Correlation of diabatic molecular orbitals of an electron in the field of three Coulomb centers

T. M. Kereselidze

Tiflis State University

(Submitted 21 March 1989)
Zh. Eksp. Teor. Fiz. **96**, 543–551 (August 1989)

A quasimolecule consisting of one negatively charged particle and three nuclei is analyzed. The diabatic potential-energy surfaces of the system are found when the distances between the particles are large and also in the limit of a bound molecule. The potential surfaces of the quasimolecule are compared. Correlation rules for the diabatic molecular orbitals are constructed. It is found that the potential-energy surfaces intersect, at a point when the particles are close together and on lines in the asymptotic region.

INTRODUCTION

Gershtein and Krivchenko[1] have denied the correlation rules for molecular orbitals (MOs) for the case of a single electron in the field of two fixed nuclei. The problem was solved through separation of variables in the Schrödinger equation in a prolate spheroidal coordinate system and keeping the number of zeros of the wave functions fixed as the distance between nuclei was varied. Correlation rules for the MOs of diatomic many-electron quasiparticles were derived in Refs. 2–6.

For the case of a single electron in the field of three fixed nuclei it is not possible to separate variables in the Schrödinger equation. It is thus not possible to determine MO correlation rules by calculating the number of zeros of the wave functions. Dowek *et al.*[7] have proposed an empirical method for determining the MO correlations of K-shell electrons of simple triatomic quasimolecules through the construction of "correlation cubes."

In the present paper we analyze a quasimolecule consisting of one negatively charged particle and three nuclei, with charges $Z_a = Z_b = 1$ and $Z_c = Z = 1,2,3,\ldots$. Systems of this type arise, for example, when the molecular hydrogen ion H_2^+ collides with H^+, He^{++}, etc., ions or when a mesomolecular ion of a hydrogen isotope[8] approaches the nuclei of various elements. This problem is also interesting in connection with research on the structure of triatomic molecules.

After the nuclei of a quasimolecule have separated, the electron may be in the field of two protons or in the field of nucleus Z. The MOs can thus be divided into a group of orbitals which are found as the H_2^+ ion approaches nucleus Z and a group of orbitals which are found as a hydrogen-like ion $A^{+(Z-1)}$ approaches two protons.

To take all types of interactions which occur in the collisions of atomic particles into account most completely, one determines the correlation among diabatic MOs.[2–7] Diabatic MOs differ from adiabatic MOs in that they are found in the approximation in which small terms are ignored in the complete Hamiltonian of the system. In the analysis below we ignore the coupling between MOs belonging to different atomic particles in the limit of separate nuclei.

It is customary to select the following three coordinates for a description of the relative positions of the nuclei: R, the distance between the two protons; L, the distance from nucleus Z to the center of mass of the protons; and γ, the angle between the R and L axes. For convenience in the calculations, however, we will introduce the coordinate system which is the most natural one in each particular case. We will then rewrite the results in terms of L, R, γ.

Our problem is thus to determine the particular orbital of the bound molecule ($L = 0$) which each of the orbitals of the separate atomic particles ($L = \infty$) becomes when the nuclei come extremely close together. This approach makes it possible to determine regions of a quasiintersection or close approach of the potential surfaces of the quasimolecule, at which nonadiabatic transitions occur.

CORRELATION OF ORBITALS IN THE $Z+H_2^+$ QUASIMOLECULE

Let us consider the quasimolecule which is formed as the ion H_2^+ approaches nucleus Z. To describe the motion of the electron and the relative position of the nuclei, we introduce two prolate spheroidal coordinate systems with foci at the positions of the nuclei of the H_2^+ ion:

$$\begin{gathered}\xi'=(r_a+r_b)/R,\quad \eta'=(r_a-r_b)/R,\quad \varphi'=\mathrm{arctg}(y/x),\\ \xi=(R_a+R_b)/R,\quad \eta=(R_a-R_b)/R,\quad \varphi=0,\\ 1\leqslant\xi'<\infty,\quad -1\leqslant\eta'\leqslant 1\quad 1\leqslant\xi<\infty,\quad -1\leqslant\eta\leqslant 1,\end{gathered}\tag{1}$$

