−4.865	2.47	1.085	1.833	1.833
Experimental[2]	−5.00	2.5	1.090		

[2] W. Weizel, *Bandenspektren* (Akad. Verlagsges. m.b.Z., Leipzig, 1931), pp. 255, 270.

the term $4/r_{AB}$, as

$$E = \frac{4}{r_{AB}} + \frac{H_{I\,I} - H_{I\,II}}{d_{I\,I} - d_{I\,II}} = \frac{4Z}{\rho} + \frac{2Z^2 + \mu Z}{\nu} \quad (9)$$

where

$$\lambda = 1 + \epsilon^2/2 + \epsilon^2 t^2/2 + s^2 s_\epsilon(1 + \epsilon^2/2)$$
$$\quad - (st_0^2/2)(\epsilon^2 + 2) - (2ss_\epsilon - t_0^2)F_2 - \epsilon^2 s^2 F_{2\epsilon}$$
$$\quad + (\epsilon + 1)st_0 F_7 - t(\epsilon F_9 + F_{10}) \qquad (10)$$

$$\mu = -27/8 + 2(t^2 - \epsilon) - 2(2 - t^2)F_1 - 2\epsilon F_{1\epsilon}$$
$$\quad + 4(2ss_\epsilon - t_0^2)F_2 + 4\epsilon s^2 F_{2\epsilon} - s_\epsilon F_6 +$$
$$\quad - 4st_0(F_7 + F_8) + 4t(F_9 + F_{10}) + 2F_{11}$$
$$\quad - 2t F_{12} - F_{13} - 2s F_{14} + 2t_0 F_{15} + s F_{16} \qquad (10a)$$

and
$$\nu = 1 - t^2 - s^2 s_\epsilon + st_0^2. \qquad (10b)$$

Minimizing (9) with respect to Z we obtain

$$Z_{min} = -(\nu/2\lambda)(4/\rho + \mu/\nu), \qquad (11)$$

and substituting this value of Z in (9) we have

$$E_{Z=min} = -(\nu/4\lambda)(4/\rho + \mu/\nu)^2. \qquad (12)$$

Expression (12) is a function of ρ and ϵ and the best set of values of ρ and ϵ, corresponding to a minimum for E, was obtained by direct substitution of different values. The procedure employed was as follows: first for a given value of ρ the best value of ϵ was obtained; then ρ was varied to get the best value of ρ for the value of ϵ obtained in the previous step; then ϵ was varied again, and so on, until the variation of neither ϵ or ρ would result in a lower value of E. However, as the numerical calculations involved are very laborious and the variations in energy very small, ρ was calculated only to two significant figures and ϵ to three. The values obtained are $\rho = 3.6$, $\epsilon = 1.17$ and $E = 4.930$, with $Z = 1.734$ and $Z' = 2.029$ at the equilibrium distance. At $r = \infty$ the corresponding values are $\epsilon = 32/27 = 1.185$ and $E = 4.848$, with $Z = 27/16 = 1.6875$ and $Z' = 2.000$. This gives for the dissociation energy the value $D_e = 2.22$ e.v. and for the internuclear distance $r_e = 1.097A$, in very good agreement with the experimental values. Table I shows the comparison of these values with Pauling's and with the experimental results.

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Appendix

Most of the integrals occurring in this work can be calculated without much trouble. I_{14} required a somewhat laborious calculation by Sugiura's[3] method and I_{13} had to be expressed as a series which, however, converges very rapidly.

The functions H and S by means of which integrals I_6 and I_{13} are expressed have been discussed by several authors.[4, 5]

The integrals bearing the subscript ϵ are obtained from the integrals without this subscript by substituting $\epsilon\rho$ instead of ρ wherever ρ occurs.

$$s = \int \psi_1 \varphi_1 d\tau_1 = e^{-\rho}\left(1 + \rho + \tfrac{1}{3}\rho^2\right),$$

$$t_0 = \int \psi_1 \xi_1 d\tau_1 = \frac{8\epsilon^{3/2}}{(1+\epsilon)^3},$$

$$t = \int \psi_1 \eta_1 d\tau_1 = \frac{8\epsilon^{3/2}}{(1-\epsilon^2)^2}\left[\epsilon e^{-\rho}\left(1 + \frac{4}{\rho(1-\epsilon^2)}\right) + e^{-\epsilon\rho}\left(1 - \frac{4\epsilon}{\rho(1-\epsilon^2)}\right)\right],$$

$$F_1 = \frac{1}{Z}\int \frac{\psi_1^2}{r_{B1}}d\tau = \frac{1}{\rho} - e^{-2\rho}\left(1 + \frac{1}{\rho}\right),$$

$$F_2 = \frac{1}{Z}\int \frac{\psi_1 \varphi_1}{r_{A1}}d\tau = e^{-\rho}(1+\rho),$$

