Molecular-orbital diabatic correlation diagrams of diatomic quasimolecules

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The effective charges of the atomic cores are calculated for quasimolecules made up of two different atoms with a degree of asymmetry $\mu = Z_a/Z_b < 4.7$, where Z_a is the atomic number of the heavy atom, and $Z_b > 20$ is that of the light atom. Correlation diagrams are constructed for the molecular orbitals of these quasimolecules. The consecutive correlation rule (the swapping rule) proposed by Barat and Lichten [Phys. Rev. A **6**, 211 (1972)] for molecular orbitals is not universally applicable. It is violated in the case of orbitals with identical n_r (or n_θ) which are close in energy. Correlation rules found here for diabatic molecular orbitals incorporate the fine structure of the levels of the quasimolecule.

The present paper is a continuation of Ref. 1, where correlation rules were found for diabatic molecular orbitals (MOs) for the inner-shell electrons of diatomic many-electron quasimolecules.

As the atoms making up a quasimolecule move closer together, the diabatic development of the MOs is determined by the effective fields acting on the electrons in the separate atoms. Determining the correlated orbitals in diatomic quasimolecules thus requires determining the effective fields in the constituent atoms.

In the present paper we calculate the effective charges of the atomic cores whose field is imposed on the electron after the atoms separate from each other. Calculations are carried out for heavy and intermediate-size quasimolecules formed from two different atoms. With these results it is possible to use the rules found in Ref. 1 to construct correlation diagrams for the MOs of a large number of quasimolecules. A comparison of these diagrams with diagrams constructed in accordance with the rules of Barat and Lichten[2] and those of Eichler *et al.*[3] shows that the empirical rule of a consecutive correlation of MOs (the "swapping rule") is not of universal applicability. In certain cases it is violated. To confirm this fact, we calculate the cross sections for charge exchange of protons with Mg^+ ions on the basis of two different models, and we compare the results with experimental data.

We derive correlation rules for diabatic MOs of diatomic many-electron quasimolecules. These rules incorporate the fine structure of the levels of the system.

1. For the case in which the shells of the atoms making up the quasimolecule lie close together along the energy scale, the effective molecular potential in that region of internuclear distances R in which the orbitals corresponding to these shells overlap can be written as a superposition of the fields acting on the electrons in each of the individual atoms. (We are using the atomic system of units):

$$V_{\text{eff}} = -\frac{Z_a^*}{r_a} - \frac{Z_b^*}{r_b} + v_a(r_a) + v_b(r_b). \qquad (1)$$

Here Z_a and Z_b ($Z_a^* \geqslant Z_b^*$) are the effective charges of the atomic cores, r_a and r_b are the distances from the electron to these cores, and v_a and v_b are spherically symmetric potentials which incorporate the difference between (on the one hand) the effective fields in the atoms and (on the other) a purely Coulomb field.

Using effective potential (1) for all internuclear distances R, we construct two different correlation rules for diabatic MOs in Ref. 1. According to the first of these rules, the quantum numbers of the correlating orbitals are related by

$$\left.\begin{array}{l} n_0 = n, \\ l_0 = l \end{array}\right\} \quad \text{for} \quad l - |m| < n\frac{Z_a^* - Z_b^*}{Z_a^*},$$

$$\left.\begin{array}{l} n_0 = n + 1 + \mathrm{Ent}\left(l - |m| - n\dfrac{Z_a^* - Z_b^*}{Z_a^*}\right), \\[2ex] l_0 = l + 1 + \mathrm{Ent}\left(l - |m| - n\dfrac{Z_a^* - Z_b^*}{Z_a^*}\right) \end{array}\right| \qquad (2)$$

$$\text{for} \quad l - |m| \geqslant n\frac{Z_a^* - Z_b^*}{Z_a^*}$$

for MOs which convert into the orbitals of the heavy atom in the limit $R \to \infty$ and

$$\left.\begin{array}{l} n_0 = n' + 1 + \mathrm{Ent}\left(l' - |m| + n'\dfrac{Z_a^* - Z_b^*}{Z_b^*}\right), \\[2ex] l_0 = l' + 1 + \mathrm{Ent}\left(l' - |m| + n'\dfrac{Z_a^* - Z_b^*}{Z_b^*}\right) \end{array}\right|$$

$$\text{for noninteger} \quad n'\frac{Z_a^*}{Z_b^*},$$

$$\left.\begin{array}{l} n_0 = l' - |m| + n'\dfrac{Z_a^*}{Z_b^*}, \\[2ex] l_0 = 2l' - |m| + n'\dfrac{Z_a^* - Z_b^*}{Z_b^*} \end{array}\right\} \qquad (3)$$

$$\text{for integer} \quad n'\frac{Z_a^*}{Z_b^*}$$

for MOs which convert into the orbitals of the light atom as $R \to \infty$.