where r_a and r_b are the distances from the electron to the foci, and R_a and R_b are the distances from nucleus Z to the foci. The coordinates ξ, η and L, γ are related by

$$\begin{aligned}\xi&=[(L^2-RL\cos\gamma+R^2/4)^{1/2}+(L^2+RL\cos\gamma+R^2/4)^{1/2}]/R,\\ \eta&=[(L^2-RL\cos\gamma+R^2/4)^{1/2}-(L^2+RL\cos\gamma+R^2/4)^{1/2}]/R.\end{aligned}$$

The wave function of the electron satisfies the Schrödinger equation

$$(H^{(0)}+V)\psi_i(\xi',\eta',\varphi')=\mathscr{E}_i(\xi,\eta,R)\psi_i(\xi',\eta',\varphi'),\tag{2}$$

where $H^{(0)}$ is the Hamiltonian for the H_2^+ ion, the operator $V = -Z/|\mathbf{r}_a - \mathbf{R}_a|$, represents the Coulomb interaction between the electron and the Z nucleus $\mathscr{E}_i = E_i - W$ is the energy of the electron, $W = 1/R + Z/R_a + Z/R_b$ is the potential energy of the nuclei, and E_i is the total energy of the quasimolecule. Here and below, we are using the atomic system of units.

We expand the wave function ψ_i in wave functions of the discrete spectrum of the molecular hydrogen ion:

$$\psi_i(\xi',\eta',\varphi')=\sum_j\sum_{\lambda_j}a_{ij\lambda_j}(\xi,\eta,R)\varphi_{j\lambda_j}(\xi',\eta',\varphi',R),\tag{3}$$

where

$$\varphi_{j\lambda_j}(\xi',\eta',\varphi',R)=(2\pi)^{-1/2}X_{j\lambda_j}(\xi',R)\,Y_{j\lambda_j}(\eta',R)\exp(i\lambda_j\varphi'),$$

and $X_{j\lambda_j}(\xi',R)$ and $Y_{j\lambda_j}(\eta',R)$ are the quasiradial and quasiangular wave functions for H_2^+. Here λ_j is the projection of the orbital angular momentum of the electron onto the molecular axis R, and j represents the set of all other quantum numbers,[9,10] [we are assuming that the continuum functions contribute little to expansion (3) even at large Z, since in this case the states of the $(Z+H_2^+)$ quasimolecule become excited states of the bound molecule]. Substituting (3) into (2), multiplying by $\varphi^*_{i\lambda_i}$, and integrating over the electron coordinates, we reduce Eq. (2) to an infinite system of coupled equations. To solve this system we need to diagonalize an infinite-dimensional energy matrix.

To determine the matrix elements of the operator $V=-Z/|\mathbf{r}_a-\mathbf{R}_a|$, we use a Neumann expansion[11]:

$$\frac{1}{|\mathbf{r}_a-\mathbf{R}_a|}=\frac{2}{R}\sum_{n=0}^{\infty}\sum_{m=0}^{n}(-1)^m\varepsilon_m(2n+1)\left[\frac{(n-m)!}{(n+m)!}\right]^2$$
$$\times P_n^m(\eta)P_n^m(\eta')P_n^m(\xi_<)Q_n^m(\xi_>)\cos m\varphi', \qquad (4)$$

where $\varepsilon_m=2-\delta_{m0}$, P_n^m and Q_n^m are the associated Legendre polynomials of respectively the first and second kinds, and $\xi_>$ and $\xi_<$ mean the larger and smaller of ξ and ξ'. After an integration over the angular variable we find

$$V_{ij}(\xi,\eta,R)=(-1)^{m+1}\frac{ZR^2}{4}\sum_{n=0}^{\infty}(2n+1)\left[\frac{(n-m)!}{(n+m)!}\right]^2$$
$$\times V_{ij}^{(n)}(\xi,\eta,R), \qquad (5)$$

