Calculation of the ground term $X^1\Sigma_g^+$ of the helium quasimolecular doubly-charged ion He_2^{++} by a simple method

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A simple method is proposed for calculating the ground term $X^1\Sigma_g^+$ of the He_2^{++} quasimolecule. It is shown that the He_2^{++} molecule possesses several quasistationary levels.

A variety of electronic states in a molecule can be obtained by successively combining its possible constituent atoms or ions. Electronic states of the quasimolecular doubly-charged ion He_2^{++} are obtained by combining the He atom with its doubly-ionized form He^{++} or by combining two He^+ ions.

We shall first investigate the behavior of the states of the quasimolecule that is formed from two helium ions as these ions come together. If the two helium ions are in their ground state, two states—$^1\Sigma_g^+$ and $^3\Sigma_u^+$—of the quasimolecule He_2^{++} are obtained by bringing the ions together. The electron shells corresponding to these states of the quasimolecule are $(1\sigma_g^2)$ and $(1\sigma_g^1\sigma_u)$, respectively. The lowest states of the doubly-ionized beryllium atom, Be^{++}, which possess the same respective symmetry and are formed by combining helium-ion nuclei, are represented (showing their electron shells) by $Be^{++}(1s^2)$ and $(Be^{++})^*(1s2p)$. Thus the $^1\Sigma_g^+$ state of the He_2^{++} quasimolecule, when the nuclei of the helium ions are ultimately united, becomes the ^1S ground state of the doubly-ionized beryllium atom, while the $^3\Sigma_u^+$ state is transformed into the ^3P excited state of Be^{++}.

We shall now investigate the behavior of the states of the quasimolecule He_2^{++} formed from a ground-state helium atom and a doubly-ionized helium atom when these two atoms come together. The approach of the He^{++} and He nuclei leads to two states—$^1\Sigma_g^+$ and $^1\Sigma_u^+$—of the quasimolecule He_2^{++}, whose electron shells corresponding to these states are $(1\sigma_u^2)$ and $(1\sigma_g 1\sigma_u)$, respectively. The lowest Be^{++} states which possess the same respective symmetry and are formed by combining He^{++} and He nuclei, are denoted by $(Be^{++})^*(2p^2)$ and $(Be^{++})^*(1s2p)$. Consequently, the ultimate union of the He^{++} and He nuclei transforms the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states of He_2^{++} into excited states of Be^{++}.

The $^1\Sigma_g^+$ state that results from the combination of two helium ions is the ground state of the He_2^{++} quasimolecule. To determine the ground level of He_2^{++} we write the Schrödinger equation for two electrons in the axisymmetric Coulomb field of two fixed nuclei each of which has a charge Z:

$$\left(-\frac{1}{2}\Delta_1-\frac{1}{2}\Delta_2-\frac{Z}{r_{A1}}-\frac{Z}{r_{A2}}-\frac{Z}{r_{B1}}-\frac{Z}{r_{B2}}+\frac{1}{r_{12}}\right)\Psi=\varepsilon_Z(R)\Psi, \qquad (1)$$

where $\epsilon_Z(R) = E_Z(R) - Z^2/R$ is the energy of electrons 1 and 2; r_{A1}, r_{A2}, r_{B1}, r_{B2} are the distances of the electrons from the nuclei A and B; R is the nuclear separation (here and hereafter atomic units are used).

By means of the scale transformation

$$r_{A1}=\frac{\rho_{A1}}{Z},\quad r_{A2}=\frac{\rho_{A2}}{Z},\quad r_{B1}=\frac{\rho_{B1}}{Z},\quad r_{B2}=\frac{\rho_{B2}}{Z},\quad R=\frac{L}{Z},$$

we obtain from (1) the Schrödinger equation for a hydrogen molecule with the electron interaction parameter $\lambda = 1/Z$:

$$\left(-\frac{1}{2}\Delta_1-\frac{1}{2}\Delta_2-\frac{1}{\rho_{A1}}-\frac{1}{\rho_{A2}}-\frac{1}{\rho_{B1}}-\frac{1}{\rho_{B2}}+\frac{\lambda}{\rho_{12}}\right)\psi=\varepsilon(\lambda,L)\psi, \qquad (2)$$

where

$$\varepsilon(\lambda,L)=\varepsilon_Z(R)\,/\,Z^2 \qquad (3)$$

is the electronic energy and L is the distance between the protons A and B. For $\lambda = 1$, Eq. (2) becomes the exact Schrödinger equation for the hydrogen molecule, while for $\lambda = 0$ it splits into two Schrödinger equations for the molecular hydrogen ion.