According to the second of these rules, the orbitals

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which are correlated are those whose quantum numbers are related by

$$\left.\begin{array}{r} n_0=n, \\ l_0=n_r+|m| \end{array}\right\} \quad \text{for} \quad n_r<n\frac{Z_a^*-Z_b^*}{Z_a^*},$$

$$\left.\begin{array}{r} n_0=n+1+\mathrm{Ent}\left(n_r-n\dfrac{Z_a^*-Z_b^*}{Z_a^*}\right), \\ l_0=n_r+|m|+1+\mathrm{Ent}\left(n_r-n\dfrac{Z_a^*-Z_b^*}{Z_a^*}\right) \end{array}\right\} \tag{4}$$

$$\text{for} \quad n_r\geqslant n\frac{Z_a^*-Z_b^*}{Z_a^*}$$

for the MOs which become the orbitals of the heavy atom as $R\to\infty$ and

$$\left.\begin{array}{r} n_0=n'+1+\mathrm{Ent}\left(n_r'+n'\dfrac{Z_a^*-Z_b^*}{Z_b^*}\right), \\ l_0=n_r'+|m|+1+\mathrm{Ent}\left(n_r'+n'\dfrac{Z_a^*-Z_b^*}{Z_b^*}\right) \end{array}\right\}$$

$$\text{for noninteger} \quad n'\frac{Z_a^*}{Z_b^*} \tag{5}$$

$$\left.\begin{array}{r} n_0=n_r'+n'\dfrac{Z_a^*}{Z_b^*}, \\ l_0=2n_r'+|m|+n'\dfrac{Z_a^*-Z_b^*}{Z_b^*} \end{array}\right\} \quad \text{for integer} \quad n'\frac{Z_a^*}{Z_b^*}$$

for MOs which become the orbitals of the light atom as $R\to\infty$. Here n_0, l_0, and m are the spherical quantum numbers of the bound atom obtained when the nuclei are extremely close together; n, l and n', l' are the spherical quantum numbers of the separate atoms; $n_r = n - l - 1$ and $n_r' = n' - l'1$ are the radial quantum numbers; and $\mathrm{Ent}(x)$ is the greatest integer in x.

Rules (4) and (5) describe the behavior of one-electron terms in very heavy quasimolecules, in which the effective fields for the inner-shell electron differ only slightly from the field of two Coulomb centers. These rules lead to maximum promotion and lowering of the energy terms belonging to a given shell. Rules (2) and (3) give a good description of the behavior of the terms in quasimolecules which are not very heavy, in which the effective fields for the inner-shell electrons do not closely approximate the field of two Coulomb centers. These rules differ from rules (4) and (5) by an interchange of the correlation (Fig. 1).

2. The non-Coulomb potentials v_a and v_b in (1) can be approximated by various analytic expressions. For example, Eichler and Wille[4] used the Thomas-Fermi model to determine the charge and field distributions in the atoms making up a quasimolecule. In the present paper we write the non-Coulomb potentials in (1) in the form $v_a = \alpha_a/r_a^2$ and $v_b = \alpha_b/r_b^2$. Our motivation for making this choice is that the Schrödinger equation for the potential $-Z^*/r + \alpha/r^2$ can be solved exactly by analytic methods, and this potential gives a good description of the energy spectrum of the inner-shell electrons of many-electron atoms.