where

$$V_{ij}^{n}(\xi,\eta,R)=P_n^m(\eta)\,[I_n^{(0)}(R)\chi_n^{(2)}(\xi,R)-I_n^{(2)}$$
$$\times(R)\chi_n^{(0)}(\xi,R)], \qquad (6)$$

$$I_n^{(k)}(R)=\int_{-1}^{1}Y_i(\eta')P_n^m(\eta')Y_j(\eta')\eta'^k\,d\eta', \qquad (7)$$

$$\chi_n^{(k)}(\xi,R)=Q_n^m(\xi)\int_1^{\xi}X_i(\xi')P_n^m(\xi')X_j(\xi')\xi'^k\,d\xi'$$
$$+P_n^m(\xi)\int_{\xi}^{\infty}X_i(\xi')Q_n^m(\xi')X_j(\xi')\xi'^k\,d\xi',$$

and $m=|\lambda_i-\lambda_j|$ [here and below, we are omitting the argument R and the index λ_j from the functions] $X_{j\lambda_j}(\xi',R)$ and $Y_{j\lambda_j}(\eta',R)$.

Using (5)–(7), and diagonalizing the finite-dimensional energy matrix, we can calculate the potential-energy surface of the quasimolecule for any configuration of the nuclei. To determine the MO correlation, however, it is sufficient to determine the potential surfaces in the two limiting cases $L\gg1$ and $L=0$. Figure 1 shows the energy terms $1\sigma^{(+)}$, $2\sigma^{(-)}$, $1\pi^{(+)}$ and $3\sigma^{(+)}$ of the ground and first three excited states of the bound molecule according to calculations from (5)–(7) for $Z=3$ and $R=a_0$ (the equilibrium distance between the H_2^+ nuclei) (for $Z=1,2$, the relative arrangement of the terms remains the same; the only change is a shift of the levels). As the basis functions we have adopted numerical wave functions of the first four states ($1s\sigma^{(+)}$, $2p\sigma^{(-)}$, $2p\pi^{(+)}$, $2s\sigma^{(+)}$) of the H_2^+ ion (the classification is based on the quantum numbers of the combined atom[9,10]). In our notation, the ± express the symmetry of the state under reflection in that plane which is perpendicular to the molecular axis and which cuts it in half (the transformation $\eta'\to-\eta'$).

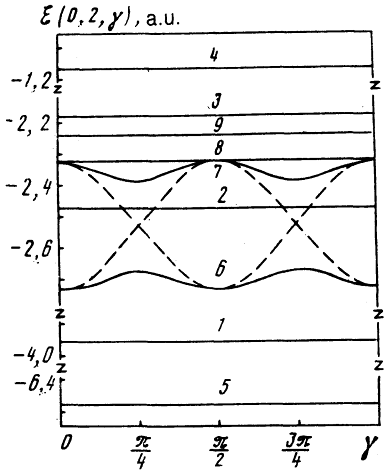

FIG. 1. Energy terms of the combined molecule according to calculations from (5)–(7) and (15), (16) for $Z=3$ and $R=2a_0$. *1–4:* The $(Z+H_2^+)$ quasimolecule. *1* — $1\sigma^{(+)}$; *2* — $2\sigma^{(-)}$; *3* — $1\pi^{(+)}$; *4* — $3\sigma^{(+)}$. *5–9:* The $(p+p+A^{+(Z-1)})$ quasimolecule. The dashed curves show terms found without consideration of the interaction between the $m=0$ and $m=\pm1$ states.

If the distance between nucleus Z and the H_2^+ ion is sufficiently large, and the condition $\xi\approx2L/R\gg1$ holds, the matrix elements in (5) can be expanded in inverse powers of ξ. Ignoring the exponentially small terms in (7), and using the asymptotic representation[12] of the associated Legendre polynomials of the second kind, $Q_n^m(\xi)$, we can write the following expression for $V_{ij}^{(n)}$:

$$V_{ij}^{(n)}(\xi,\eta,R)=\frac{(-1)^m2^nn!\,(n+m)!}{(2n+1)!}P_n^m(\eta)A_{ij}^{(n)}(R)\left[\frac{1}{\xi^{n+1}}\right.$$
$$\left.+\frac{(n+m+1)(n+m+2)-m(2n+3)}{2(2n+3)}\frac{1}{\xi^{n+3}}+\dots\right], \qquad (8)$$