We must solve (2) with the electron interaction parameter $\lambda = \frac{1}{2}$. Calculating the electronic energy $\epsilon(\lambda, L)$ for $\lambda = 0, \frac{1}{2}, 1$, and 2, we obtain: $\epsilon(0, L) = 2\epsilon_{H_2^+}(L)$, where $\epsilon_{H_2^+}(L)$ is the electronic energy of H_2^+; $\epsilon(\frac{1}{2}, L) = \frac{1}{4}\epsilon_{He_2^{++}}(L/2)$, where $\epsilon_{He_2^{++}}(L/2)$ is the desired electronic energy of the He_2^{++} quasimolecule; $\epsilon(1, L) = \epsilon_{H_2}(L)$, where $\epsilon_{H_2}(L)$ is the electronic energy of the hydrogen molecule. With further increase of λ one electron is detached, and for the energy $\epsilon(\lambda, L)$ we obtain the expression $\epsilon(\lambda > 2, L) = \epsilon_{H_2^+}(L)$. The value of the interaction parameter λ at which electron detachment occurs increases with the internuclear distance L. At large separations L we have the asymptotic relation

$$\lambda\sim\frac{L}{2}+1+\frac{\beta}{4L}+\left(\frac{\beta^2}{4}-\frac{\beta}{2}\right)\frac{1}{L^3}+o\left(\frac{1}{L^5}\right),$$

where β is the polarizability of the hydrogen atom.

Knowing the energy levels of the systems resulting from the ultimate union of the nuclei, we can calculate the electronic energy $\epsilon(\lambda, L)$ for $L = 0$ and different values of λ:

$\varepsilon(0,0)=2E_{He^+}=-4$, E_{He^+} – ground level of He^+;
$\varepsilon(\frac{1}{2},0)=\frac{1}{4}E_{Be^{++}}=-3.41$, $E_{Be^{++}}$ – ground level of Be^{++};
$\varepsilon(1,0)=E_{He}=-2.90$, E_{He} – ground level of He;
$\varepsilon(2,0)=4E_{H^-}=-2.09$, E_{H^-} – ground level of H^-;
$\varepsilon(\lambda>2.0)=E_{He^+}=-2.$

The behavior of the $\epsilon(\lambda, 0)$ curve is shown in Fig. 1; $\epsilon(0, L) = 2\epsilon_{H_2^+}(L)$ is taken to be the zero energy level. The $\epsilon(\lambda, 0)$ curve intersects the boundary of the continuous spectrum, $\epsilon(\lambda > 2.0) = -2$, at $\lambda = 2.13$. For larger λ, $\epsilon(\lambda, 0)$ becomes a quasistationary level, because a potential barrier appears.

It is seen in Fig. 1 that within the interval 0 to 1 the $\epsilon(\lambda, 0)$ curve is almost linearly dependent on λ. The curves for large L lie below that curve and their behav-

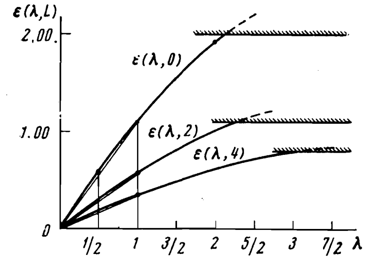

FIG. 1

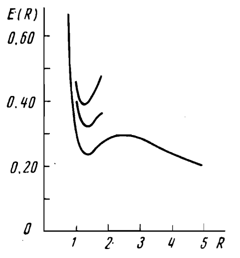

FIG. 2

FIG. 1. Electronic energy $\epsilon(\lambda, L)$ as a function of the parameter λ for different values of L.

FIG. 2. Total energy $E_{He_2^{++}}(R)$ of the quasimolecule He_2^{++}. The upper curves were calculated using the variational method of Kolos and Roothaan. [3]

ior will be similar. Therefore in the given interval (0—1) a $\epsilon(\lambda, L)$ curve can be replaced sufficiently accurately by a straight line; after this, for $\lambda = ½$ and arbitrary L the electronic energy can be written as

$$\varepsilon(1/2, L) \approx \varepsilon_{H_2^+}(L) + 1/2\varepsilon_{H_2}(L). \tag{4}$$

It should be noted here that for large internuclear distances L, since each electron can be closer to either nucleus, in the vicinity of the point $\lambda = 0$ the derivative of the electronic energy with respect to λ, $\epsilon'_\lambda(\lambda, L)$, has the constant value 5/16. However, calculations show that this region of small λ decreases exponentially as L increases.

