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On the asymptotic behavior of Hartree–Fock orbitals

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Summary. Handy et al. have shown that the asymptotic behavior of Hartree–Fock orbitals is controlled by the energy of highest occupied molecular orbital, except for the atomic case in which only s-orbitals are occupied. However, their proof is not complete at one point. This point is clarified, and a more unified derivation is given. Further, we discuss the preexponential factor r^{α} of the leading asymptotic term $r^{\alpha}\exp[-\beta r]$, where $\beta = (-2\varepsilon_{\mathrm{HOMO}})^{1/2}$ and $\varepsilon_{\mathrm{HOMO}}$ is the orbital energy of HOMO. New results are obtained for linear molecules, and the results of several authors for atoms and non-linear molecules are reproduced.

Key words: Hartree–Fock orbital – Wave function – Asymptotic behavior – Molecular orbital – HOMO

1. Introduction

The investigation of the long-range behavior of wave functions is important because the long-range behavior of the charge densities is one of the indispensable points in the search for an unknown energy density functional. Also, the long-range behavior of wave functions is important in the discussion of interacting systems, because the long-range part of wave functions plays an essential role when intermolecular potentials and energy transfer are considered. Since the exponent of most diffuse function determines the asymptotic behavior in the basis function expansion approach, the investigation of this behavior is significant for the determination of basis sets. The variation principle is almost always used to determine wave functions. It is difficult, however, to determine tails of wave functions from the variation principle because the long-range behavior of wave functions has little effect on energy values. Recently, we studied wave function tails by application of the exterior electron model [1].

The upper bound of total wave functions has been discussed and atomic and molecular wave functions have been found to decay exponentially [2], $\exp[-(2I)^{1/2}r]$, where I is the first ionization potential and r is the radial distance from the origin. When a molecule has an inversion center, this defines the origin. However, when the molecule does not have an inversion center, we can, for example, take the center of nuclear charges as the origin. For natural orbitals, the decay of the wave function is also exponential [3]. The asymptotic behavior is also studied from the view point of the momentum space [4–6]. Lassettre studied the analytic behavior of momentum eigenfunctions, under various potentials including the Hartree–Fock potential, in the complex momentum plane, and found the relation of the singular points in the plane with the asymptotic behavior of coordinate space eigenfunctions [4]. Koga applied the zero potential criterion to the Hartree–Fock wave functions, and suggested that the Hartree–Fock approximation cannot describe the correct long-range behavior of many-electron wave functions [5]. Casida and Chong discussed momentum distributions with the "large r approximation", and claimed that the important large r parts of molecular orbitals behave like the Hartree orbitals rather than the Hartree–Fock orbitals [6]. These conclusions are based on the following results of Handy et al. [7]. However, there is an incomplete point in the discussion in [7].

In this paper, the incomplete point is clarified and the asymptotic behavior is analysed with a matrix treatment of the differential equation. The present treatment is more general and unified, although the results are the same as those obtained by Handy et al.: (1) The asymptotic behavior of the Hartree–Fock orbital is found to be controlled by the orbital energy of the highest occupied molecular orbital (HOMO) except for the atoms that only have s-orbitals. (2) The behavior of each orbital of the atoms whose orbitals are all s-type is determined by the energy of each orbital. Further, we obtain the preexponential factor r^{α_i} of the leading term of the asymptotic form $r^{\alpha_i}\exp[-\beta_i r]$. Our treatment yields new results for linear molecules, and reproduces the known results for atoms [8] and non-linear molecules [9].

2. An example counter to the previous treatment

For a closed-shell system with N doubly occupied orthonormal orbitals ψ_i $(i = 1, 2, \ldots, N)$, Hartree-Fock equations for polyatomic molecules are

$$\left[-\tfrac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{|\boldsymbol{r}-\boldsymbol{R}_A|} + \int \frac{d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|}\left(2\sum_{\substack{j=1\\(j\neq i)}}^{N} |\psi_j(\boldsymbol{r}')|^2 + |\psi_i(\boldsymbol{r}')|^2\right) - \varepsilon_i\right]\psi_i(\boldsymbol{r})$$

$$= \sum_{\substack{j=1\\(j\neq i)}}^{N} \psi_j(\boldsymbol{r}) \int \frac{d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|}\psi_j^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}') \quad (i = 1, 2, \ldots, N), \tag{1}$$

where $\boldsymbol{R}_A$ and Z_A are the position vector and the nuclear charge of the nucleus A, respectively, and ε_i is the orbital energy for ψ_i.

