

# Correlation rules for diabatic molecular orbitals in diatomic quasimolecules

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(Submitted 15 January 1984)

Zh. Eksp. Teor. Fiz. **87**, 741–749 (September 1984)

Rigorous correlation rules are obtained for molecular orbitals of diatomic multielectron quasimolecules. It is shown that the previously known Barat-Lichten and Eichler-Wille rules are adiabatic and diabatic molecular-orbital correlation rules for states corresponding to identical shells in the limit of separated atoms.

**1.** Correlation diagrams in diatomic quasimolecules establish a correspondence between the energy levels of the system in the limit of separated atoms and a united one. The use of correlation diagrams for analysis of various inelastic processes that occur when slow atomic molecules collide was initiated by Fano and others,<sup>1,2</sup> who were the first to explain the mechanism whereby free electrons are produced in close atomic collision on account of the displacement of the molecular orbital (MO) and formation of vacancies in the inner shells of the colliding molecules.

The variables of the Schrödinger equations for one electron in the field of two immobile nuclei with charges  $Z_a$  and  $Z_b$  can be separated in a prolate spheroidal coordinate system. This makes it possible to obtain rigorous rules for the correspondence of the system orbitals in the limits of the separated atoms and the united one.<sup>3–7</sup> At  $Z_a = Z_b$  these relations are

$$n_0 = n_1 + 2n_2 + |m| + 1, \quad l_0 = 2n_2 + |m| \quad (1a)$$

for symmetric MO and

$$n_0 = n_1 + 2n_2 + |m| + 2, \quad l_0 = 2n_2 + |m| + 1 \quad (1b)$$

for antisymmetric MO.

Here  $n_1$  and  $n_2$  are parabolic quantum numbers that describe the MO in the limit of separated atoms, and  $n_0$ ,  $l_0$ , and  $m$  are the spherical quantum numbers of the united atom.

The correlation rules (1) are not valid for multielectron quasimolecules, for in this case the variables of the Schrödinger equations do not separate in a prolate spheroidal coordinate frame.<sup>8</sup> Barat and Lichten proposed for this case the following MO correlation rule:

$$n_r^{\text{UA}} = n_r^{\text{IA}}, \quad (2)$$

where  $n_r^{\text{UA}}$  and  $n_r^{\text{IA}}$  are, respectively, the number of zeros of the radial wave function of the electron in a united atom and an isolated atom. It was shown, however, first in Ref. 10 and later in Ref. 11, that the use of the rule (2) leads to diagrams that do not contain many quasicrossings of the MO. Eichler, Wille, *et al.*<sup>12,13</sup> proposed, on the basis of numerical calculations of the energy terms of various quasimolecules, another MO correlation rule, substantially different from (2):

$$n_r^{\text{UA}} = n_\theta^{\text{IA}}, \quad (3)$$

where  $n_\theta^{\text{IA}}$  is the number of zeros of the angular wave func-

tion of the electron in an isolated atom.

Both the Barat-Lichten rule and the Eichler-Wille rule are empirical, and their use to construct MO correlation diagrams calls for additional assumptions, since condition (2) or (3) is satisfied by an infinite set of orbitals. We obtain in this paper rigorous and unambiguous MO correlation rules for multielectron quasimolecules, and determine those assumptions with which the foregoing rules are connected.

**2.** In a multielectron quasimolecule each electron moves in an effective axisymmetric field produced by the nuclei together with all the remaining electrons. These fields are generally speaking different for different electrons of the quasimolecule and depend on the distance  $R$  between the quasimolecule nuclei.

The molecular orbitals of a multielectron quasimolecule can be made up of a generally speaking infinite number of two-center Coulomb orbitals whose correlation rules are known. If, however, the effective fields in the atoms of the quasimolecule do not differ greatly from the Coulomb fields, each orbital to which a definite principal number  $n$  corresponds can be represented in the form of a linear combination of Coulomb MO with the same value of  $n$ . The contribution of each of these Coulomb MO to the sought orbital is determined by solving a finite system of homogeneous linear equations.<sup>14</sup> This approximation is valid for electrons that fill the inner shells of the atomic particles of the quasimolecule,<sup>9</sup> for a highly excited electron located mainly far from the quasimolecule nuclei,<sup>14</sup> as well as for all electrons of light quasimolecules.

