Investigation of the energy terms of a system of two metastable helium atoms

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The behavior of the ${}^1\Sigma_g^+$ terms of a system of two metastable helium atoms is investigated for small internuclear distances *R*. It is shown that the system does not form a stable molecule, since the total energy curve intersects a whole band of terms in the vicinity of the minimum; consequently, in addition to the previously known autoionization channel, a new channel of inelastic collisions of the second kind becomes open at small distances.

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The present paper is a continuation of[1], in which the ground term $X^1\Sigma_g^+$ of the doubly charged ion of the helium quasimolecule He_2^{++} was obtained. It was shown that this term has a minimum at the internuclear distance R = 0.71 Å. Because of the strong Coulomb repulsion of the nuclei, the bottom of the wall is 6.34 eV above the value of the energy of two isolated He^+ ions. Calculation shows that the potential well contains several (four) quasidiscrete vibrational levels. The lifetimes of the levels to decay due to the tunnel effect amount to the following, according to the estimates of[1]: for the ground vibrational level, 10^{-16} sec, for the upper level—the fourth—10^{-12} sec. The dissociation energy of the quasimolecule is equal to 1.69 eV.

Thus, in the decay of the quasimolecule He_2^{++} into two He^+ ions, an energy of about 8 eV is released. This means that this system could be a good accumulator of energy. However, since the quasimolecule is electrically charged, it is not possible to accumulate such a gas in significant quantities. Therefore, the question arises as to whether this property of the He_2^{++} quasimolecule is preserved if it is completely neutralized to some other state by the addition of two electrons. In other words, could two helium atoms in any electron state form a quasi-stable system with a large (on a chemical scale) decay energy?

It is well known that two helium atoms in the ground state have one purely repulsive term.[2,3] Some of the energy terms, which correspond at infinity to a helium atom in the ground state and a helium atom in an excited state, lead to the formation of a quasistable He_2^* molecule, with a maximal decay energy from a fraction of an electron volt to one electron volt.[4-11]

The next terms energetically are the quasimolecular terms corresponding at infinity to two metastable helium atoms. There are literature papers on the calculation of the energy terms of such a system.[12, 13] There the terms were calculated at medium and large internuclear distances ($R > 4a_0$) in connection with investigation of the Penning effect for the collision of two metastable helium atoms.

At small distances ($R < 4a_0$), some of the terms (this will be discussed in detail below) should have a second minimum. We are interested in the location of these minima relative to the energy of the isolated atoms. Such a problem is usually solved by the variational method with the use of a multiparameter wave function.

In the present study, we consider a simplified model in view of the large number of electrons. It is assumed in this model that the inner electrons of the quasimolecule form a "rigid" system with the electron shell of He_2^{++}, while the outer electrons move in the averaged field of the nuclei and the inner electrons. The total energy of the electrons is composed of the electron energy of the quasimolecule He_2^{++} and the energy of the outer electrons, which is determined by the variational method. Anticipating somewhat, we shall show that the accuracy of the given model is entirely sufficient for unique solution of the problem posed.

We now consider the behavior of the energy terms of the system of two metastable helium atoms as the constituent atoms approach one another. If two singlet helium atoms (1s, 2s, ${}^1S_0$) approach each other, then a single term ${}^1\Sigma_g^+$ is obtained. The quasimolecule electron shell corresponding to this state has the symmetry $(1\sigma_g)^2(2\sigma_g)^2$. In the limiting union of the nuclei, this term transforms into the ground term ${}^1S_0$ of the Be atom ($1s^2$, $2s^2$) (we consider adiabatic terms). If one of the atoms is in the triplet spin state of He (1s, 2s, ${}^3S_1$), then the number of ${}^3\Sigma^+$ terms is doubled, and they differ in parity. In the limiting union of the nuclei, these terms transform into excited states of the beryllium atom. If both metastable helium atoms are in triplet spin states, we then have three terms: ${}^5\Sigma_g^+$, ${}^3\Sigma_\mu^+$ and ${}^1\Sigma_g^+$—with respective total spins s = 2, 1, 0. The first two of these terms give excited states of the beryllium atom, and the last transforms into the ground state ${}^1S_0$.

