The Normal State of the Helium Molecule-Ions He₂⁺ and He₂⁺⁺

Linus Pauling, *Gates Chemical Laboratory, California Institute of Technology*

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With the use of wave functions constructed from hydrogen-like single-electron functions with an effective nuclear charge Z, the application of the variation method of treating the wave equation for the normal state of He₂⁺, involving a three-electron bond, leads to the values $Z = 1.833$, $r_0 = 1.085A$, $D_e = 2.47$ v.e., and $\omega_0 =$ approximately 1950 cm⁻¹. The experimentally determined values (from the He₂ spectrum) are $r_0 = 1.090A$, $D_e = 2.5$ v.e., and $\omega_{\frac{1}{2}} = 1628$ cm⁻¹. A similar discussion of He₂⁺⁺, with a covalent-plus-ionic wave function, shows that the energy curve has a minimum at $r_0 = 0.75A$, $\omega_0 =$ approximately 3200 cm⁻¹, with a maximum 1.4 v.e. higher at about 1.1A. This configuration could act as the core for excited states of He₂⁺ and doubly-excited states of He₂, some of which would be capable of existence with either one of two moments of inertia, one corresponding to $r_0 = 0.75A$ and the other to about the same values of r_0 as for the analogous states in excited H₂⁺ or doubly-excited H₂.

The Normal State of He₂⁺

IT has been pointed out[1] that the degeneracy represented by the two symbols He: ·He⁺ and He·⁺ : He, in which each dot represents a 1s electron, would lead to attraction and the formation of a bond between the two atoms, which may be called a three-electron bond; and it was suggested that as a rule such a bond should be about as strong as a one-electron bond, such as that in H₂⁺, and weaker than an electron-pair bond, as in H₂. The following wave-mechanical treatment of the ion He₂⁺ was made to verify (or disprove) these statements. The treatment used is closely analogous to that applied to the hydrogen molecule by Heitler and London,[2] Sugiura,[3] and Wang,[4] and to the hydrogen molecule-ion by Pauling[5] and Finkelstein and Horowitz.[6] In these cases the equilibrium internuclear distances obtained agree with experiment to within a few percent, and the dissociation energies to within about 25 percent; similar agreement can hence be expected for the helium molecule-ion calculations. The integrals which occur in the calculations are all well known, being given, for example, in reference 5, so that it has

seemed unnecessary to give explicit expressions for the energy integrals discussed in the following pages.

With $a_0 = 0.529A$, e, and $e^2/a_0 = 27.06$ v.e. as units of length, electrical charge, and energy, Schrödinger's equation becomes $\nabla^2\psi + 2(W - V)\psi = 0$, with $V = \Sigma z_i z_j / r_{ij}$, in which $z = -1$ for an electron, 2 for a helium nucleus, and the summation includes each pair of charges once. The value of the energy integral $\int \Psi^* H \Psi d\tau / \int \Psi^* \Psi d\tau$, with $H = -\frac{1}{2}\nabla^2 + V$, for an arbitrary function Ψ is known to be greater than or equal to the energy W_0 of the lowest state of the system.

A simple wave function for the system of two helium nuclei A and B and three electrons 1, 2, and 3 can be 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, by assuming that each electron interacts only with one nucleus. The two antisymmetric functions Ψ_I and Ψ_{II}, represented by the scheme

	ψ	φ	Σm_s		
I	$+-$	$+$	$+\frac{1}{2}$	He :	·He⁺
II	$+$	$+-$	$+\frac{1}{2}$	He ·⁺	: He

can then be constructed by Slater's method,[7] as well as two other functions with $\Sigma m_s = -\frac{1}{2}$ which do not combine with these, and which give rise to the other components of the doublet levels. Because of the identity of the nuclei the nuclear-symmetric and nuclear-antisymmetric functions $\Psi_S = \Psi_I + \Psi_{II}$ and $\Psi_A = \Psi_I - \Psi_{II}$ provide better

[1] L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

[2] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[3] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

[4] S. C. Wang, Phys. Rev. **31**, 579 (1928).

[5] Linus Pauling, Chem. Rev. **5**, 173 (1928).

[6] B. N. Finkelstein and G. E. Horowitz, Zeits. f. Physik **48**, 118 (1928).

[7] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

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approximations to the correct wave functions than do Ψ_I and Ψ_{II} individually. The energy integral for these functions is

$$E = (H_{I\ I} \pm H_{I\ II})/(d_{I\ I} \pm d_{I\ II}),$$

with

$$H_{I\ I} = \int \psi(1)\psi(2)\varphi(3)H\psi(1)\psi(2)\varphi(3)d\tau$$
$$- \int \psi(1)\psi(2)\varphi(3)H\varphi(1)\psi(2)\psi(3)d\tau$$
$$H_{I\ II} = \int \psi(1)\psi(2)\varphi(3)H\psi(1)\varphi(2)\varphi(3)d\tau$$
$$- \int \psi(1)\psi(2)\varphi(3)H\varphi(1)\varphi(2)\psi(3)d\tau,$$

and with similar expressions for the d's, with 1 in place of H.