We determine below the MO of multielectron quasimolecules within the limits of the separated and united atoms. From these results we shall deduce the general MO correlation rules and obtain equations that connect the quantum numbers of the correlating atomic orbitals (AO).

**3.** Consider a quasimolecule made up of two identical atoms. The molecular orbitals of such a quasimolecule break up into symmetric and antisymmetric.<sup>7</sup> We designate the Coulomb MO by the parabolic quantum numbers  $n_1$ ,  $n_2$ , and  $m$ , where  $m$  is the projection of the orbital momentum of the electron on the axis joining the quasimolecule nuclei. We can then write for symmetric (or antisymmetric) MO

$$\Phi_{i,m}^{(\pm)}(\mathbf{r}, R) = \sum_{n_1, n_2} a_{n_1 n_2}^{(\pm)}(R) \varphi_{n_1 n_2 m}^{(\pm)}(\mathbf{r}, R), \quad (4)$$

$$i=1, 2, 3, \dots, n-|m|.$$

Here  $\varphi_{n_1 n_2 m}^{(\pm)}(\mathbf{r}, R)$  are two-center Coulomb wave functions, and the summation is over parabolic quantum numbers that meet the condition  $n_1 + n_2 + |m| + 1 = n$ , where  $n$  is the principal quantum number of the determined orbital.

It can be seen from the expansion (4) that if  $n = |m| + 1$  we have  $n_1 = n_2 = 0$  and the sought orbitals coincide with the Coulomb MO in the approximation used. Taking into account the explicit form of the Coulomb wave functions and the connection between the parabolic and spherical coordinates, these MO can be represented in the limit of the separated atoms as a linear combination of the following AO (the quasimolecule axis is assumed to be directed from the nucleus  $a$  to the nucleus  $b$ ):

$$\begin{aligned} \Phi_{1,m}^{(\pm)}(\mathbf{r}, \infty) &= \varphi_{00m}^{(\pm)}(\mathbf{r}, \infty) = \frac{1}{\sqrt{2}}(\varphi_{00m}^a \pm \varphi_{00m}^b) \\ &= \frac{1}{\sqrt{2}}(\psi_{n,|m|,m}^a \pm \psi_{n,|m|,m}^b), \end{aligned} \quad (5)$$

where  $\varphi_{00m}^{a,b}$  and  $\varphi_{nlm}^{a,b}$  are the Coulomb wave functions of an electron located in an isolated atom  $a$  and  $b$ , in parabolic and spherical coordinates, respectively.

The atomic orbitals into which the indicated MO go over are determined in the limit of the united atom from the correlation rules (1) for Coulomb orbitals:

$$\Phi_{1,m}^{(\pm)}(\mathbf{r}, 0) = \begin{cases} \varphi_{00m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+1,|m|,m} \\ \varphi_{00m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+2,|m|+1,m} \end{cases}. \quad (6)$$

Here  $\psi_{n_0 l_0 m}$  are the wave functions, in spherical coordinates, of an electron in a united atom.