where

$$A_{ij}^{(n)}(R)=I_n^{(0)}(R)\int_1^{\infty}X_i(\xi')P_n^m(\xi')X_j(\xi')\xi'^2\,d\xi'$$
$$-I_n^{(2)}(R)\int_1^{\infty}X_i(\xi')P_n^m(\xi')X_j(\xi')\,d\xi'. \qquad (9)$$

From the orthonormality of the H_2^+ wave functions follows $A_{ij}^{(0)}(R)=8\delta_{ij}/R^3$.

Noting that the off-diagonal matrix element is $A_{ij}^{(0)}(R)=0$, and transforming from ξ and η to L and γ, we find the following expression for the potential-energy surfaces of the quasimolecule in second-order perturbation theory[13]:

$$\mathscr{E}_i(L,R,\gamma)=\varepsilon_i(R)-\frac{Z}{L}-\frac{Z}{2L^3}Q_i(R)P_2(\cos\gamma)$$
$$-\frac{Z^2}{2L^4}[\alpha_i^{(+)}(R)\sin^2\gamma+4\alpha_i^{(-)}(R)\cos^2\gamma], \tag{10}$$

$$Q_i(R)=\frac{R^5}{24}\left[A_{ii}^{(2)}(R)+\frac{4}{R^3}\right], \tag{11}$$

$$\alpha_i^{(\pm)}(R)=\frac{R^8}{512}\sum_j{}' \frac{|A_{ij}^{(1)}(R)|^2}{\varepsilon_j(R)-\varepsilon_i(R)}. \tag{12}$$

Here $\varepsilon_i(R)$ are the energy terms of the H_2^+, $Q_i(R)$ is the quadrupole moment of the H_2^+ ion, and $\alpha_i^{\parallel}(R)=4\alpha_i^{(-)}(R)$ and $\alpha_i^{\perp}(R)=\alpha_i^{(+)}(R)$ are the components of the H_2^+ polarizability tensor respectively parallel and perpendicular to the molecular axis. The summation in (12) is over the matrix elements between wave functions of identical symmetry (under the transformation $\eta'\to-\eta'$) for $\alpha_i^{(+)}(R)$ and between wave functions of opposite symmetry for $\alpha_i^{(-)}(R)$. The prime on the summation sign means that the term with $j=i$ must be omitted from the sum for $\alpha_i^{(+)}(R)$.

Expression (10) holds under the condition that the off-diagonal matrix element in (8) is small in comparison with the term difference $\varepsilon_j(R)-\varepsilon_i(R)$. Accordingly, in regions of the internuclear distance R in which the term $\varepsilon_i(R)$ is crossed or merges with other H_2^+ terms, expression (10) cannot be used. Expression (10) is also inapplicable for H_2^+ states with a nonzero projection of the angular momentum of the electron, since terms with $\lambda\neq0$ are doubly degenerate.[9] In these regions of R, and for states with a nonvanishing angular-momentum projection, it is necessary to solve a system of coupled equations with matrix elements (8). If, for a state with $\lambda_i\neq0$, we restrict the expansion to two H_2^+ wave functions, one with a positive angular-momentum projection and one with a negative projection, we find the following expression for the potential-energy surfaces of the quasimolecule:

$$\mathscr{E}_i(L,R,\gamma)=\varepsilon_i(R)-\frac{Z}{L}-\frac{Z}{2L^3}Q_i(R)P_2(\cos\gamma)$$
$$\pm\frac{Zk!\,R^{k+3}}{8[(2k)!]^2}\frac{A_{ii}^{(k)}(R)}{L^{k+1}}P_k^{\,k}(\cos\gamma), \tag{13}$$

where $k=2\lambda_i$. It follows from (13) that the splitting of the surfaces is important only for the π terms of H_2^+. In a linear configuration of the nuclei ($\gamma=0,\pi$), and in the limit of the bound molecule, potential energy surfaces (13) again degenerate.