The angular parts of the kinetic energy, nuclear attraction potential, and Coulomb operators are all negligible compared with ε_i at a large r. On the other hand, the right hand side of Eq. (1), that corresponds to the exchange operators, cannot be neglected. This was pointed out by Handy et al. [7]. Then, the general asymptotic form of the Hartree–Fock equations is reduced to

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} - \varepsilon_i\right)\psi_i(\boldsymbol{r}) \sim \sum_{\substack{j=1\\(j\neq i)}}^{N} K_{ji}(\boldsymbol{r})\psi_j(\boldsymbol{r}) \quad (i = 1, 2, \ldots, N), \tag{2}$$

where

$$K_{ji}(\boldsymbol{r}) = \int \frac{d\boldsymbol{r}'}{|\boldsymbol{r} - \boldsymbol{r}'|} \psi_j^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}') \quad (i = 1, 2, \dots, N). \tag{3}$$

The following equation was deduced from Eq. (2) in Ref. 7:

$$\left(\prod_{j=1}^{N} \Delta_j\right)\psi_i \sim 0 \quad (i = 1, 2, \dots, N), \tag{4}$$

where

$$\Delta_j = -\frac{1}{2}\frac{d^2}{dr^2} - \varepsilon_j. \tag{5}$$

In their derivation, Handy et al. assumed [7] that $K_{Ni}K_{jN}\psi_j$ goes to zero more quickly than $K_{ji}\Delta_N\psi_j$. However, this assumption is not always valid as is shown in the following discussion.

The Laplace expansion [10, 11] for $1/|\boldsymbol{r} - \boldsymbol{r}'|$ is

$$\begin{aligned} \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} &= 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \frac{r'^l}{r^{l+1}} Y_l^{m*}(\theta, \phi) Y_l^m(\theta', \phi') \quad (r' < r) \\ &= 4\pi \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \frac{r^l}{r'^{l+1}} Y_l^{m*}(\theta, \phi) Y_l^m(\theta', \phi') \quad (r' > r), \end{aligned} \tag{6}$$

where $Y_l^m(\theta, \phi)$ denotes the spherical harmonic. When this expansion is substituted for K_{ji}, we obtain

$$\begin{aligned} K_{ji} = 4\pi &\sum_{l=0}^{\infty} \frac{1}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}(\theta, \phi) \\ &\times \left[\frac{1}{r^{l+1}} \int_{r'=0}^{r} dr'\, r'^{l+2} \int \sin\theta'\, d\theta'\, d\phi'\, Y_l^m(\theta', \phi')\psi_j^*(r', \theta', \phi')\psi_i(r', \theta', \phi') \right. \\ &\left. + r^l \int_{r'=r}^{\infty} dr'\, r'^{1-l} \int \sin\theta'\, d\theta'\, d\phi'\, Y_l^m(\theta', \phi')\psi_j^*(r', \theta', \phi')\psi_i(r', \theta', \phi') \right]. \end{aligned} \tag{7}$$

Let us consider the atomic case:

$$\psi_i(r, \theta, \phi) = R_i(r) Y_{l_i}^{m_i}(\theta, \phi). \tag{8}$$

Substitution of Eq. (8) into Eq. (7) gives

$$\begin{aligned} K_{ji}\psi_k = 4\pi Y_{l_k}^{m_k}(\theta, \phi) &\sum_{l=0}^{\infty} \frac{1}{2l+1} \\ &\times \sum_{m=-l}^{l} Y_l^{m*}(\theta, \phi) \int Y_{l_j}^{m_j*}(\theta', \phi') Y_{l_i}^{m_i}(\theta', \phi') Y_l^m(\theta', \phi') \sin\theta'\, d\theta'\, d\phi' \\ &\times \left[\frac{R_k(r)}{r^{l+1}} \int_0^{\infty} r'^{l+2} R_j(r') R_i(r')\, dr' \right. \\ &\left. - \frac{R_k(r)}{r^{l+1}} \int_r^{\infty} r'^{l+2} R_j(r') R_i(r')\, dr' + r^l R_k(r) \int_r^{\infty} \frac{R_j(r') R_i(r')}{r'^{l-1}}\, dr' \right]. \end{aligned} \tag{9}$$