$$F_6 = \frac{1}{Z}\int \frac{\psi_1 \varphi_1 \psi_2 \varphi_2}{r_{12}}d\tau_1 d\tau_2 = \frac{\rho^5}{15}\left[9H(2, 2, \rho) - 6H(2, 0, \rho) + H(0, 0, \rho) - 3S(1, 2, \rho) + S(1, 0, \rho)\right],$$

$$F_7 = \frac{1}{Z}\int \frac{\psi_1 \xi_1}{r_{A1}}d\tau_1 = \frac{4\epsilon^{3/2}}{(1+\epsilon)^2},$$

$$F_8 = \frac{1}{Z}\int \frac{\psi_1 \xi_1}{r_{B1}}d\tau_1 = \frac{4\epsilon^{3/2}}{\rho(1+\epsilon)^3}\{2 - e^{-(\epsilon+1)\rho}[(1+\epsilon)\rho + 2]\},$$

$$F_9 = \frac{1}{Z}\int \frac{\psi_1 \eta_1}{r_{B1}}d\tau_1 = \frac{4\epsilon^{3/2}}{\rho(1-\epsilon^2)^2}\{2e^{-\epsilon\rho} - e^{-\rho}[(1-\epsilon^2)\rho + 2]\},$$

$$F_{10} = \frac{1}{Z}\int \frac{\psi_1 \eta_1}{r_{A1}}d\tau_1 = \frac{4\epsilon^{3/2}}{\rho(1-\epsilon^2)^2}\{2\epsilon e^{-\rho} + e^{-\epsilon\rho}[(1-\epsilon^2)\rho - 2\epsilon]\},$$

$$F_{11} = \frac{1}{Z}\int \frac{\psi_1^2 \eta_2^2}{r_{12}}d\tau_1 d\tau_2 = \frac{1}{\rho} + \epsilon^3\left\{\frac{\epsilon e^{-2\rho}}{(\epsilon^2-1)^2}\left[-1 - \frac{\epsilon^2-3}{(\epsilon^2-1)\rho}\right]\right.$$
$$\left. + e^{-2\epsilon\rho}\left[-\frac{1}{\epsilon^2}\left(1 + \frac{1}{\epsilon\rho}\right) + \frac{1}{(\epsilon^2-1)^2}\left(\epsilon^2 - 2 + \frac{\epsilon(\epsilon^2-3)}{(\epsilon^2-1)\rho}\right)\right]\right\},$$

$$F_{12} = \frac{1}{Z}\int \frac{\psi_1^2 \psi_2 \eta_2}{r_{12}}d\tau_1 d\tau_2 = \frac{8\epsilon^{5/2}e^{-\rho}}{\rho(1-\epsilon^2)^2} + 4\epsilon^{3/2}e^{-\epsilon\rho}\left[\frac{1}{1-\epsilon^2} - \frac{15-\epsilon^2}{(9-\epsilon^2)^2} - \frac{2\epsilon}{\rho}\left(\frac{1}{(1-\epsilon^2)^2} + \frac{\epsilon^2-21}{(9-\epsilon^2)^3}\right)\right]$$
$$+ \frac{8\epsilon^{5/2}e^{-3\rho}}{(9-\epsilon^2)^2}\left(-1 + \frac{\epsilon^2-21}{\rho}\right),$$

[3] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).
[4] N. Rosen, Phys. Rev. **38**, 2099 (1931).

[5] C. Zener and V. Guillemin, Phys. Rev. **34**, 999 (1929), etc.

$$F_{13} = \frac{1}{Z}\int \frac{\psi_1\eta_1\psi_2\eta_2}{r_{12}}d\tau_1 d\tau_2 = \epsilon^3\rho^5\left\{\frac{1}{15}\left[9II(2, 2, \alpha\rho) - 6II(2, 0, \alpha\rho) + II(0, 0, \alpha\rho) - 3S(1, 2, \alpha\rho)\right.\right.$$

$$+ S(1, 0, \alpha\rho)\Big] + \frac{(\epsilon-1)^2\rho^2}{840}\big[7II(4, 0, \alpha\rho) - 47II(2, 0, \alpha\rho) + 9II(0, 0, \alpha\rho) - 21II(4, 2, \alpha\rho)$$

$$+ 60II(2, 2, \alpha\rho) + 21S(1, 4, \alpha\rho) + 21S(3, 2, \alpha\rho) - 43S(1, 2, \alpha\rho) - 7S(3, 0, \alpha\rho) + 12S(1, 0, \alpha\rho)$$

$$+ 50II(3, 3, \alpha\rho) - 60II(3, 1, \alpha\rho) + 18II(1, 1, \alpha\rho) - 100S(2, 3, \alpha\rho) + 50S(0, 3, \alpha\rho) + 60S(2, 1, \alpha\rho)$$