The energy levels of an electron moving in a spherically symmetric field with a potential energy $-Z^*/r + \alpha/r^2$ are given by[5]

$$E_{n_r} = -\frac{Z^{*2}}{2(n_r+s_l)^2}, \tag{6}$$

where $s_l = \frac{1}{2}\left[(l+\frac{1}{2})^2+2\alpha\right]^{1/2}$. To determine the effective charge Z^* and the parameter α, we fit the energy levels in (6) to the one-electron levels of the atoms making up a quasimolecule as calculated by the Hartree-Fock self-consistent-field method.[6,7]

It is a simple matter to fit energy levels (6) to the K-shell levels of atoms. In this case we can set $\alpha = 0$; we then have $Z^* = (-2E_{1s})^{1/2}$. Once we have specified the value of Z^* for L shells of atoms, we determine the parameter α by requiring that (6) (with $l = 0$ and $n_r = 1$) coincide with the energy of the $2s$ level of the atom. Using these values of Z^* and α, we then use (6) (now with $l = 1$ and $n_r = 0$) to calculate the energy of the next level. From the set of various values of Z^* we choose the value which is most successful in reproducing the energy of the atomic $2p$ level. For a shell with more than two levels (the M, N, etc., shells), the effective charge Z_a^* is found by fitting the levels in (6) to those atomic levels which lie closest to the levels of the other atom of the quasimolecule, which determine the effective charge Z_b^*.

Using this approach, we have calculated the effective charges for the inner shells of quasimolecules made up of two different atoms with a degree of asymmetry $\mu = Z_a/Z_b < 4.7$ (Z_a is the atomic number of the heavy atom, and $Z_b > 20$ is that of the light atom). The results of these calculations are given in Tables I and II. From the results in these tables and the degree of asymmetry μ, we can determine the following quantities, which appear in the rules (2), (3) and (4), (5):

$$n\frac{Z_a^*-Z_b^*}{Z_a^*}, \quad n'\frac{Z_a^*-Z_b^*}{Z_b^*}.$$

We can then go on to identify the correlated MOs in the quasimolecule of interest, made up of either two neutral atoms or positive ions. These tables can legitimately be used for charged quasimolecules because the removal of one, two, or several outer electrons causes only slight changes in the values of the Hartree-Fock energies for the inner-shell electrons of many-electron atoms.[8]

From these tables we can draw a conclusion of practical importance: If the degree of asymmetry of the atoms making up the quasimolecule satisfies $\mu \leqslant 1.66$, the correlation of the MOs does not depend on the effective charges of the atomic cores. This correlation is governed by the correlation rules for slightly asymmetric quasimolecules.[9] (It follows in particular that in order to analyze the formation of vacancies in inner electron shells of the fragments during the fission of the nuclei of heavy elements[10] it is necessary to use the MO correlation diagram for slightly asymmetric quasimolecules,[11] since the condition $\mu < 1.66$ holds for all the fission products.[12])

For symmetric and slightly asymmetric quasimolecules, the correlation diagrams constructed by rules (2), (3) and (4), (5) are precisely the same as those constructed by

TABLE I. The quantity $n(Z_a^* - Z_b^*)/Z_a^*$ for quasimolecules made up of two different atoms.

n	$0 < n \frac{\overset{*}{Z_a} - \overset{*}{Z_b}}{\overset{*}{Z_a}} \leqslant 1$	$1 < n \frac{\overset{*}{Z_a} - \overset{*}{Z_b}}{\overset{*}{Z_a}} \leqslant 2$	$2 < n \frac{\overset{*}{Z_a} - \overset{*}{Z_b}}{\overset{*}{Z_a}} \leqslant 3$	$3 < n \frac{\overset{*}{Z_a} - \overset{*}{Z_b}}{\overset{*}{Z_a}} \leqslant 4$
1	$\mu > 1$	—	—	—
2	$1 < \mu \leqslant 2{,}48$	$\mu > 2{,}48$	—	—
3	$1 < \mu \leqslant 1{,}85$	$1{,}85 < \mu \leqslant 4{,}5$	$\mu > 4{,}5$	—
4	$1 < \mu \leqslant 1{,}66$	$1{,}66 < \mu \leqslant 3{,}4$	$3{,}4 < \mu \leqslant ?$	$\mu > ?$

the Barat-Lichten and Eichler-Wille rules. For asymmetric quasimolecules, the correlations found for MOs belonging to different atoms at $R = \infty$, with identical values of n_r (or n_θ), from rules (2), (3) [or (4), (5)] are often not the same as those found from the Barat-Lichten (or Eichler-Wille) rules. These differences arise when the energy levels of the separate atoms corresponding to these MOs are nearly in resonance.