The first term in the bracket [ ] of Eq. (9) is $O(R_k(r)/r^{l+1})$, where O denotes "of the order of". It is noted that the first term is zero when $l=0$ because of the orthogonality of orbitals. Both the second and third terms are $O(r^2R_i(r)R_j(r)R_k(r))$. Let us consider the ratio of the second and third terms to the first term:

$$\frac{r^2R_i(r)R_j(r)R_k(r)}{R_k(r)/r^{l+1}}=r^{l+3}R_i(r)R_j(r)\to 0 \quad (r\to\infty). \tag{10}$$

This estimation shows the second and third terms go to zero more quickly than the first term. The smallest l for which the angular integral does not vanish determines the order $(l+1)$ of $1/r$ in $R_k(r)/r^{l+1}$. The integral with respect to angular variables θ' and ϕ' can be expressed by Wigner 3–j symbols. Thus, the angular integral does not vanish for $|l-l_j|\leqslant l_i\leqslant l+l_j$, $m_j=m+m_i$ and $l+l_i+l_j+m+m_i+m_j$ is even. When $l_i=l_j=0$, i.e., ψ_i and ψ_j are s-type, the first integral with respect to r in [ ] is zero for $l=0$, and the angular integral vanishes for $l\neq 0$. Therefore, if both ψ_i and ψ_j are s-type, $K_{ji}(r)\psi_k(r)\ll\psi_k(r)$. In the other cases, $K_{ji}(r)\psi_k(r)=O(\psi_k(r)/r^n)$, where $n=3$ when $l_i=l_j\neq 0$, and $n=|l_i-l_j|+1$ when $l_i\neq l_j$, according to the angular integral. Thus,

$$K_{ji}(r)\psi_k(r)=\begin{cases} o(\psi_k(r)/r^p) & (l_i=l_j=0)\\ O(\psi_k(r)/r^3) & (l_i=l_j\neq 0)\\ O(\psi_k(r)/r^{|l_i-l_j|+1}) & (l_i\neq l_j),\end{cases} \tag{11}$$

where o indicates an infinitesimal of higher order, p is an arbitrary positive number.

In order to clarify the incomplete point in the treatment of Handy et al., let us consider a Ne atom, for example. If we choose $p=4$, the above discussion leads to $K_{2s,1s}\psi_{2s}\ll\psi_{2s}/r^4$, $K_{2p,1s}\psi_{2s}=O(\psi_{2s}/r^2)$, and $K_{2s,2p}\psi_{2s}=O(\psi_{2s}/r^2)$. If we assume that i, j and N are the 1s, 2s and 2p orbitals, respectively, $K_{Ni}K_{jN}\psi_j=(O(\psi_{2s}/r^4))$ does not vanish as quickly as $K_{ji}\Delta_N\psi_j$ $(\ll\psi_{2s}/r^4)$. This discussion for Ne indicates that the proof is not valid for atoms that have at least two s-orbitals and another orbital with non s-symmetry such as Mg, Ar and Ca atoms.

3. A treatment with a matrix form

To fully derive Eq. (4), we rewrite Eq. (2) in a matrix form

$$\frac{d^2\boldsymbol{\psi}}{dr^2}=A\boldsymbol{\psi}, \tag{12}$$

where

$$\frac{d^2\boldsymbol{\psi}}{dr^2}={}^t\left(\frac{d^2}{dr^2}\psi_1,\frac{d^2}{dr^2}\psi_2,\ldots,\frac{d^2}{dr^2}\psi_N\right), \tag{13}$$