On placing Z equal to 2, there are obtained the curves shown in Fig. 1 representing the energy
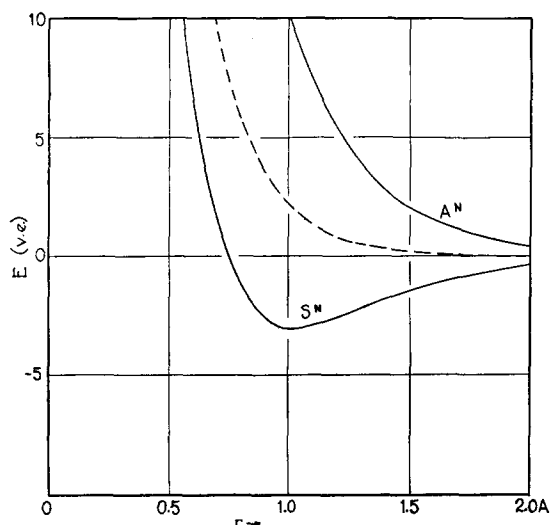

FIG. 1. Energy curves for attractive and repulsive states of He_2^+. The dashed curve corresponds to a non-existent state, resonance between He : $\cdot He^+$ and He$\cdot^+$: He being excluded.

as a function of r, the internuclear distance, the energy at $r = \infty$ being taken as zero. As in Heitler and London's treatment of the interaction of two normal hydrogen atoms, the nuclear-antisymmetric state does not lead to the formation of a stable molecule, the forces between the atoms being repulsive at all distances. The nuclear-symmetric state gives a potential function with a pronounced minimum at $r_0 = 1.01A$, with a dissociation energy of 2.9 v.e.

In Fig. 1 the dashed curve represents the energy $H_{I\ I}/d_{I\ I}$, corresponding to the wave function Ψ_I or Ψ_{II} alone. Comparison of this curve

with that for $\Psi_I + \Psi_{II}$ provides justification for the statement that the three-electron bond results from resonance of the system between the two degenerate states represented by the symbols He : $\cdot He^+$ and He$\cdot^+$: He. It is evident that for unlike atoms for which the energy difference of the states $A : \cdot B$ and $A. : B$ is greater than the resonance energy between these two states, the correct wave functions approximate Ψ_I and Ψ_{II}, and do not lead to the formation of a stable three-electron bond.

A more accurate treatment of He_2^+ results on minimizing the energy with respect to the effective nuclear charge Z. On introducing the variable $\rho = Zr$, the process of minimizing with respect to Z can be carried out analytically, as pointed out by Wang,[4] with subsequent determination of the minimum relative to ρ by numerical calculation. This treatment leads to $Z = 1.833$, with the equilibrium internuclear distance $r_0 = 1.085A$. The dissociation energy to $He + He^+$ (energy -9.630 Rhc, for $Z = 43/24$) is found to be $D_e = 2.47$ v.e., and the vibrational frequency approximately 1950 cm^{-1}, obtained from values of the energy calculated in the neighborhood of r_0 by holding Z constant. The experimental values of these quantities,[8] from measurements of the spectrum of He_2 in states consisting of a normal He_2^+ ion and an outer electron, are $r_0 = 1.090A$, $D_e = 2.5$ v.e., and $\omega_{1/2} = 1628$ cm^{-1}, in excellent agreement with the theoretical values. The dissociation energy is nearly equal to that for H_2^+, $D_e = 2.76$ v.e., as expected.

Although the variation treatment leads to an energy value for the system greater than or equal to the energy of the lowest state of the system, the calculated value of D_e given above is not a lower limit to the true value, inasmuch as an approximate wave function has been used both for $r = r_0$ and $r = \infty$, and it is not known at which point the error is greater.

A closer approximation to the wave function could be obtained by using different values of Z for He : and $\cdot He^+$; because of the complexity of the calculations and the small expected improvement, this treatment has not been carried out.

[8] W. Weizel, Bandenspektren, Akad. Verlagsges. m.b.h. Leipzig, 1931, pp. 255, 270.

The Normal State of He_2^{++} and the Spectrum of He_2^+

The wave functions for He_2^{++} which can be constructed from $1s$ hydrogen-like functions are, as for H_2 also, the following:

	ψ	φ		
I	$+$	$-$	H .	. H
II	$-$	$+$	H .	. H
III	$+-$		H:⁻	H⁺
IV		$+-$	H⁺	:H⁻

From these we obtain the nuclear-symmetric functions $(\Psi_I - \Psi_{II}) + \alpha(\Psi_{III} + \Psi_{IV})$ and $(\Psi_I - \Psi_{II}) - \beta(\Psi_{III} + \Psi_{IV})$, and similar nuclear-antisymmetric functions. The first function provides a close approximation to the wave function for normal H_2, the ionic parameter α being equal[9] to 0.256, with $Z = 1.193$ and $r_0 = 0.750A$. On minimizing the energy integral for this function for He_2^{++} with respect to α, Z, and ρ, the values $\alpha = 0.435$, $Z = 2.124$, and $r_0 = 0.75A$ are obtained. The course of the energy as a function of r, calculated for these values of α and Z, is shown in Fig. 2. It is seen that at large distances the two
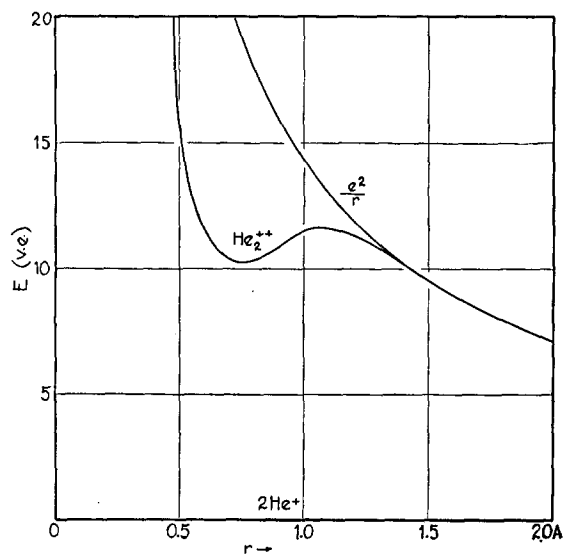

FIG. 2. The energy curve for normal He_2^{++}.

He^+ ions repel each other with the force e^2/r^2; at about 1.3A the resonance interaction of the

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[9] S. Weinbaum, private communication; J. C. Slater, Phys. Rev. 35, 509 (1930).

electrons becomes important, causing the force to become attractive at about 1.1A, and leading to the formation of a molecule which is probably sufficiently metastable to give rise to a band spectrum. The predicted constants for this state are $r_0 = 0.75A$, $D = 1.4$ v.e. (distance from minimum to maximum), and $\omega_0 = 3200$ cm⁻¹, with four vibrational levels occurring, the fourth (and perhaps the others also) probably showing pronounced predissociation characteristics. There are no experimental data existent with which to compare these values. However, excited states of He_2^+ consisting of this state of He_2^{++} with an outer electron, and having approximately these values of r_0, D, and ω_0, should give rise to well-defined He_2^+ bands, bearing approximately the same relation to the He_2 bands that the He^+ spectrum does to the H spectrum; it is hoped that these bands will be observed by the experimental spectroscopists.

It is interesting to note that of these states of He_2^+ about one-half should be capable of existence with either of two moments of inertia; that is, the electronic energy curves should show two minima. At $r = 0.75A$ the two He^+ ions are held together by an electron-pair bond formed by the two atom-cores, the outer electron being roughly hydrogen-like, and contributing little to the bond. This gives rise to states of He_2^+ which resemble closely in their values of r_0 and ω_0 the normal state of He_2^{++} just discussed, in the same way that many known states of He_2 and of H_2 resemble the normal states of He_2^+ and of H_2^+, respectively. At larger distances, of 3 or 4A, the He^+ ions simulate protons with regard to their interaction both with each other and with an outer electron; and if the outer electron is in a nuclear-symmetric state, it will hold them together in the same way that the protons in excited states of H_2^+ are held together by the excited electron. This statement can be made without carrying out the calculation of the energy curves, inasmuch as previous calculations for atoms with one electron in a non-penetrating orbit outside of a K-shell, such as Li $1s^2 2p$, He $1s2p$, etc., have shown that the interaction of the outer and inner electrons has very little influence in changing the wave function and energy value from those corresponding to complete screening,

and the calculations given above for $He^+ + He^+$ show that at these internuclear distances the interaction of the two atom-cores is essentially equal to that of two protons. The energy corresponding to resonance between the two states $\cdot He^* \cdot He \cdot^+$ and $\cdot He^+ \cdot He \cdot^*$ will accordingly cause the potential curves for various excited states to show minima, corresponding to stable states of $\cdot He \cdot He \cdot^+$, with a one-electron bond formed by the excited electron. These states will be very closely similar to the excited states of H_2^+, but with quadrupled moments of inertia. States of He_2 with two excited electrons would in some cases also show two minima, one at $r = 0.75A$, and one at some larger value, approx-imately equal to that for the corresponding state of doubly-excited H_2.

Certain relations between equilibrium distances for bonds formed by K electrons may be pointed out. The electron-pair bond in He_2^{++} leads to the same value for r_0 (0.75A) as for H_2 (0.750A). The three-electron bond in He_2^+ leads to $r_0 = 1.09A$, nearly equal to the value $r_0 = 1.06A$ for the one-electron bond in H_2^+. The oscillational frequencies in He_2^{++} and He_2^+ are approximately three-quarters of those for H_2 and H_2^+, respectively.

I am indebted to Mr. Sidney Weinbaum for carrying out many of the calculations involved in this work.