According to the Barat-Lichten rules, the MOs which are correlated are those whose quantum numbers satisfy the condition $n_r^{\mathrm{OA}} = n_r^{\mathrm{PA}}$, where n_r^{OA} is the number of zeros of the radial wave function of the electron in the combined atom, and n_r^{PA} is the corresponding number in the separate atom. According to the Eichler and Wille rules, on the other hand, the quantum numbers of the correlated MOs must satisfy the condition $n_r^{\mathrm{OA}} = n_\theta^{\mathrm{PA}}$, where n_θ^{PA} is the number of zeros of the angular wave function of the electron in the separate atom. The rules $n_r^{\mathrm{OA}} = n_r^{\mathrm{PA}}$ (or $n_r^{\mathrm{OA}} = n_\theta^{\mathrm{PA}}$) are not sufficient to unambiguously determine the correlated MOs. For this reason, both Barat and Lichten, on the one hand, and Eichler and Wille, on the other, introduce an auxiliary empirical rule. According to the latter rule, each energy level of the individual atoms, starting from the lowest, is correlated with the lowest unoccupied level of the combined atom which satisfies the condition $n_r^{\mathrm{OA}} = n_r^{\mathrm{PA}}$ (or $n_r^{\mathrm{OA}} = n_\theta^{\mathrm{PA}}$).

The correlation swapping rule for MOs requires going from the limit of separate atoms to the limit of the combined atom without disrupting the arrangement of levels with identical n_r (or n_θ). According to rules (2), (3) and (4), (5), in contrast, a low-lying level of the separate atom can correlate with a high-lying level of the combined atom; the same is true of a high-lying level of the separate atom with a low-lying of the combined atom. For the orbitals of the combined atom which correlate with orbitals of the separate atoms with identical n_r (or n_θ), rules (2), (3) [or (4), (5)] lead to the same results as are found by the Barat-Lichten (or Eichler-Wille) rules. The reason is that rules (2), (3) and (4), (5) contain the Barat-Lichten and Eichler-Wille rules [as can be verified easily by subtracting the second equation from the first in (2), (3) and again in (4), (5)].

To illustrate the violation of the MO swapping rule we consider the behavior of the $3d\sigma$ orbital of the Al^{++} ion ($2p^6 3d$) and that of the $3s\sigma$ orbital of the Mg^+ ion ($2p^6 3s$) in $(\mathrm{AlH})^{+++}$ and $(\mathrm{MgH})^{++}$ quasimolecules. The $3d$ levels ($n_r = 0$, $E = -0.517$ a.u.; Ref. 13) and $3s$ levels ($n_\theta = 0$, $E = -0.525$ a.u.; Ref. 13) are nearly in resonance with the $1s$ level ($n_r = n_\theta = 0$, $E = -0.5$ a.u.) of the hydrogen atom. Fitting levels (6) to the $3p$ level ($E = -0.801$ a.u.; Ref. 13) and the $3d$ level of the Al^{++} ion and also to the $3s$ and $3p$ levels ($E = -0.390$ a.u.; Ref. 13) of the Mg^+ ion, we find $Z_a^* = 2.628$, $\alpha = -0.959$ for the aluminum ion and $Z_a^* = 2.627$, $\alpha = -0.125$ for the magnesium ion. For the hydrogen atom the corresponding values are $Z_b^* = 1$, $\alpha = 0$.

Figure 1 shows diabatic correlation diagrams constructed for MOs from rules (2), (3) for the $(\mathrm{AlH})^{+++}$ quasimolecule and from rules (4), (5) for the $(\mathrm{MgH})^{++}$ quasimolecule. [The correlation of the $3s\sigma$ orbital of the Al^{++} ion in the $(\mathrm{AlH})^{+++}$ quasimolecule and the correlation of the $3d\sigma$ orbital of the Mg^+ ion in the $(\mathrm{MgH})^{++}$ quasimolecule are determined from the first equations in (2) and (4). For this reason, the correlation of these orbitals does not depend on the effective charges, whose values are found by fitting levels (6) to the levels corresponding to the other orbitals of the M shell.] The behavior of the terms according to the MO swapping rule is illustrated by the dashed lines in Fig. 1. We see that this rule leads to an additional crossing of terms at intermediate internuclear distances (at large distances, there is a term crossing as a result of a difference between the charges of the ions).