$$\boldsymbol{\psi}={}^t(\psi_1,\psi_2,\ldots,\psi_N), \tag{14}$$

$$A=\begin{bmatrix} e_1 & f_{12}(r) & f_{13}(r) & \cdots & f_{1N}(r)\\ f_{21}(r) & e_2 & f_{23}(r) & \cdots & f_{2N}(r)\\ f_{31}(r) & f_{32}(r) & e_3 & \cdots & f_{3N}(r)\\ \cdots & \cdots & \cdots & \cdots & \cdots\\ f_{N1}(r) & f_{N2}(r) & f_{N3}(r) & \cdots & e_N \end{bmatrix}, \tag{15}$$

and

$$e_i = -2\varepsilon_i, \tag{16}$$

$$f_{ij}(r) = -2K_{ji}(r). \tag{17}$$

The f_{ij} for atoms shows a stronger decay than $1/r^2$ [8], so, as pointed out in the previous section:

$$f_{ij} = \begin{cases} o(1/r^p) & (l_i = l_j = 0) \\ O(1/r^3) & (l_i = l_j \neq 0) \\ O(1/r^{|l_i - l_j| + 1}) & (l_i \neq l_j). \end{cases} \tag{18}$$

In linear molecules, since $|m_i|$ specifies the symmetry of an orbital i, ψ_i is expanded in the following form:

$$\psi_i = \sum_{l_i = |m_i|}^{\infty} R_{il_i}(r) Y_{l_i}^{m_i}(\theta, \phi). \tag{19}$$

From this form of the orbital, the order n of $1/r$ for f_{ij} is derived through a discussion similar to that for atoms:

$$f_{ij}(r) = \begin{cases} O(1/r^2) & (m_i = m_j) \\ O(1/r^{|m_i - m_j| + 1}) & (m_i \neq m_j). \end{cases} \tag{20}$$

The derivation is presented in the Appendix. In non-linear molecules,

$$\psi_i = \sum_{l_i = 0}^{\infty} \sum_{m_i = -l_i}^{l_i} R_{il_im_i}(r) Y_{l_i}^{m_i}(\theta, \phi), \tag{21}$$

because there are no limitations on l and m. Since only the term with $l = 0$ vanishes in $K_{ji}\psi_i$ owing to the orthogonality of orbitals,

$$f_{ij}(r) = O(1/r^2). \tag{22}$$

Consequently, $f_{ij}(r)$ is at most the order of $1/r^2$ in all cases.

If we tentatively assume that $f_{ij}(r)$ is a constant, i.e., A is a constant matrix, we can define the characteristic polynomial of A:

$$f_A(x) = |A - xE|, \tag{23}$$

where E is the N-dimensional unit matrix. When we rewrite the characteristic polynomial $f_A(x)$ as follows:

$$f_A(x) = \sum_{k=0}^{N} a_k x^{N-k} \tag{24}$$

and the coefficients a_k are

$$a_k = (-1)^{N-k} \sum_{i_1 < i_2 < i_3 < \cdots < i_k} \det \begin{pmatrix} e_{i_1} & f_{i_1i_2} & f_{i_1i_3} & \cdots & f_{i_1i_k} \\ f_{i_2i_1} & e_{i_2} & f_{i_2i_3} & \cdots & f_{i_2i_k} \\ f_{i_3i_1} & f_{i_3i_2} & e_{i_3} & \cdots & f_{i_3i_k} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ f_{i_ki_1} & f_{i_ki_2} & f_{i_ki_3} & \cdots & e_{i_k} \end{pmatrix}. \tag{25}$$

Since $f_{**} \ll e_*$ holds for a sufficiently large r, we can neglect the third and higher order of f_{**}:

$$\begin{cases} a_0 = (-1)^N \\ a_1 = (-1)^{N-1} \sum_{i=1}^{N} e_i \\ a_2 = (-1)^{N-2} \sum_{i<j}^{N} e_i e_j + O(f_{**}^2) \\ a_3 = (-1)^{N-3} \sum_{i<j<k}^{N} e_i e_j e_k + O(f_{**}^2) \\ \dots \\ a_N = \prod_{i=1}^{N} e_i + O(f_{**}^2). \end{cases} \tag{26}$$

The characteristic equation is therefore

$$\prod_{j=1}^{N} (x - e_j) + O(f_{**}^2)(\text{polynomial of } x) = 0. \tag{27}$$