Using the numerical wave functions for H_2^+, along with (11) and (12) we have calculated the quadrupole moments and the polarizability of the molecular hydrogen ion at the equilibrium internuclear distance, $R=2a_0$. For the ground state and the first three excited states of H_2^+ we found

$$Q_0=0{,}939,\ Q_1=4{,}614,\ Q_2=0{,}402,\ Q_3=1{,}864,$$
$$\alpha_0^{\parallel}=5{,}071,\ \alpha_0^{\perp}=1{,}766.$$

The calculated values of the polarizability ($np\sigma^{(-)}$ and $np\pi^{(+)}$ wave functions with $n\leqslant5$ are involved in the expansion) agree well with the values found in Ref. 14 through an expansion of the two-center Coulomb Green's function in the complete system of Sturm functions of the purely discrete spectrum.[15]

Let us find the MO correlation rules. It follows from (5)–(7) that none of the off-diagonal matrix elements $V_{ij}(\xi,\eta,R)$ vanishes identically for a given value of the parameter R and arbitrary values of ξ and η. Only with $\xi=1$ or with $\eta=\pm1$ and $\eta=0$ are some of the matrix elements $V_{ij}(\xi,\eta,R)$ identically zero for arbitrary values of the two other parameters. These values of ξ and η correspond to configurations of nuclei with more symmetry, specifically, the linear configuration ($\xi=1$ and $\eta=\pm1$) and the configuration of an isosceles triangle ($\eta=0$). For a configuration of nuclei with higher symmetry, only those H_2^+ orbitals which have the corresponding symmetry will contribute to MO expansion (3).

The wave functions for H_2^+ are classified as either symmetric or antisymmetric, depending on whether the quasiangular function $Y_j(\eta')$ changes sign when η' is replaced by $-\eta'$ (Refs. 9 and 10). For the associated Legendre polynomials $P_n^m(\eta')$, the change in sign resulting from the replacement of η' by $-\eta'$ depends on the parity of $n-m$ (Ref. 12). Accordingly, for off-diagonal matrix elements taken between the wave functions of opposite symmetry in (5) there are no Legendre polynomials with even $n-m$; i.e., the summation is carried out over those values of n for which the difference $n-m$ is an odd number. The associated Legendre polynomials $P_n^m(\eta)$ with odd $n-m$ contain the variable η as a factor.[12] The off-diagonal matrix elements taken between wave functions of opposite symmetry therefore vanish in the case $\eta=0$. As a result, the molecular orbitals (3) reduce to symmetric and antisymmetric ones for the isosceles-triangle configuration.

For the isosceles-triangle configuration, each MO (3) thus has a definite symmetry under reflection, which is preserved when we go from the limit of separate atomic particles to the limit of the bound molecule. For each value of the parameter R, the correlation of MOs of the same symmetry occurs in accordance with the rule that terms do not cross. This conclusion follows from the fact that for given values of R and η a change in the parameter ξ alone cannot lead to the satisfaction of two term-crossing conditions.[16]

For a linear configuration of nuclei ($\xi=1$ and $\eta=\pm1$), the off-diagonal matrix elements between states with different values of λ are zero [the Legendre polynomials are $P_n^m(\xi)\sim(\xi^2-1)^{m/2}$ and $P_n^m(\eta)\sim(1-\eta^2)^{m/2}$; Ref. 12]. Each MO (3) is thus characterized by a definite value of the projection of the orbital angular momentum of the electron onto the molecular axis at all distances between the nuclei. In the case of a linear configuration of the nuclei, the MOs with identical λ are thus correlated. For each value of the parameter R the correlation of the MOs with identical λ is in accordance with the rule that terms of identical symmetry do not cross.

If the configuration of the nuclei does not have a higher symmetry, the correlation of all the MOs in (3) conforms to the term noncrossing rule. As the symmetry of the configuration of nuclei is lowered, the crossing energy terms thus move apart.