$$- 30S(0, 1, \alpha\rho)\Big] + \frac{(\epsilon-1)^4\rho^4}{192}\left[\frac{1}{315}\big[-27II(4, 2, \alpha\rho) + 9II(4, 0, \alpha\rho) + 63II(2, 2, \alpha\rho) - 51II(2, 0, \alpha\rho)\right.$$

$$+ 10II(0, 0, \alpha\rho) + 27S(1, 4, \alpha\rho) - 54S(1, 2, \alpha\rho) + 15S(1, 0, \alpha\rho) + 27S(3, 2, \alpha\rho) - 9S(3, 0, \alpha\rho)\Big]$$

$$+ \frac{2}{4725}\big[-675II(5, 3, \alpha\rho) + 2100II(3, 3, \alpha\rho) + 405II(5, 1, \alpha\rho) - 2385II(3, 1, \alpha\rho) + 675II(1, 1, \alpha\rho)$$

$$- 180S(0, 5, \alpha\rho) + 675S(2, 5, \alpha\rho) + 1642S(0, 3, \alpha\rho) - 3975S(2, 3, \alpha\rho) + 675S(4, 3, \alpha\rho)$$

$$- 1050S(0, 1, \alpha\rho) + 2358S(2, 1, \alpha\rho) - 405S(4, 1, \alpha\rho)\big] + \frac{1}{2205}\big[6321II(4, 4, \alpha\rho)$$

$$- 14805II(4, 2, \alpha\rho) + 3465II(4, 0, \alpha\rho) + 9075II(2, 2, \alpha\rho) - 4545II(2, 0, \alpha\rho) - 621II(0, 0, \alpha\rho)$$

$$+ 10591S(1, 4, \alpha\rho) - 12642S(3, 4, \alpha\rho) - 12810S(1, 2, \alpha\rho) + 14535S(3, 2, \alpha\rho) + 2949S(1, 0, \alpha\rho)$$

$$\left.\left.- 3465S(3, 0, \alpha\rho)\big]\right] + \cdots\right\} \quad \text{where} \quad \alpha = \frac{1+\epsilon}{2},$$

$$F_{14} = \frac{1}{Z}\int \frac{\psi_1\varphi_1\xi_2\eta_2}{r_{12}}d\tau_1 d\tau_2 = \frac{1}{5}\left\{\epsilon e^{-(\epsilon+1)\rho}\left(-\frac{\rho^3}{3} - \frac{6\epsilon^3 + 8\epsilon + 4}{3\epsilon(\epsilon+1)}\rho^2 - \frac{6\epsilon^2(\epsilon^2 + \epsilon + 1) + 3\epsilon + 2}{\epsilon^2(\epsilon+1)^2}\rho\right.\right.$$

$$+ \frac{6\epsilon^5 + 6\epsilon^4 - 11\epsilon^3 + 10\epsilon^2 + 15\epsilon - 1}{\epsilon^3(\epsilon+1)^3}\bigg) + \frac{6}{\rho}\bigg[ss_\epsilon\left(C + \log(2\rho) - \log\frac{\epsilon+1}{\epsilon}\right)$$

$$\left.\left.- \big[s_\epsilon s' Ei(-2\rho) + ss_\epsilon' Ei(-2\epsilon\rho)\big] + s's_\epsilon' Ei[-2(\epsilon+1)\rho]\bigg]\right\},$$

$$F_{15} = \frac{1}{Z}\int \frac{\psi_1\xi_1\psi_2\varphi_2}{r_{12}}d\tau_1 d\tau_2 = \frac{8\epsilon^{3/2}e^{-\rho}}{(1+\epsilon)^3}(\rho+1)$$

$$+ \frac{32\epsilon^{3/2}}{(1+\epsilon)^4(3+\epsilon)^2}\left[e^{-\rho}\left(-2\epsilon - 5 + \frac{6\epsilon+14}{(\epsilon+1)(\epsilon+3)\rho}\right) - e^{-(2+\epsilon)\rho}\left(1 + \frac{6\epsilon+14}{(\epsilon+1)(\epsilon+3)\rho}\right)\right],$$

$$F_{16} = \frac{1}{Z}\int \frac{\psi_1\xi_1\varphi_2\eta_2}{r_{12}}d\tau_1 d\tau_2 = \frac{64\epsilon^3}{(1+\epsilon^6)\rho} - \epsilon^3 e^{-(\epsilon+1)\rho}\left[\frac{64}{(1+\epsilon)^6\rho} + \frac{44}{(1+5)^5} + \frac{12\rho}{(1+\epsilon)^4} + \frac{4\rho^2}{3(1+\epsilon)^3}\right].$$