Thus, a solution of Eq. (27), i.e., an eigenvalue of the constant matrix A, is

$$x = e_i + O(f_{**}^2). \tag{28}$$

If we assume that $\boldsymbol{p}_i = {}^t(p_{1i}, p_{2i}, \dots, p_{Ni})$ is the corresponding eigenvector, the equation

$$[A - (e_i + O(f_{**}^2))]\boldsymbol{p}_i = 0, \tag{29}$$

is valid, i.e.,

$$\begin{cases} \sum_{j \neq i}^{N} f_{ij} p_{ji} = O(f_{**}^2) \\ (e_j - e_i) p_{ji} + \sum_{k \neq j}^{N} f_{jk} p_{ki} = O(f_{**}^2) \quad (j \neq i) \end{cases} \tag{30}$$

holds for the components of $\boldsymbol{p}_i$. If we substitute the following p_{ji} into Eq. (30):

$$p_{ii} = 1 + O(f_{**}^2), \tag{31a}$$

and

$$\begin{cases} p_{ji} = 0 & (j \neq i, e_j = e_i) \\ p_{ji} = \dfrac{f_{ji}}{e_i - e_j} + O(f_{**}^2) & (e_j \neq e_i), \end{cases} \tag{31b}$$

Eq. (30) holds. Therefore, if we neglect the second order of f_{**}, a solution of Eq. (12) with constant matrix A is

$$\psi_i \sim \exp[-e_i^{1/2} r] + \sum_{\substack{j \neq i \\ e_j \neq e_i}}^{N} \frac{f_{ji}}{e_i - e_j} \exp[-e_j^{1/2} r]. \tag{32}$$

It is noted that this solution is obtained under the assumption that f_{ij} is constant. Therefore, the validity of the solution must be examined. When we substitute Eq.

(32) into Eq. (12), we find that Eq. (4) holds if we neglect the second and higher terms of f_{**}. Thus,

$$\psi_i \sim \exp[-e_i^{1/2}r] + \sum_{\substack{j\neq i\\ e_j\neq e_i}}^{N} \frac{f_{ji}(r)}{e_i - e_j} \exp[-e_j^{1/2}r]. \tag{33}$$

Although the solution seems to show that the orbital energy of the j-th orbital is not responsible for the asymptotic behavior of the i-th orbital when $f_{ij}(r) = 0$, the term $\exp[-e_j^{1/2}r]$ is included in the general asymptotic form of ψ_i because of the existence of the second or higher orders of f_{**}. The form of ψ_i at large r does not include the term corresponding to the orbital energy ε_j only when the products $f_{ik}(r)f_{kj}(r), f_{ik}(r)f_{kl}(r)f_{lj}(r), \ldots, f_{ik_1}(r)f_{k_2k_3}(r)\ldots f_{k_{N-2}j}(r)$ are all zero, i.e., ψ_i belongs to a block, say A_I, different from that to which ψ_j belongs, where A_I is the I-th block in the block diagonal form of A. Thus, all orbitals that belong to the same block are controlled by the energy of the highest orbital (h) in the relevant block.

4. The leading term of asymptotic forms for atoms, linear and non-linear molecules

In order to discuss the asymptotic behavior in more detail, we consider the following equation taking the order of $1/r$ into account [8, 9]

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{Z+1}{r} - \varepsilon_i\right]\psi_i \sim \sum_{j\neq i}^{N} K_{ji}\psi_j, \tag{34}$$

where $Z = \sum_A Z_A - 2N$ is the charge of the system. As for ψ_h, we can neglect the contribution from the exchange parts:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{Z+1}{r} - \varepsilon_h\right]\psi_h \sim 0. \tag{35}$$