The MO correlation rules which have been found [along with (10)–(13) and the terms of the bound molecule] make it possible to determine the behavior of the potential-energy surfaces of the $(Z + H_2^+)$ quasimolecule. For $Z = 1,2,3$ and $R = 2a_0$, for example, we find that the potential surfaces of the first four states of the quasimolecule do not cross each other. The only effect in this direction is that some of the surfaces approach each other in configurations of nuclei with higher symmetry [see (10)–(13)].

CORRELATION OF ORBITALS IN THE QUASIMOLECULE $p+p+A^{+(Z-1)}$

Let us examine the quasimolecule which is produced when a hydrogen-like ion $A^{+(Z-1)}$ and two protons approach each other. We place the center of the coordinate system at the position of the ion, and we run the polar axis along the L axis. We can then write the following expression for the operator which represents the interaction of the electron with the two protons:

$$V = -\sum_{l=0}^{\infty}\sum_{m=0}^{l} \varepsilon_m \frac{(l-m)!}{(l+m)!}\left\{\begin{pmatrix} \dfrac{r^l}{R_a^{l+1}} \\ \dfrac{R_a^l}{r^{l+1}} \end{pmatrix} \right.$$

$$\times\ P_l^m(\cos\theta_a)\cos[m(\varphi_a - \varphi)]$$

$$\left. + \begin{pmatrix} \dfrac{r^l}{R_b^{l+1}} \\ \dfrac{R_b^l}{r^{l+1}} \end{pmatrix} P_l^m(\cos\theta_b)\cos[m(\varphi_b - \varphi)]\right\}$$

$$\times\ P_l^m(\cos\theta). \tag{14}$$

Here $\varepsilon_m = 2 - \delta_{m0}; r,\theta,\varphi$ are the spherical coordinates of the electron; θ_a and θ_b are the angles between the polar axis and the vectors $\mathbf{R}_a$ and $\mathbf{R}_b$; and $\varphi_{a,b} = \mp\pi/2$ are the angles between the xz plane and the plane which passes through the nuclei. The upper terms in parentheses in (14) are used for $r < R_a, R_b$; the lower for $r > R_a, R_b$. The coordinates R_a, R_b and θ_a, θ_b are related to L, R, γ by

$$R_{a,b} = (L^2 \mp RL\cos\gamma + R^2/4)^{1/2},$$
$$\cos\theta_{a,b} = (L \mp {}^1/_2 R\cos\gamma)(L^2 \mp RL\cos\gamma + R^2/4)^{-1/2}.$$

We expand the unknown MOs in wave functions of the discrete spectrum of the hydrogen-like ion, and we reduce the original Schrödinger equation to an infinite system of coupled equations. For matrix elements of the interaction operator (14) we find

$$V_{n_i l_i m_i}^{n_j l_j m_j} = -\sum_{l=0}^{\infty}\frac{(l-m)!}{(l+m)!}[B_l(R_a)P_l^m(\cos\theta_a)e^{\pm im\pi/2}$$
$$+ B_l(R_b)P_l^m(\cos\theta_b)e^{\mp im\pi/2}]J_l, \tag{15}$$

where

$$J_l = \int_0^{\pi}\Theta^*_{l_i m_i}(\theta)P_l^m(\cos\theta)\Theta_{l_j m_j}(\theta)\sin\theta\,d\theta,$$

$$B_l(x) = \frac{1}{x^{l+1}}\int_0^x R_{n_i l_i}(r)R_{n_j l_j}(r)r^{l+2}\,dr + x^l$$

$$\times\int_x^{\infty} R_{n_i l_i}(r)R_{n_j l_j}(r)r^{-l+1}\,dr, \tag{16}$$

$m = |m_i - m_j|$, and $R_{nl}(r)$ and $\Theta_{lm}(\theta)$ are the radial and angular wave functions of the hydrogen-like ion. The upper sign in the exponential function in (15) is used in the case $m_i > m_j$ and the lower in the case $m_i < m_j$.