The effective fields acting on the electron of interest in the $(\mathrm{AlH})^{+++}$ and $(\mathrm{MgH})^{++}$ quasimolecules are approximately the same as the field of two Coulomb centers. Consequently, the behavior of the diabatic MOs of the electron of interest at intermediate internuclear distances should be the same as the behavior of two-center Coulomb MOs in this region. Analysis of the energy terms of an electron in the

TABLE II. The quantity $n'(Z_a^* - Z_b^*)/Z_b^*$ for quasimolecules made up of two different atoms.

n'	$0 < n' \frac{\overset{*}{Z_a} - \overset{*}{Z_b}}{\overset{*}{Z_b}} < 1$	$1 \leqslant n' \frac{\overset{*}{Z_a} - \overset{*}{Z_b}}{\overset{*}{Z_b}} < 2$	$2 \leqslant n' \frac{\overset{*}{Z_a} - \overset{*}{Z_b}}{\overset{*}{Z_b}} < 3$
1	$1 < \mu \leqslant 2{,}48$	$2{,}48 < \mu \leqslant 4{,}5$	$4{,}5 < \mu \leqslant ?$
2	$1 < \mu \leqslant 1{,}85$	$1{,}85 < \mu \leqslant 3{,}4$	$3{,}4 < \mu \leqslant 3{,}9$
3	$1 < \mu \leqslant 1{,}66$	$1{,}66 < \mu \leqslant 1{,}9$	$1{,}9 < \mu \leqslant 2{,}1$

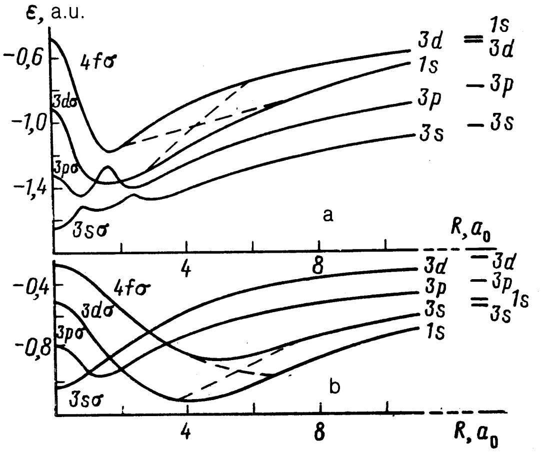

FIG. 1. Diabatic correlation diagrams of MOs. a—Constructed from rules (2) and (3) for an $(AlH)^{+++}$ quasimolecule; b—calculated from rules (4) and (5) for an $(MgH)^{++}$ quasimolecule. Only the σ terms are shown.

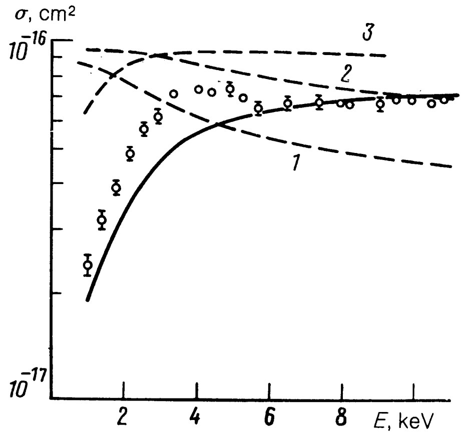

FIG. 2. Cross sections for the charge exchange of protons with Mg^+ ions. Solid line: Calculated from the Rosen-Zener model. Dashed lines: Calculated from the Landau-Zener model. 1—$\tau = 0.05$; 2—$\tau = 0.1$; 3—$\tau = 0.2$.

field of two nuclei with charges $Z_a = 3$ and $Z_b = 1$ (Ref. 14) shows that the $3d\sigma$ and $4f\sigma$ terms (classified in accordance with the quantum numbers of the combined atom do not cross in the region $R = (3\text{–}6)a_0$.