Since this equation no longer has $\exp[-\beta_h r]$, where $\beta_h = e_h^{1/2} = (-2\varepsilon_h)^{1/2}$, as a solution we have to search for a solution of the form

$$(r^{\alpha_h} + O(r^{\alpha_h - 1}))\exp(-\beta_h r). \tag{36}$$

Handler et al. [8] and Davis et al. [9] have shown that

$$\alpha_h = (Z+1)/\beta_h - 1. \tag{37}$$

When the system is neutral, $\alpha_h = 1/\beta_h - 1$ because Z is the charge of the system. This result indicates that the asymptotic behavior of ψ_i is

$$\psi_i \sim r^{\alpha_h - \lambda}\exp[-\beta_h r], \tag{38}$$

where λ is the lowest order of $1/r$ of $f_{ih}(r)$, $f_{ik_1}(r)f_{k_1h}(r)$, $f_{ik_1}(r)f_{k_1k_2}(r)f_{k_2h}(r), \ldots, f_{ik_1}(r)f_{k_1k_2}(r)\ldots f_{k_{m-2}h}(r)$ (usually, the order of $f_{ih}(r)$) when $i \neq h$, and $\lambda = 0$ when $i = h$. The general result in Eq. (38) leads to the results for atoms, linear molecules, and non-linear molecules.

The result in Eq. (38) combined with Eq. (18) reproduces the form obtained by Handler et al. [8] for atoms that have an orbital other than s-orbitals:

$$\psi_i \sim \begin{cases} r^{\alpha_H}\exp[-\beta_H r] & (i = H) \\ r^{\alpha_H - 3}\exp[-\beta_H r] & (l_i = l_H \neq 0, i \neq H) \\ r^{\alpha_H - 2(l_{\min}+1)}\exp[-\beta_H r] & (l_i = l_H = 0, i \neq H) \\ r^{\alpha_H - |l_i - l_H| - 1}\exp[-\beta_H r] & (l_i \neq l_H), \end{cases} \tag{39}$$

where H denotes the HOMO of the atom, not of the block, and $\beta_H = (-2\varepsilon_H)^{1/2}$, $\alpha_H = (Z+1)/\beta_H - 1$, $l_{\min}$ is the smallest nonzero orbital quantum number of the atom considered. For atoms that have only s-orbitals, the leading term of asymptotic form is

$$\psi_i \sim r^{\alpha_i} \exp[-\beta_i r], \tag{40}$$

where $\beta_i = (-2\varepsilon_i)^{1/2}$ and $\alpha_i = (Z+1)/\beta_i - 1$.

For linear molecules, we obtain the following results from Eq. (20):

$$\psi_i \sim \begin{cases} r^{\alpha_H} \exp[-\beta_H r] & (i = H) \\ r^{\alpha_H - 2} \exp[-\beta_H r] & (m_i = m_H, i \neq H) \\ r^{\alpha_H - |m_i - m_H| - 1} \exp[-\beta_H r] & (m_i \neq m_H). \end{cases} \tag{41}$$

The second and third results for $\psi_i \neq \psi_H$ are new ones, since although Davis et al. discussed the asymptotic form for molecules [9], they did not explicitly consider the case of linear molecules.

For non-linear molecules, the result obtained by Davis et al. [9] is reproduced from Eq. (22):

$$\psi_i \sim \begin{cases} r^{\alpha_H} \exp[-\beta_H r] & (i = H) \\ r^{\alpha_H - 2} \exp[-\beta_H r] & (i \neq H). \end{cases} \tag{42}$$

In summary, the behavior of ψ_i is determined by the energy of the HOMO in most cases although the preexponential factors are different. The preexponential factors are usually determined by the order of r for f_{iH}. On the other hand, the behavior of the orbitals in the atoms that have only s-orbitals is determined by their own orbital energy because the matrix element f_{ij} vanishes when both of i and j orbitals are s-type. In the previous treatment [7], the Be atom was considered separately. In this treatment, however, the exceptional behavior of the Be atom emerges from the general consideration. Moreover, new results are obtained for the leading asymptotic form in non-linear molecules.

From an analysis similar to the above, the asymptotic forms of all orbitals in the open shell RHF scheme can be shown to be $\sim r^{\alpha_H - \lambda} \exp[-(-2\varepsilon_H)^{1/2} r]$, where λ is determined in the same way as in the closed shell RHF scheme. In this open shell scheme, the Li atom has the asymptotic behavior $\psi_{1s} \sim r^{\alpha_{1s}} \exp[-(-2\varepsilon_{1s})^{1/2} r]$ and $\psi_{2s} \sim r^{\alpha_{2s}} \exp[-(-2\varepsilon_{2s})^{1/2} r]$.