Molecular orbitals with  $n = |m| + 2$  are made up of two Coulomb MO:  $\varphi_1^{(\pm)} = \varphi_{10m}^{(\pm)}(\mathbf{r}, R)$  and  $\varphi_2^{(\pm)} = \varphi_{01m}^{(\pm)}(\mathbf{r}, R)$ . For the energy terms of the quasimolecule and for the expansion coefficients in (4) we obtain in this case

$$\varepsilon_{1,2}(R) = \frac{1}{2} \{ H_{11} + H_{22} \mp [(H_{11} - H_{22})^2 + 4H_{12}^2]^{1/2} \}; \quad (7)$$

$$a_{1,0}(R) = \left\{ \frac{1}{2} \left[ 1 \mp \frac{H_{11} - H_{22}}{[(H_{11} - H_{22})^2 + 4H_{12}^2]^{1/2}} \right] \right\}^{1/2}, \quad (8a)$$

$$a_{0,1}(R) = \pm \left\{ \frac{1}{2} \left[ 1 \pm \frac{H_{11} - H_{22}}{[(H_{11} - H_{22})^2 + 4H_{12}^2]^{1/2}} \right] \right\}^{1/2}, \quad (8b)$$

where  $H_{ij}(R)$  are real matrix elements of the one-electron Hamiltonian of the system, taken over the wave functions  $\varphi_1^{(\pm)}$  and  $\varphi_2^{(\pm)}$ . These equations are valid for both symmetric and antisymmetric MO.

Recognizing that  $H_{11} = H_{22}$  in the limit of separated atoms and determining the coefficients from (8), we can write for the sought MO as  $R \rightarrow \infty$ :

$$\begin{aligned} \Phi_{1,m}^{(\pm)}(\mathbf{r}, \infty) &= \frac{1}{\sqrt{2}} \left( \frac{\varphi_{10m}^a \pm \varphi_{10m}^b}{\sqrt{2}} + \frac{\varphi_{01m}^a \pm \varphi_{01m}^b}{\sqrt{2}} \right) \\ &= \frac{1}{\sqrt{2}} (\psi_{n,|m|,m}^a \pm \psi_{n,|m|,m}^b), \\ \Phi_{2,m}^{(\pm)}(\mathbf{r}, \infty) &= \frac{1}{\sqrt{2}} \left( \frac{\varphi_{10m}^a \pm \varphi_{10m}^b}{\sqrt{2}} - \frac{\varphi_{01m}^a \pm \varphi_{01m}^b}{\sqrt{2}} \right) \\ &= \frac{1}{\sqrt{2}} (\psi_{n,|m|+1,m}^a \mp \psi_{n,|m|+1,m}^b). \end{aligned} \quad (9)$$

The notation used here is the same as in Eq. (5).

In the limit of the united atom, each of the Coulomb MO,  $\varphi_{10m}^{(\pm)}(\mathbf{r}, R)$  and  $\varphi_{01m}^{(\pm)}(\mathbf{r}, R)$ , goes over into a definite AO. As follows from (1), these AO are then different. The effective fields have in the united atom spherical symmetry, so that in this limit the off-diagonal matrix element in (8) is zero (because of the orthogonality of the electron wave functions),  $H_{11} - H_{22} < 0$ , and the sought MO go over into the following AO:

$$\begin{aligned} \Phi_{1,m}^{(\pm)}(\mathbf{r}, 0) &= \begin{cases} \varphi_{10m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+2,|m|,m} \\ \varphi_{10m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+3,|m|+1,m} \end{cases}, \\ \Phi_{2,m}^{(\pm)}(\mathbf{r}, 0) &= \begin{cases} \varphi_{01m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+3,|m|+2,m} \\ \varphi_{01m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+4,|m|+3,m} \end{cases}. \end{aligned} \quad (10)$$

Here  $\psi_{n_0 l_0 m}$  are the wave functions of the electron in the united atom and their spherical quantum numbers are determined from the correlation rules (1).

The molecular orbitals with  $n = |m| + 3$  take the form of linear combinations of the Coulomb MO, viz.,  $\varphi_1^{(\pm)} = \varphi_{20m}^{(\pm)}(\mathbf{r}, R)$ ,  $\varphi_2^{(\pm)} = \varphi_{02m}^{(\pm)}(\mathbf{r}, R)$ ,  $\varphi_3^{(\pm)} = \varphi_{11m}^{(\pm)}(\mathbf{r}, R)$ . The secular equation leads in this case to a cubic equation whose discriminant for each value of the parameter  $R$  is larger than zero (irreducible case). The cubic equation has therefore three real and different roots for each value of  $R$ .<sup>15</sup> This means that the energy terms of the sought orbitals do not cross, so that their relative placement does not change when the distance  $R$  between nuclei is changed.