Thus, of the six terms, the two terms ${}^1\Sigma_g^+$ obtained on the union of two singlet and two triplet helium atoms give the ground term of the beryllium atom in the limit of the combined nuclei. The differences in the values of these terms at R = ∞ and R = 0 are greater than the analogous difference for the term ${}^1\Sigma_g^+$ of the quasimolecule He_2^{++}; therefore the total energies corresponding to these terms should have minima at small distances. As for the remaining four terms, they evidently do not lead to the appearance of minima on the total-energy curves, since in the limit of the combined nuclei they give excited states of the beryllium atom. Thus, only the two terms ${}^1\Sigma_g^+$ of all the terms considered can have quasidiscrete vibrational levels.

To determine these terms, we write the Schrödinger equation for the four electrons in an axially symmetric Coulomb field of the two fixed nuclei a and b with charges $Z_a = Z_b = 2$:

$$(H(1,\,2)+H(3,\,4)+V)\Psi=\mathscr{E}_{He_2}(R)\Psi. \tag{1}$$

Here

$$H(i,k)=-\frac{\Delta_i}{2}-\frac{\Delta_k}{2}-\frac{2}{r_{ai}}-\frac{2}{r_{bi}}-\frac{2}{r_{ak}}-\frac{2}{r_{bk}}+\frac{1}{r_{ik}}$$

$$V=\frac{1}{r_{13}}+\frac{1}{r_{14}}+\frac{1}{r_{23}}+\frac{1}{r_{24}},$$

r_{ai}, r_{ak}, r_{bi}, and r_{bk} are the distances of the ith and kth electrons from the respective nuclei a and b, $\mathscr{E}_{He_2}(R) = E_{He_2}(R) = 4/R$ is the electron energy, and R is the distance between the nuclei (here and below we use atomic units).

We shall seek a solution of Eq. (1) in the form

$$\Psi=\Phi(1,2)F(3,4), \tag{2}$$

where $\Phi(1, 2)$ is the wave function of the electrons of the quasimolecule He_2^{++}.

Substituting (2) in (1), multiplying on the left by $\Phi^*(1, 2)$, and integrating over the coordinates of the electrons 1, 2, we obtain for F(3, 4),

$$(H(3,4)+v(3,4))F(3,4)=\mathscr{E}(R)F(3,4). \tag{3}$$

Here $v(3, 4) = \langle\Phi(1, 2)|V|\Phi(1, 2)\rangle$, and $\mathscr{E}(R) = \mathscr{E}_{He_2}(R) - \mathscr{E}_{He_2^{++}}(R)$ is the energy of the electrons 3 and 4. In (2), we have not taken into account the permutational symmetry between electrons of different shells; therefore, in place of the two terms $^1\Sigma_g^{++}$ we obtain a single term.

We represent the wave function $\Phi(1, 2)$ in the form of the product of hydrogen 1s-functions in the field of nuclei a and b with charges $Z_a = Z_b = 2$:

$$\Phi(1,2)=\varphi_a(1)\varphi_b(2). \tag{4}$$

We then obtain the following equation for F(3, 4):

$$\left(-\frac{\Delta_3}{2}-\frac{\Delta_4}{2}-\frac{1}{r_{a3}}-v_a(3)-\frac{1}{r_{b3}}-v_b(3)-\frac{1}{r_{a4}}-v_a(4)-\frac{1}{r_{b4}}-v_b(4)+\frac{1}{r_{34}}\right)F(3,4)=\mathscr{E}(R)F(3,4), \tag{5}$$

where

$$v_a(i)=\exp(-4r_{ai})(2+1/r_{ai}),\quad v_b(i)=\exp(-4r_{bi})(2+1/r_{bi}). \tag{6}$$

(In (4), we did not carry out symmetrization between electrons 1 and 2 and, by the same token, we did not consider exponentially small terms in Eq. (5).)

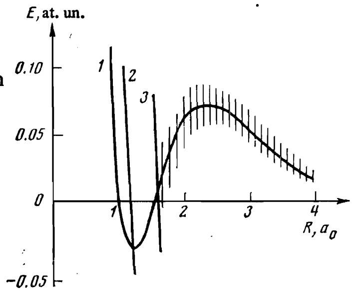
We solve Eq. (5) by the variational method. We construct the wave function F(3, 4) out of hydrogen 2s-wave functions with effective charge Z, which we shall vary:

$$F(3,4)=[2(1+s^2)]^{-1/2}(\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)),$$

$$s=\langle\psi_a|\psi_b\rangle.$$

The calculations were performed on a computer. For given R in the range $1 \leq Z \leq 2.5$, a set of values of $\mathscr{E}(Z, R)$ was computed with a step $\Delta Z = 0.01$, and the minimum was selected from this set. The exchange interaction integral of the electrons was computed numerically.