It is important to determine the true correlation of MOs in quasimolecules made up of hydrogen atoms and the ions of metal atoms. The reason is that the behavior of the MOs of these quasimolecules determines the mechanism for the neutralization of protons by positive atomic impurity ions in a thermonuclear hydrogen plasma. There is a high probability that this neutralization will allow fast hydrogen atoms to escape from the plasma to the wall. This escape is the reason for the sputtering of the wall material.[15]

Figure 2 shows the cross section for the charge-exchange of protons with Mg^+ ions as calculated in the rectilinear-path approximation in the c.m. frame. The exchange interaction is found from

$$\Delta(R) = AR^{2/\gamma}\exp[-R(1+\gamma)/2],$$

where

$$\gamma = (-2E_{Mg^+})^{1/2},\quad A = 2a\exp\left(-\frac{1}{2}-\frac{1}{\gamma}\right)$$

(Ref. 16) and $a = 2.4$ (Ref. 15). The transition goes by the Rosen-Zener mechanism with a probability

$$W = {}^1/_2\,\mathrm{ch}^{-2}(\pi\varkappa(R_1)/2\gamma v_R)$$

(v_R is the radial velocity of the motion[17]), near the point $R_1 = 4.9a_0$, where $\Delta(R)$ becomes equal to $\chi(R)$, which is the difference between the terms of the initial and final states of the system. (Transitions are unlikely at small values of R, since the system passes through this region diabatically at the collision velocities under consideration here. In the asymptotic region, the charge-exchange cross section calculated in the Landau-Zener approximation near the term crossing point $R_0 = 19.01a_0$ is negligibly small.[18])

Under the assumption that terms cross at the point $R = R_1$ in the region of intermediate internuclear distances, we have calculated the charge-exchange cross sections from the Landau-Zener model. The probability for a transition during one passage through the crossing point is found from

$$w = \exp(-\tau/v_R),$$

where the parameter τ was assigned values close to the actual values. These cross sections are shown by the dashed lines in Fig. 2. Also shown in this figure are measurements of the cross section for the formation of Mg^{++} ions in collisions of protons with Mg^+ ions.[19]

A comparison of these cross sections shows that the results calculated from the Rosen-Zener model agree well with the experimental data, while the cross sections calculated from the Landau-Zener model differ significantly from the measured values at all values considered for the parameter τ. This result indicates that the Landau-Zener mechanism does not operate, so the terms do not cross at intermediate internuclear distances. The experiments thus confirm that the correlation of MOs in the $(MgH)^{++}$ quasimolecule is described by rules (4), (5).

3. Let us find some MO correlation rules which incorporate the fine structure of the levels of the quasimolecule. In the effective potential (1) we need to consider the terms V_a and V_b in this case. They give rise to splitting of the atomic levels in accordance with the total angular momentum of the electron, **j**. Since the projection of this total angular momentum of the electron onto the molecular axis $\Omega = |m_j|$ is related to the projection of the orbital angular momentum m and the spin projection m_s of the electron onto the same axis by $\Omega = |m + m_s|$, we can write the following expression[20] for MOs which belong to the given shell of the separate atom, at $R = \infty$:

$$\Phi_{i\Omega}^{a(b)}(\mathbf{r},R) = \sum_{m_s}\sum_{n_2=0}^{n-\Omega+m_s-1} C_{in_2m_s}^{a(b)}(R)\,\varphi_{n,n_2,\Omega-m_s}^{a(b)}(\mathbf{r},R)\,\chi_{1/2,m_s}, \tag{7}$$

where $i = 1, 2,\ldots, 2(n-\Omega)$; $\varphi_{n_1n_2m}^{a(b)}$ are screened two-center Coulomb MOs, which are the solutions of the Schrödinger equation with potential (1) without v_a, and v_b; and $\chi_{1/2,m_s}$ by the spin wave functions of the electron. The expansion coefficients in (7) and the MO energies are found by diagonalizing the $2(n-\Omega)$-dimensional matrix of the Hamiltonian of the quasimolecule.

In the limit of separate atoms, the screened Coulomb MOs $\varphi_{n_1n_2m}$ convert into parabolic Coulomb functions. If we express these parabolic Coulomb functions in terms of spherical Coulomb functions,[5] the expansion (7) takes the following form at $R=\infty$:

$$\Phi_{i\Omega}^{a(b)}(\mathbf{r},\infty)=\sum_{m_s}\sum_{l=\Omega-m_s}^{n-1}A_{ilm_s}^{a(b)}\psi_{n,l,\Omega-m_s}^{a(b)}(\mathbf{r})\chi_{1/2,m_s}, \tag{8}$$

where

$$A_{ilm_s}^{a(b)}=\sum_{n_2=0}^{n-\Omega+m_s-1}(-1)^{n_1}\left\langle\frac{n-1}{2},\frac{n-1}{2},\frac{n_2-n_1+\Omega-m_s}{2},\right.$$
$$\left.\frac{n_1-n_2+\Omega-m_s}{2}\right|l,\Omega-m_s\Big\rangle C_{in_2m_s}^{a(b)},$$