In the limit of separated atoms, the following relation holds between the one-electron Hamiltonian elements taken over the wave functions  $\varphi_1^{(\pm)}$ ,  $\varphi_2^{(\pm)}$  and  $\varphi_3^{(\pm)}$

$$H_{11}^{(\pm)} = H_{22}^{(\pm)}, \quad H_{13}^{(\pm)} = H_{23}^{(\pm)}.$$

The cubic equation breaks up therefore as  $R \rightarrow \infty$  into a linear and a quadratic equation, whose solutions are

$$\begin{aligned} \varepsilon_1^{(\pm)} &= H_{33}^{(\pm)} + \left( \frac{2(|m|+2)}{|m|+1} \right)^{1/2} H_{13}^{(\pm)}, \quad \varepsilon_2^{(\pm)} = H_{11}^{(\pm)} - H_{12}^{(\pm)}, \\ \varepsilon_3^{(\pm)} &= H_{33}^{(\pm)} - \left( \frac{2(|m|+1)}{|m|+2} \right)^{1/2} H_{13}^{(\pm)}. \end{aligned} \quad (11)$$

By determining the expansion coefficients of (4) for each of these energy values, we find that in the limit of separated atoms the sought MO are linear combinations of the following AO:

$$\begin{aligned}
\Phi_{1,m}^{(\pm)}(\mathbf{r}, \infty) &= \left( \frac{|m|+2}{2(2|m|+3)} \right)^{1/2} (\varphi_{20m}^{(\pm)} + \varphi_{02m}^{(\pm)}) \\
&\quad + \left( \frac{|m|+1}{2|m|+3} \right)^{1/2} \varphi_{11m}^{(\pm)} - \\
&= \frac{1}{\sqrt{2}} (\psi_{n,|m|,m}^a \pm \psi_{n,|m|,m}^b), \\
\Phi_{2,m}^{(\pm)}(\mathbf{r}, \infty) &= \frac{1}{\sqrt{2}} (\varphi_{20m}^{(\pm)} - \varphi_{02m}^{(\pm)}) = \frac{1}{\sqrt{2}} (\psi_{n,|m|+1,m}^a \mp \psi_{n,|m|+1,m}^b), \\
\Phi_{3,m}^{(\pm)}(\mathbf{r}, \infty) &= \left( \frac{|m|+1}{2(2|m|+3)} \right)^{1/2} (\varphi_{20m}^{(\pm)} + \varphi_{02m}^{(\pm)}) \\
&\quad - \left( \frac{|m|+2}{2|m|+3} \right)^{1/2} \varphi_{11m}^{(\pm)} \\
&= \frac{1}{\sqrt{2}} (\psi_{n,|m|+2,m}^a \pm \psi_{n,|m|+2,m}^b).
\end{aligned} \tag{12}$$

In the limit of a united atom, owing to the spherical symmetry of the field and to the orthogonality of the angular wave functions of the electrons, the off-diagonal matrix elements of the one-electron Hamiltonian are zero (in analogy with the preceding case with  $n = |m| + 2$ ). The cubic equation breaks up then into three linear equations with roots  $\varepsilon_1^{(\pm)} = H_{11}^{(\pm)}$ ,  $\varepsilon_2^{(\pm)} = H_{33}^{(\pm)}$  and  $\varepsilon_3^{(\pm)} = H_{22}^{(\pm)}$ . Therefore each of the MO goes over as  $R \rightarrow 0$  into a Coulomb orbital whose connection with the AO is determined by the correlation rules (1):

$$\Phi_{1,m}^{(\pm)}(\mathbf{r}, 0) = \begin{cases} \varphi_{20m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+3,|m|,m} \\ \varphi_{20m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+4,|m|+1,m} \end{cases}, \tag{13}$$

$$\Phi_{2,m}^{(\pm)}(\mathbf{r}, 0) = \begin{cases} \varphi_{11m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+4,|m|+2,m} \\ \varphi_{11m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+5,|m|+3,m} \end{cases},$$

$$\Phi_{3,m}^{(\pm)}(\mathbf{r}, 0) = \begin{cases} \varphi_{02m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+5,|m|+4,m} \\ \varphi_{02m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+6,|m|+5,m} \end{cases}.$$