The calculations showed that the model used above for the energy of the upper 2s-electron of the helium atom gives a value $E_{He} = -4.11$ eV with an effective charge Z = 1.19. For comparison, the experimental values of the energy of this same electron in the singlet and triplet states are $E_{He}^{sing} = -3.97$ eV and $E_{He}^{trip} = -4.76$ eV, respectively. For the energy of two outer electrons of the beryllium atom, our calculation gives $E_{Be} = -28.24$ eV (effective charge 2.30) and the experimental value is equal to $E_{Be}^{exp} = -27.53$ eV. In the latter case, our calculation gives a value somewhat lower than the experimental value. This is due to the fact that in the limit of the united nuclei, averaging of the field takes place with hydrogen 1s-functions with charge Z = 2. The latter in turn leads to a slower drop in the potentials (6) and a stronger "compression" of the outer 2s-electrons toward the nucleus. As the nuclear separation increases, this error is rapidly reduced. The remaining error is determined entirely by the approximation which leads to a single term in place of the two terms $^1\Sigma_g^+$. This approximation leads in the final analysis to a greatly reduced error, since we are interested in the position of the minimum relative to the energy of the isolated atoms, and not the location of the term as a whole.



Behavior of the $^1\Sigma_g^+$ term–curve 1–of two metastable helium atoms as a function of the internuclear distance R in the region $R \leqslant 4a_0$. Curves 2 and 3 are respectively the $^1\Sigma_g^+$ and $^2\Sigma_g^+$ terms of the systems He(1s²) + He(1s, 2s) and He(1s²) + He⁺(1s).

As the energy of the inner electrons, we use the values of the electron energy of the quasimolecule He_2^{++} obtained in[14]. The curve of the total energy is shown in the figure. The energy of the noninteracting atoms is chosen as the zero point. As is seen from the figure, the curve for R = 1.25a₀ has a minimum, and that for R = 2.3a₀ a maximum. The minimum is located 1.01 eV below the energy of the noninteracting atoms. The height of the repulsive "hump" is 1.93 eV.

Thus, in spite of the strong Coulomb repulsion of the nuclei, the addition of two 2s-electrons to the quasimolecule He_2^{++} leads to a shift in the position of the minimum from the region of positive energies to the region of negative energies (relative to the noninteracting atoms).

We now investigate the question: can the well lead to the formation of a stable molecule? For this, we compare the calculated curve with the energy terms of the system $He(1s^2) + He^+(1s)$ and determine the internuclear distances R at which intersection of the terms takes place. This system has two terms: $^2\Sigma_g^+$ and $^2\Sigma_\mu^+$, the first of which is purely repulsive, while the second ensures the existence of a stable He_2^+ molecule. The terms considered intersect the term $^1\Sigma_g^+$ at the distances $R \approx 1.6a_0$ and $R \approx 0.7a_0$, respectively[15,16], from which it follows that at internuclear distances $R > 1.6a_0$ the term $^1\Sigma_g^+$ acquires a "width" due to the possibility of autoionization transition to the term $^2\Sigma_g^+$ of the system He_2^+ (the autoionization transition to the term $^2\Sigma_u^+$ is considerably less probable, since it requires a change in the parity of the outgoing particle).

In addition to these terms, the term $^1\Sigma_g^+$ intersects in the region of the minimum with a whole band of terms that correspond at infinity to two helium atoms, one of which is single-electron-excited.[4-11] Due to these transitions, a predissociation of the system takes place with a decay time of the order of the time of nuclear motion. (We note that all the considered terms intersect the term $^1\Sigma_g^+$ in the region where they are almost vertical; therefore, the shift of the term $^1\Sigma_g^+$ by the amount of the error has almost no effect on the point of intersection.)

Thus, analysis of the terms shows that two metastable helium atoms do not form a stable system (or, consequently, a quasistable one either), since the aforementioned channel of inelastic collisions of the second kind is opened up in the collision of the atoms at small distances:

$$\mathrm{He}(1s,\ 2s)+\mathrm{He}(1s,\ 2s)\longrightarrow\mathrm{He}(1s^2)+\mathrm{He}(1s,\ nl)+\Delta E$$

with a large energy release $\Delta E \sim 20$ eV.

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