In the UHF scheme, the asymptotic behavior of α and β orbitals is determined by the highest occupied α spin orbital ψ^{α}_{H} and the highest occupied β spin orbital ψ^{β}_{H}, respectively. It is noted that when the outermost shell is half or less filled in the ground state of the atom, the orbital quantum number of ψ^{α}_{H} is different from that of ψ^{β}_{H}. For example, in the Na atom, the behavior of the α orbitals is controlled by the energy of ψ^{α}_{3s}, whereas that of β orbitals is controlled by the energy of ψ^{β}_{2p}. In particular, in the B, C and N atoms the behavior of the α orbitals is controlled by the energy of ψ^{α}_{2p} because these atoms have ψ^{α}_{1s}, ψ^{α}_{2s} and ψ^{α}_{2p} orbitals, whereas the behavior of each β orbital is controlled by the energy of each orbital because only ψ^{β}_{1s} and ψ^{β}_{2s} orbitals are occupied. In molecular cases, for example O_2, the behaviors of α and β orbitals are controlled by the energy of $1\pi_g$ and $1\pi_u$ orbitals, respectively. In the Li atom, each orbital (ψ^{α}_{1s}, ψ^{α}_{2s}, and ψ^{β}_{1s}) is controlled by the energy of each orbital, which is similar to the behavior in the open RHF scheme.

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Appendix

In linear molecules, since ψ_i is represented by Eq. (19)

$$\psi_i = \sum_{l_i = |m_i|}^{\infty} R_{il_i}(r) Y_{l_i}^{m_i}(\theta, \phi), \tag{A1}$$

the equation corresponding to Eq. (19) is

$$\begin{aligned} K_{ji}\psi_k = 4\pi & \sum_{l_k = |m_k|}^{\infty} Y_{l_k}^{m_k}(\theta, \phi) \sum_{l=0}^{\infty} \frac{1}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}(\theta, \phi) \\ & \times \sum_{l_i = |m_i|}^{\infty} \sum_{l_j = |m_j|}^{\infty} \int Y_{l_j}^{m_j *}(\theta', \phi') Y_{l_i}^{m_i}(\theta', \phi') Y_l^m(\theta', \phi') \sin\theta' \, d\theta' \, d\phi' \\ & \times \left[\frac{R_{kl_k}(r)}{r^{l+1}} \int_0^{\infty} r'^{l+2} R_{jl_j}(r') R_{il_i}(r') \, dr' - \frac{R_{kl_k}(r)}{r^{l+1}} \right. \\ & \quad \left. \times \int_r^{\infty} r'^{l+2} R_{jl_j}(r') R_{il_i}(r') \, dr' + r^l R_{kl_k}(r) \int_r^{\infty} \frac{R_{jl_j}(r') R_{il_i}(r')}{r'^{l-1}} \, dr' \right]. \end{aligned} \tag{A2}$$

The difference of Eq. (A2) from Eq. (19) is the presence of additional summations with respect to l_i and l_j. The term with $m \neq |m_i - m_j|$ and the term with $l = 0$ vanish, respectively from the evaluation of the angular integral and because of orthogonality of orbitals. When $m_i = m_j$, the term with $l = m = 0$ is precluded, and all the terms with $l \geqslant 1$ do not vanish because the terms with $l \geqslant 1$ necessarily include the term $m = |m_i - m_j| (=0)$. Thus,

$$K_{ji}\psi_k = O(\psi_k / r^2). \tag{A3}$$

It is noted that this result is valid even for $m_i = m_j = 0$ unlike the case of $l_i = l_j = 0$. When $m_i \neq m_j$, the terms with $l < |m_i - m_j|$ are precluded, but all the terms with $l \geqslant |m_i - m_j|$ do not vanish because such terms always include the term $m = |m_i - m_j|$. Therefore,

$$K_{ji}\psi_k = O(\psi_k / r^{|m_i - m_j| + 1}). \tag{A4}$$

Consequently, $f_{ij}(r)$ behaves as

$$f_{ij}(r) = \begin{cases} O(1/r^2) & (m_i = m_j) \\ O(1/r^{|m_i - m_j| + 1}) & (m_i \neq m_j), \end{cases} \tag{A5}$$

which is identical with Eq. (20).

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