The molecular orbitals with  $n = |m| + 4$  are constructed of four Coulomb MO:  $\varphi_1^{(\pm)} = \varphi_{30m}^{(\pm)}(\mathbf{r}, R)$ ,  $\varphi_2^{(\pm)} = \varphi_{03m}^{(\pm)}(\mathbf{r}, R)$ ,  $\varphi_3^{(\pm)} = \varphi_{21m}^{(\pm)}(\mathbf{r}, R)$  and  $\varphi_4^{(\pm)} = \varphi_{12m}^{(\pm)}(\mathbf{r}, R)$ . The secular equation leads in this case to a fourth-degree equation with four real and different roots for each value of  $R$ .<sup>15</sup> Using the symmetry of the Coulomb parabolic functions, we can show that in the limit of the separated atoms this equation breaks up into two quadratic equations with solutions

$$\begin{aligned}
\varepsilon_1^{(\pm)} &= H_{11}^{(\pm)} + H_{12}^{(\pm)} + \left( \frac{3(|m|+1)}{|m|+3} \right)^{1/2} (H_{13}^{(\pm)} + H_{14}^{(\pm)}), \\
\varepsilon_2^{(\pm)} &= H_{11}^{(\pm)} - H_{12}^{(\pm)} + \left( \frac{|m|+1}{3(|m|+3)} \right)^{1/2} (H_{13}^{(\pm)} - H_{14}^{(\pm)}), \\
\varepsilon_3^{(\pm)} &= H_{11}^{(\pm)} + H_{12}^{(\pm)} - \left( \frac{|m|+3}{3(|m|+1)} \right)^{1/2} (H_{13}^{(\pm)} + H_{14}^{(\pm)}), \\
\varepsilon_4^{(\pm)} &= H_{11}^{(\pm)} - H_{12}^{(\pm)} - \left( \frac{3(|m|+3)}{|m|+1} \right)^{1/2} (H_{13}^{(\pm)} - H_{14}^{(\pm)}).
\end{aligned} \tag{14}$$

After determining for each of these energy values the expansion coefficients in (4), we get for the sought MO as  $R \rightarrow \infty$