If the distances between the hydrogen-like ion and the protons are large ($R_{a,b} \gg 1$, $0 \leqslant R < \infty$), the potential-energy surfaces of the quasimolecule are conveniently determined in a basis of parabolic functions. In this case the first two terms of the interaction operator (14) are diagonal with respect to each group of mutually degenerate states,[16] and the third term has nonzero off-diagonal matrix elements

$$V_{n_1 n_2 m_i}^{n_1' n_2' m_j} = -\frac{3n(n-1)^{1/2}}{4Z}\left(\frac{\sin\theta_a}{R_a^2} - \frac{\sin\theta_b}{R_b^2}\right)$$

between states with parabolic quantum numbers $n_2' = n_2, |n_2 \pm 1|$, and $m_j = m_i \pm 1$.

After diagonalizing the energy matrix for each group of degenerate states, we find the following expression for the potential-energy surfaces of the quasimolecule[17]:

$$\mathscr{E}_{n_1 n_2 m_i}(R_a, R_b, \alpha) = -\frac{Z^2}{2n^2} - \frac{1}{R_a} - \frac{1}{R_b} + \frac{3n\Delta}{2Z}\cdot$$
$$\cdot\left(\frac{1}{R_a^4} + \frac{1}{R_b^4} + \frac{2\cos\alpha}{R_a^2 R_b^2}\right)^{1/2}, \tag{17}$$

where $n = n_1 + n_2 + |m| + 1$, $\Delta = n_1 - n_2$, and α is the angle between the vectors $\mathbf{R}_a$ and $\mathbf{R}_b$. For $R_{ab} \approx L \gg R/2$, the last expression becomes the known expression for the linear Stark effect.

Incorporating the following terms of the expansion in (14) results in a twofold splitting of the potential-energy surfaces with $m_i \neq 0$. The MOs which correspond to the surfaces in the case of an isosceles-triangle configuration have opposite symmetries under reflection in that plane perpendicular to the axis connecting the protons which cuts this axis in half (the transformation $\varphi \to -\varphi$). If the configuration of nuclei is axisymmetric, the degeneracy in the direction of the projection of the angular momentum of the electron is not lifted. In this case we find the following expression for the potential-energy surfaces of the quasimolecule:

$$\mathscr{E}_{n_1 n_2 m_i}(R_a, R_b) = -\frac{Z^2}{2n^2} - \frac{1}{R_b} - \frac{1}{R_a} + \frac{3n\Delta}{2Z}\left(\frac{1}{R_b^2} \pm \frac{1}{R_a^2}\right)$$
$$-\frac{n^2(6\Delta^2 - n^2 + 1)}{2Z^2}\left(\frac{1}{R_b^3} + \frac{1}{R_a^3}\right)$$
$$+\frac{n^3\Delta(109\Delta^2 - 39n^2 - 9m_i^2 + 59)}{16Z^3}$$
$$\times\left(\frac{1}{R_b^4} \pm \frac{1}{R_a^4}\right) - \frac{n^4(17n^2 - 3\Delta^2 - 9m_i^2 + 19)}{16Z^4}$$
$$\times\left(\frac{1}{R_b^2} \pm \frac{1}{R_a^2}\right)^2. \tag{18}$$

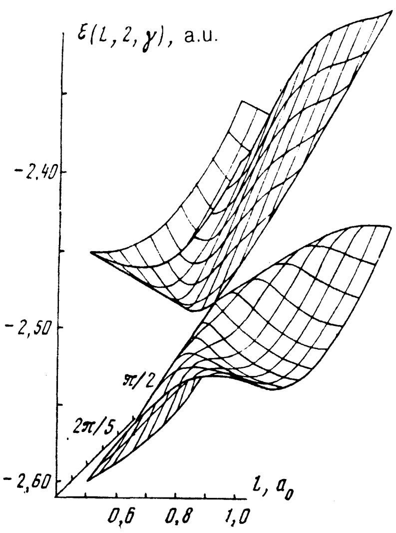

FIG. 2. Potential-energy surfaces $\mathcal{E}_{010}^{(+)}(L,2,\gamma)$ and $\mathcal{E}_{001}^{(-)}(L,2,\gamma)$ of the $(p+p+A^{+(Z-1)})$ quasimolecule according to calculations from (15) and (16) for $Z=3$ and $R=2a_0$ in the crossing region.