$\langle\ldots\rangle$ are the Clebsch-Gordan coefficients, and ψ_{nlm} are the spherical Coulomb functions. In the basis of spherical Coulomb functions, the $2(n-\Omega)$-dimensional energy matrix is block-diagonal (atomic orbitals with identical values of the orbital angular momentum l and with spin projections $m_s=1/2$ and $m_s=-1/2$ are coupled; Ref. 21). For each $l=\Omega-3/2+i$ $(i=1,2,3,\ldots,n-\Omega+1/2)$ we obtain two levels, with total angular momenta $j=l-1/2$ and $j=l+1/2$ (an exceptional case is $l=\Omega-1/2$, for which we have a single level, with $j=l+1/2$).

The levels of the separate atoms with the two-center screened Coulomb terms can be compared with and without allowance for the splitting of the Coulomb terms in regions in which they cross. Noting that v_a and v_b split terms with identical values of $|m|$, while V_a and V_b split terms with $\Delta|m|=0,\pm1$ (Ref. 22), we find the following results for the quantum numbers of the correlating MOs:

$$n_2=j-\Omega,\qquad |m|=l-j+\Omega. \tag{9}$$

If we ignore the splitting of the Coulomb molecular terms, we find the following results for the quantum numbers of the correlating MOs:

$$n_2=n-l-1,\qquad |m|=l-j+\Omega. \tag{10}$$

In this approximation, each orbital of a given shell of the separate atom thus converts into one of the screened Coulomb MOs with quantum numbers n, $n_2=j-\Omega$ (or $n_2=n-l-1$), and $|m|=l-j+\Omega$ as the nuclei move close together. These quantum numbers are related to the quantum numbers of the combined atom, n_0 and l_0, by the correlation rules for two-center screened Coulomb MOs.[23]

In the combined atom, there are two levels, with total angular momenta $j_0=l_0-1/2$ and $j_0=l_0+1/2$, corresponding to each value of the orbital angular momentum l_0 (an exceptional case is $l_0=\Omega-1/2$, in which we have a single level with $j_0=l_0+1/2$). At small internuclear distances, the relative order of magnitude of the screened Coulomb molecular terms is determined by the well-known nonrelativistic formula for the levels of a one-electron quasimolecule at small values of R (Ref. 14). At given values of n_0, l_0, and Ω, the Coulomb molecular term with $|m|=\Omega-1/2$ lies below the term with $|m|=\Omega+1/2$. A comparison of these terms with the levels of the combined atom leads to the following relations between j_0 and l_0:

$$\begin{aligned}&j_0=l_0+{}^1/_2, &&\text{if}\quad l_0=\Omega-{}^1/_2,\\ &j_0=l_0+|m|-\Omega, &&\text{if}\quad l_0\neq\Omega-{}^1/_2.\end{aligned} \tag{11}$$

Some correlation rules for diabatic MOs which incorporate the fine structure of the quasimolecular levels are found by replacing n_2 and $|m|$ in the correlation rules for screened Coulomb MOs [Eqs. (4) and (5) in Ref. 1] by their values from (9) and (10).

Substituting in the values of n_2 and $|m|$ from (9), we find

$$\left.\begin{aligned}n_0&=n,\\ l_0&=l\end{aligned}\right\}\quad\text{for}\quad j-\Omega<n\frac{Z_a^*-Z_b^*}{Z_a^*},$$

$$\left.\begin{aligned}n_0&=n+1+\operatorname{Ent}\left(j-\Omega-n\frac{Z_a^*-Z_b^*}{Z_a^*}\right),\\ l_0&=l+1+\operatorname{Ent}\left(j-\Omega-n\frac{Z_a^*-Z_b^*}{Z_b^*}\right)\end{aligned}\right\}\quad\text{for}\quad j-\Omega\geqslant n\frac{Z_a^*-Z_b^*}{Z_a^*} \tag{12}$$