$$\begin{aligned}
\Phi_{1,m}^{(\pm)} &= \frac{1}{2} \left[ \left( \frac{|m|+3}{2|m|+3} \right)^{1/2} (\varphi_{30m}^{(\pm)} + \varphi_{03m}^{(\pm)}) \right. \\
&\quad \left. + \left( \frac{3(|m|+1)}{2|m|+3} \right)^{1/2} (\varphi_{21m}^{(\pm)} + \varphi_{12m}^{(\pm)}) \right] \\
&= \frac{1}{\sqrt{2}} (\psi_{n,|m|,m}^a \pm \psi_{n,|m|,m}^b), \\
\Phi_{2,m}^{(\pm)} &= \frac{1}{2} \left[ \left( \frac{3(|m|+3)}{2|m|+5} \right)^{1/2} (\varphi_{30m}^{(\pm)} - \varphi_{03m}^{(\pm)}) \right. \\
&\quad \left. + \left( \frac{|m|+1}{2|m|+5} \right)^{1/2} (\varphi_{21m}^{(\pm)} - \varphi_{12m}^{(\pm)}) \right] \\
&= \frac{1}{\sqrt{2}} (\psi_{n,|m|+1,m}^a \mp \psi_{n,|m|+1,m}^b), \\
\Phi_{3,m}^{(\pm)} &= \frac{1}{2} \left[ \left( \frac{3(|m|+1)}{2|m|+3} \right)^{1/2} (\varphi_{30m}^{(\pm)} + \varphi_{03m}^{(\pm)}) \right. \\
&\quad \left. - \left( \frac{|m|+3}{2|m|+3} \right)^{1/2} (\varphi_{21m}^{(\pm)} + \varphi_{12m}^{(\pm)}) \right] \\
&= \frac{1}{\sqrt{2}} (\psi_{n,|m|+2,m}^a \pm \psi_{n,|m|+2,m}^b), \\
\Phi_{4,m}^{(\pm)} &= \frac{1}{2} \left[ \left( \frac{|m|+1}{2|m|+5} \right)^{1/2} (\varphi_{30m}^{(\pm)} - \varphi_{03m}^{(\pm)}) \right. \\
&\quad \left. - \left( \frac{3(|m|+3)}{2|m|+5} \right)^{1/2} (\varphi_{21m}^{(\pm)} - \varphi_{12m}^{(\pm)}) \right] \\
&= \frac{1}{\sqrt{2}} (\psi_{n,|m|+3,m}^a \mp \psi_{n,|m|+3,m}^b).
\end{aligned} \tag{15}$$

In the limit of the united atom, the off-diagonal matrix elements are zero, and the fourth-degree equation breaks up into linear equations with roots  $\varepsilon_1^{(\pm)} = H_{11}^{(\pm)}$ ,  $\varepsilon_2^{(\pm)} = H_{33}^{(\pm)}$ ,  $\varepsilon_3^{(\pm)} = H_{44}^{(\pm)}$  and  $\varepsilon_4^{(\pm)} = H_{22}^{(\pm)}$ . Therefore the MO go over in this limit into the following AO:

$$\begin{aligned}
\Phi_{1,m}^{(\pm)}(\mathbf{r}, 0) &= \begin{cases} \varphi_{30m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+4,|m|,m} \\ \varphi_{30m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+5,|m|+1,m} \end{cases}, \\
\Phi_{2,m}^{(\pm)}(\mathbf{r}, 0) &= \begin{cases} \varphi_{21m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+5,|m|+2,m} \\ \varphi_{21m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+6,|m|+3,m} \end{cases}, \\
\Phi_{3,m}^{(\pm)}(\mathbf{r}, 0) &= \begin{cases} \varphi_{12m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+6,|m|+4,m} \\ \varphi_{12m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+7,|m|+5,m} \end{cases}, \\
\Phi_{4,m}^{(\pm)}(\mathbf{r}, 0) &= \begin{cases} \varphi_{03m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+7,|m|+6,m} \\ \varphi_{03m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+8,|m|+7,m} \end{cases}.
\end{aligned} \tag{16}$$

The molecular orbitals with  $n = |m| + i$ , where  $i = 5, 6, \dots$  are made up respectively of five, six, etc., Coulomb MO. We shall not present the equations for these orbitals, since they are correlated in accord with the same rules as the orbitals considered above.

The equations presented confirm that in symmetric (or homonuclear) multielectron quasimolecules the relations between the quantum numbers of the correlating MO are  $n_r^{UA} = n_r^{IA}$ ,  $n_\theta^{UA} = 2n_\theta^{IA}$  for symmetric orbitals and  $n_r^{UA} = 2n_\theta^{IA} + 1$  for antisymmetric orbitals, where  $n_\theta^{UA}$  is the

number of zeros of the angular wave function of the electron in the united atom. The first of these relations coincides with the condition proposed in Ref. 9 for MO correlation. The relations obtained determine uniquely the state of the united atom into which each of the state of an isolated atom goes over in the limit of joining of the quasimolecule nuclei:

$$n_0 = n + l - |m|, \quad l_0 = 2l - |m| \quad (17)$$

for symmetric MO and

$$n_0 = n + l - |m| + 1, \quad l_0 = 2l - |m| + 1 \quad (18)$$

for antisymmetric MO.