From (3) and (4) we obtain an expression for the ground level of the quasimolecule He_2^{++}:

$$\varepsilon_{He_2^{++}}(R) \approx 2(2\varepsilon_{H_2^+}(2R) + \varepsilon_{H_2}(2R)). \tag{5}$$

At R = 0 we estimate a maximum relative error ≈ 1% here; this is probably not much reduced at R ~ 1. At very large R the error decreases as $1/R^4$. It must also be noted that the error is negative for all internuclear distances.

From Eq. (5), taking into account the Coulomb nuclear repulsion for the total energy of He_2^{++}, we obtain

$$E_{He_2^{++}}(R) \approx 2(2\varepsilon_{H_2^+}(2R) + \varepsilon_{H_2}(2R)) + 2/R). \tag{6}$$

To calculate the ground level of He_2^{++} we used Kolos and Wolniewicz's variational calculation of the hydrogen-molecule ground level[1] and Bates' numerical calculation of the ground level of the molecular hydrogen ion.[2] The results are given in the table and the corresponding curve is shown in Fig. 2. This curve, representing the total energy of the He_2^{++} ground state, is seen to possess a maximum and a minimum; at infinite separation of the nuclei it approaches a constant value, which is the total energy of the $He^+ + He^+$ system. Figure 2 also shows total-energy curves of ground-state He_2^{++} that were calculated in the region of the minimum by means of the variational method of Kolos and Roothaan,[3] using wave functions with forty and with nine parameters, respectively. From the (lowest) calculated curve the following values of the quasimolecule's parameters are obtained (R_0 is the equilibrium separation, D is the dissociation energy, and ω is the vibrational frequency): $R_0 = 1.34 = 0.71$ Å, D = 0.062 = 1.69 eV, and $\omega = 0.016 = 3504\ \text{cm}^{-1}$. It is easily perceived thereby that the potential well of the quasimolecule contains four quasistationary vibrational levels: $E_0 = 0.241 = 6.55$ eV, $E_1 = 0.257 = 6.99$ eV, $E_2 = 0.273 = 7.42$ eV, and $E_3 = 0.289 = 7.86$ eV. The respective lifetimes are of the following orders: $\tau_0 \sim 10^{16}$ sec, $\tau_1 \sim 10^6$ sec, $\tau_2 \sim 10^{-3}$ sec, and $\tau_3 \sim 10^{-12}$ sec.

R	$-E_{He_2^{++}}(R)$	R	$-E_{He_2^{++}}(R)$
0.50	2,056	2.50	3,705
0.75	3.342	2.75	3.709
1,00	3.687	3.00	3.716
1.25	3.763	3.25	3.726
1.50	3.758	3.50	3.737
1.75	3.736	4.00	3.760
2.00	3.717	4.50	3.783
2.25	3.707	5.00	3.802

The approximate formula (5) for the electronic energy of He_2^{++} gives values that lie below the true values. However, it can be shown that this underestimation of the electronic energy is not responsible for the minimum of the total-energy curve. The reason lies in the fact that the total-energy curve of He_2^{++} possesses an inflection point where its electronic energy is replaced by the electronic energy of the hydrogen molecule.

The He_2^{++} molecule can be formed by ionizing the stable He_2^+ molecule, which has the parameters $R_0 = 2.06 = 1.09$ Å, D = 0.092 = 2.5 eV, and $\omega = 0.0074 = 1627\ \text{cm}^{-1}$. The ground state of this molecule will be $X^2\Sigma_u$. By analyzing the ground-state potential curves of these two systems it is shown that, according to the Franck-Condon principle, ionization of ground-state He_2^+ produces He_2^{++} in vibrational excited states. It should also be noted that there is a small probability of obtaining ground-state He_2^{++} by ionizing He_2^+ in a vibrational excited state.

Calculations show that the ground state $X^1\Sigma_g^+$ of the He_2^{+++} system is a monotonic function of the internuclear distance R and thus possesses no inflection point. Consequently, the He_2^{+++} system possesses no quasistationary states. The maximum charge (Z) at which a single electron can still bind the two nuclei is 1.40.

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[1] W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).

[2] Advances in Atomic and Molecular Physics, D. R. Bates and I. Estermann, eds., Vol. 1, Academic Press, New York and London, 1965.

[3] W. Kolos and C. Roothaan, Rev. Mod. Phys. **32**, 205 (1960).

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11