for MOs which convert into the heavy atom in the limit $R\to\infty$ and

$$\left.\begin{aligned}n_0&=n'+1+\operatorname{Ent}\left(j'-\Omega+n'\frac{Z_a^*-Z_b^*}{Z_b^*}\right),\\ l_0&=l'+1+\operatorname{Ent}\left(j'-\Omega+n'\frac{Z_a^*-Z_b^*}{Z_b^*}\right)\end{aligned}\right\}$$

$$\text{for noninteger}\quad n'\frac{Z_a^*}{Z_b^*},$$

$$\left.\begin{aligned}n_0&=j'-\Omega+n'\frac{Z_a^*}{Z_b^*},\\ l_0&=l'+j'-\Omega+n'\frac{Z_a^*-Z_b^*}{Z_b^*}\end{aligned}\right\}\quad\text{for integer}\quad n'\frac{Z_a^*}{Z_b^*} \tag{13}$$

for MOs which convert into the orbitals of the light atom as $R\to\infty$.

Substituting in the values of n_2 and $|m|$ from (10), we find the correlation rules

$$\left.\begin{aligned}n_0&=n,\\ l_0&=n-j+\Omega-1\end{aligned}\right\}\quad\text{for}\quad n_r<n\frac{Z_a^*-Z_b^*}{Z_a^*},$$

$$\left.\begin{aligned}n_0&=n+1+\operatorname{Ent}\left(n_r-n\frac{Z_a^*-Z_b^*}{Z_a^*}\right),\\ l_0&=n-j+\Omega+\operatorname{Ent}\left(n_r-n\frac{Z_a^*-Z_b^*}{Z_a^*}\right)\end{aligned}\right\}\quad\text{for}\quad n_r\geqslant n\frac{Z_a^*-Z_b^*}{Z_a^*} \tag{14}$$

for MOs which convert into the orbitals of the heavy atom as $R\to\infty$ and

$$\left.\begin{aligned} n_0&=n'+1+\mathrm{Ent}\left(n_r'+n'\,\frac{Z_a^*-Z_b^*}{Z_b^*}\right),\\ l_0&=n'-j'+\Omega+\mathrm{Ent}\left(n_r'+n'\,\frac{Z_a^*-Z_b^*}{Z_b^*}\right)\end{aligned}\right\}$$

$$\text{for noninteger}\quad n'\,\frac{Z_a^*}{Z_b^*}, \qquad (15)$$

$$\left.\begin{aligned} n_0&=n'-l'-1+n'\,\frac{Z_a^*}{Z_b^*},\\ l_0&=2n'-j'-l'+\Omega-2+n'\,\frac{Z_a^*-Z_b^*}{Z_b^*}\end{aligned}\right\}\quad \text{for integer}\quad n'\,\frac{Z_a^*}{Z_b^*}$$

for MOs which convert into the orbitals of the light atom as $R\rightarrow\infty$. We see from (11) that we have $j_0 = l_0 + 1/2$ in both cases if $l_0 = \Omega - 1/2$, or we have $j_0 = l_0 + l - j$ (or $j_0 = l_0 + l' - j'$) if $l_0 \neq \Omega - 1/2$.

Rules (12) and (13) do not allow a crossing of terms with identical values of n and different values of l, while rules (14) and (15) allow such crossings. For this reason, (12), (13) and (14), (15) may be thought of as respectively adiabatic and diabatic correlation rules for MOs belonging to a common shell. If we subtract the second equation from the first in (12) and (13), we find $n_r^{\mathrm{OA}} = n_r^{\mathrm{PA}}$: the Barat-Lichten MO correlation rule. Making the corresponding subtraction in (14) and (15), we find $n_r^{\mathrm{OA}} = j - \Omega$, which is the relativistic analog of the Eichler-Wille MO correlation rule.

Rules (12), (13) and (14), (15) are a generalization of rules (2), (3) and (4), (5) to relativistic MOs. The rules found here are valid for quasimolecules which are not too heavy, with $Z_a + Z_b \ll \alpha^{-1}$, where $\alpha \approx 1/137$ is the fine-structure constant. Nevertheless, a comparison with results calculated on the terms of heavy quasimolecules[24] shows that these rules also apply to quasimolecules with $Z_a + Z_b \lesssim 137$.

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