It can be seen from (17) and (18) that the terms with like  $n$  and  $m$  but with different  $l$  do not cross, so that the obtained MO correlation rules are adiabatic for these states.

4. In the foregoing construction of the MO we did not take into account the behavior of the Coulomb terms as functions of the distance  $R$  between the nuclei. At large  $R$  (noticeably exceeding the effective length of the AO) the positions of these terms are determined mainly by the linear Stark effect. For given  $n$  and  $m$ , the Coulomb terms with larger  $n_2$  lie below the terms with the smaller  $n_2$  (Ref. 7). It follows from Eqs. (1) that in the limit of the unit atom the higher of these terms are those corresponding to larger  $n_2$ . Therefore Coulomb terms with identical  $n$  and  $m$  but with different  $n_2$  cross at finite  $R$ .

In the region where the Coulomb levels cross, the one-electron terms of a multielectron quasimolecule come very close together (it is assumed that the effective fields in the quasimolecule differ little from the field of two Coulomb centers). If the quasicrossings of the terms are regarded as crossings, each molecular orbital with given  $n$ ,  $l$ , and  $m$  constructed above in the limit of separated atoms will correspond to an AO different than the one that follows from Eqs. (17) and (18).

It is easily seen that in this case the MO (9) with  $n = |m| + 2$  go over in the limit of the united atom into the following AO:

$$\Phi_{1,m}^{(\pm)}(\mathbf{r}, 0) = \begin{cases} \varphi_{01m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+3, |m|+2, m} \\ \varphi_{01m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+4, |m|+3, m} \end{cases}, \quad (19)$$

$$\Phi_{2,m}^{(\pm)}(\mathbf{r}, 0) = \begin{cases} \varphi_{10m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+2, |m|, m} \\ \varphi_{10m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+3, |m|+1, m} \end{cases},$$

and the MO with  $n = |m| + 3$  are transformed as  $R \rightarrow 0$  into the following orbital of the united atom:

$$\Phi_{1,m}^{(\pm)}(\mathbf{r}, 0) = \begin{cases} \varphi_{02m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+5, |m|+4, m} \\ \varphi_{02m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+6, |m|+5, m} \end{cases}, \quad (20)$$

$$\Phi_{2,m}^{(\pm)}(\mathbf{r}, 0) = \begin{cases} \varphi_{11m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+4, |m|+2, m} \\ \varphi_{11m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+5, |m|+3, m} \end{cases},$$

$$\Phi_{3,m}^{(\pm)}(\mathbf{r}, 0) = \begin{cases} \varphi_{20m}^{(+)}(\mathbf{r}, 0) = \psi_{|m|+3, |m|, m} \\ \varphi_{20m}^{(-)}(\mathbf{r}, 0) = \psi_{|m|+4, |m|+1, m} \end{cases}.$$

We shall not present the equations for the AO into which the MO with  $n = |m| + 4$ ,  $|m| + 5$ , ..., etc., go over as

$R \rightarrow 0$ , since these orbitals are correlated in accordance with the same rules as the considered MO. As for the molecular orbitals with  $n = |m| + 1$ , their correlation is determined by Eqs. (5) and (6).

It can be seen from the equations above as well as from (5) and (6) that if the quasicrossings of the terms are regarded as crossings, the MO that correlate are those whose quantum numbers satisfy the relations  $n_r^{\text{UA}} = n_\theta^{\text{IA}}$ ,  $n_\theta^{\text{UA}} = 2n_r^{\text{IA}}$  for symmetric orbitals and  $n_\theta^{\text{UA}} = 2n_r^{\text{IA}} + 1$  for antisymmetric orbitals. The first of these relations coincides with the MO correlation condition proposed in Ref. 13.