The upper sign is used in (18) if the nucleus Z is not between the protons ($\alpha=0$), and the lower sign is used if the nucleus is between the protons ($\alpha=\pi$).

In the limit of the bound molecule, the degeneracy with respect to the direction of the projection of the angular momentum of the electron is lifted for all values of the angle γ except $\gamma=0$ and π. Figure 1 shows the energy terms of the first five states of the bound molecule according to calculations from (15) and (16) for $Z=3$, $R=2a_0$, and $0\leqslant\gamma\leqslant\pi$ (The wave functions of the hydrogen-like ion with $n\leqslant 2$ are used in the expansion of the MOs). The dashed lines show the terms found without consideration of the interaction between the states with $m_i=0$ and $m_i=\pm 1$. At $\gamma=\pi/2$, these terms correspond to states which are symmetric under reflection. An exceptional case is the first excited level, which corresponds to an antisymmetric state. At $\gamma=0$ and π, the second and third excited levels are π terms, and the others σ terms. For $Z=1, 2$, the relative positions of these terms remain the same. The positions of these terms with respect to the levels of the $(Z+H_2^+)$ molecule change.

The correlation among the MOs in the $(p+p+A^{+(Z-1)})$ quasimolecule conforms to the rules derived in the preceding section of this paper. Let us use these rules to analyze the potential-energy surfaces with $n=2$. It follows from the MO correlation rules that in the case of an isosceles-triangle configuration the antisymmetric term $\mathcal{E}_{001}^{(-)}(L,2,\pi/2)$ which is obtained after the splitting of the level with $n_1=0$, $n_2=0$, and $m_i=1$ goes over into the first excited level of the bound molecule in the case $L=0$, while the symmetric term $\mathcal{E}_{010}^{(+)}(L,2,\pi/2)$, which is a lower-lying term in the case $L\gg 1$, becomes the second excited level of the bound molecule. These terms thus cross. For a linear configuration of nuclei, the order of the terms at $L\gg 1$ and $L=0$ is the same. Accordingly, the terms do not cross for $\gamma=0$, π. Figure 2 shows the potential-energy surfaces $\mathcal{E}_{010}^{(+)}(L,2,\gamma)$ and $\mathcal{E}_{001}^{(-)}(L,2,\gamma)$ calculated from (15) and (16) for $Z=3$. We see that the potential-energy surfaces intersect at the point $\gamma=\pi/2$, $L=0.67a_0$. The observed intersect of surfaces should lead to the appearance of an oscillatory structure in the total scattering cross section[18,19] when H_2^+ ions oriented in a direction perpendicular to the velocity collide with nuclei Z.

At $L\gg R/2$ we find from (17)

$$\mathcal{E}_{n_1n_2m_i}(L,R,\gamma)=-Z^2/2n^2-2/L+3n\Delta/ZL^2.$$

It thus also follows from (10) that the potential-energy surface $\mathcal{E}_0(L,R,\gamma)$ of the ground state of the $(Z+H_2^+)$ quasimolecule intersects the potential-energy surfaces of the $((p+p+A^{+(Z-1)})$ quasimolecule only if $Z>2$. The intersections occur on lines for $L\gg 1$. This circumstance is responsible for the low probability for charge exhange if the mesomolecular ions of hydrogen isotopes with the nuclei of helium and hydrogen atoms in the mesonic catalysis of nuclear fusion reactions in a deuterium-tritium mixture.[8]

This study shows that the potential-energy surfaces of the quasimolecule depend strongly on the angle γ. The probabilities for inelastic processes during collisions of H_2^+ with nuclei should therefore depend strongly on the orientation of the molecules. An experimental study of this question in the example of a system for which precise calculations are possible would present the opportunity to test the theoretical ideas. We note in conclusion that the method proposed here might be used to determine the correlations of the MOs of triatomic quasimolecules with several electrons.

I wish to thank O. B. Firsov and M. I. Chibisov for a discussion of these results.

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Translated by Dave Parsons