The relations obtained determine uniquely the united-atom state into which of the states of the isolated atom goes over in the limit of unification of the quasimolecule nuclei:

$$n_0 = 2n - l - 1, \quad l_0 = 2n - 2l + |m| - 2 \quad (21)$$

for symmetric MO and

$$n_0 = 2n - l, \quad l_0 = 2n - 2l + |m| - 1 \quad (22)$$

for antisymmetric MO.

The rules (21) and (22) are the diabatic MO-correlation rules.

5. We consider now a quasimolecule made up of two different atoms and assume that the effective fields in which the electrons are located in each of the atoms differ little from one another and from the Coulomb field. The molecular orbitals of such a quasimolecule do not break up into symmetric and antisymmetric. Since the atoms are different, the quasimolecule levels that are doubly degenerate at given  $n$ ,  $l$ , and  $m$  split in the limit of separated atoms.

We represent the sought MO in the form

$$\Phi_{j,m}(\mathbf{r}, R) = a_i^{(+)}(R) \Phi_{i,m}^{(+)}(\mathbf{r}, R) + a_i^{(-)}(R) \Phi_{i,m}^{(-)}(\mathbf{r}, R), \quad (23)$$

$$j = 1, 2,$$

where  $\Phi_{i,m}^{(+)}(\mathbf{r}, R)$  and  $\Phi_{i,m}^{(-)}(\mathbf{r}, R)$  are the symmetric and antisymmetric MO defined in (4). Assume that the one-electron levels of the atom  $a$  are below the corresponding levels of the atom  $b$ . To determine the expansion coefficients in (23) we can use the equations of the two-center approximation (8), where  $H_{ij}(R)$  are matrix elements of the one-electron Hamiltonian of the quasimolecule, taken over the wave functions  $\varphi_1 = \Phi_{i,m}^{(+)}(\mathbf{r}, R)$  and  $\varphi_2 = \Phi_{i,m}^{(-)}(\mathbf{r}, R)$ .

In the limit of separated atoms we have  $H_{11} = H_{22}$  and the MO go over into the following AO:

$$\Phi_{1,m}(\mathbf{r}, \infty) = \frac{1}{\sqrt{2}} (\Phi_{i,m}^{(+)} + \Phi_{i,m}^{(-)}) = \psi_{n,l,m}^a, \quad (24)$$

$$\Phi_{2,m}(\mathbf{r}, \infty) = \frac{1}{\sqrt{2}} (\Phi_{i,m}^{(+)} - \Phi_{i,m}^{(-)}) = \psi_{n,l,m}^b,$$

where  $\psi_{n,l,m}^a$  and  $\psi_{n,l,m}^b$  are the wave functions of the electron in the isolated atoms  $a$  and  $b$ .

In the united-atom limit, owing to the spherical symmetry of the field and to the orthogonality of the angular wave functions of the electron, the off-diagonal matrix element in (8) is zero,  $H_{11} - H_{22} < 0$ , and we can write for the MO

$$\begin{aligned}\Phi_{1,m}(\mathbf{r}, 0) &= \Phi_{i,m}^{(+)}(\mathbf{r}, 0) = \psi_{n_0, l_0, m}, \\ \Phi_{2,m}(\mathbf{r}, 0) &= \Phi_{i,m}^{(-)}(\mathbf{r}, 0) = \psi_{n_0', l_0', m},\end{aligned}\quad (25)$$

where the spherical quantum numbers  $n_0$  and  $l_0$  are connected with the quantum numbers  $n$ ,  $l$ , and  $m$  by relation (18) or (22).

It follows from the obtained equations that the correlation rules of MO of an asymmetric molecule coincide with rules (17) and (18). If the quasicrossings of the terms are regarded as crossings these rules coincide with the (21) and (22). Relation (17) or (21) should be used for the orbitals of an atom whose energy levels lie lower, and (17) or (21) for higher levels.

The authors thank O. B. Firsov, Yu. N. Demkov, and M. I. Chibisov for a discussion of the results derived in the paper.

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Translated by J. G. Adashko