Asymptotic behavior of atomic Hartree–Fock orbitals

George S. Handler and Darwin W. Smith

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Harris J. Silverstone

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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The restricted Hartree–Fock equations are solved at large r for closed shell atomic states. Except for states containing only s orbitals, the Hartree–Fock orbitals obey the formula,

$$\phi_i(\mathbf{r}) \sim k_i Y_{l_i}^{m_i}(\theta,\phi) r^{\beta-\lambda-1}\exp(-\zeta r)$$

where $-1/2\zeta^2 = \epsilon_{\rm ho}$, the highest occupied orbital energy, where β = (nuclear charge − number of electrons $+1-\zeta)/\zeta$, where $\lambda+1=0$ for the highest occupied orbital where, $\lambda = |l_i - l_{\rm ho}|$ if $l_i \neq l_{\rm ho}$, where $\lambda = 2$ if $l_i = l_{\rm ho} \neq 0$ and $i \neq$ ho, where $\lambda = 2l_{\rm min}+1$ if $l_i = l_{\rm ho} = 0$, and where $l_{\rm min}$ is the smallest nonzero l value of the occupied Hartree–Fock orbitals.

INTRODUCTION

Accurate descriptions of atomic wavefunctions at large distances from the nucleus are needed for a careful treatment of scattering[1] and of long-range forces.[2] Handy *et al.*[3] pointed out the somewhat surprising fact that at large r the radial parts of the restricted Hartree–Fock (RHF) atomic orbitals $\phi_i(\mathbf{r})$ do not behave like

$$f_i(r)\exp[-(-2\epsilon_i)^{1/2}r]\,, \tag{1}$$

but rather like

$$\sum_j f_{ij}(r)\exp[-(-2\epsilon_j)^{1/2}r]\,, \tag{2}$$

where the ϵ_j are the orbital energies of the N occupied orbitals. While form (1) is valid for atoms containing only s orbitals, many workers in the field had previously overlooked the fact the exchange potential couples radial equations for different angular momenta, leading to form (2) in the general case of atoms containing orbitals of angular momenta not all of s type.

No explicit solutions for the preexponential factors f_{ij} in Eq. (2) were given by Handy *et al.*[3]; they merely pointed out that the f_{ij} are functions of r which behave less strongly than exponentials at large r. The purpose of this paper is to derive the asymptotic form of the f_{ij}.

A number of authors have questioned the significance of the long-range exchange effect. For example, Weber *et al.*[4] considered form (2) to be a mathematical artifact of the Hartree–Fock method; they state that form (1) is more reasonable. However, the Hartree–Fock model is well defined and the matter of its behavior is of intrinsic interest for the study of its structure, given its widespread use.

DERIVATION OF THE LEADING TERMS FOR THE CLOSED SHELL NOT-ALL-s-ORBITAL CASE

Consider first a closed shell state. In the RHF equations,

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \sum_{j=1}^{N}(2J_j - K_j) - \epsilon_i\right)\phi_i = 0\,, \tag{3}$$

the Coulomb operators J_j approach $1/r$ for large r, while the exchange contributions depend on i, j, and the relative l values. To evaluate the exchange contributions, we use the Laplace expansion of $1/r_{12}$,[5]

$$K_j\phi_i = \phi_j(\mathbf{r})\int dV'\,\phi_j(\mathbf{r}')^* \sum_{l,m}\frac{4\pi}{2l+1}Y_l^m(\theta,\phi)^* \times Y_l^m(\theta',\phi')\,\frac{r_<^l}{r_>^{l+1}}\,\phi_i(\mathbf{r}')\,. \tag{4}$$

Each RHF orbital ϕ_j and ϕ_i in the integrand contributes a spherical harmonic factor. The integration over the triple product of spherical harmonics vanishes unless $|l_i - l_j| \le l \le l_i + l_j$, and $l_i + l_j + l$ is even. To evaluate the exchange contributions *asymptotically*, we formally set the variable $r_<$ in the Laplace expansion equal to the integration variable r', integrate, and keep in the sum over l the leading nonvanishing term:

$$K_j\phi_i \sim r^{-\lambda-1}\phi_j(\mathbf{r})\sum_m Y_\lambda^m(\theta,\phi)^* d_{ji\lambda m}\,, \tag{5}$$

$$\lambda = |l_i - l_j|\,, \quad d_{ji\lambda m} = \frac{4\pi}{2\lambda+1}\langle\phi_j|r^\lambda Y_\lambda^m|\phi_i\rangle\,, \quad (l_i \neq l_j)\,, \tag{6}$$

$$\lambda = 2\,, \quad d_{ji\lambda m} = \tfrac{4}{5}\pi\langle\phi_j|r^2 Y_2^m|\phi_i\rangle\,, \quad (l_i = l_j \neq 0,\ \ i \neq j)\,, \tag{7}$$

$$\lambda = 0\,, \quad d_{ji\lambda m} = (4\pi)^{1/2}\,, \quad (i = j)\,. \tag{8}$$

Equations (7) and (8) reflect that d_{ji00} is essentially an overlap or normalization integral when $l_i = l_j$. In the ss' case—that is, in the case that $i \neq j$ and $l_i = l_j = 0$, $K_j\phi_i$ is exponentially small compared with either ϕ_i or ϕ_j. For large r, the RHF equations become

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{d}{dr} - \frac{1}{r}(Z - 2N + 1) - \epsilon_i + O\left(\frac{1}{r^2}\right)\right]\phi_i \sim \sum_{j(\neq i)} r^{-\lambda-1}\phi_j \sum_m Y_\lambda^{m*} d_{ji\lambda m}\,. \tag{9}$$

These equations permit an asymptotic solution[3] [dominated by the term with the smallest exponential in Eq. (2)] of the form,

$$\phi_i \sim [k_i r^{\beta_i} + a_i r^{\beta_i - 1} + O(r^{\beta_i - 2})]e^{-\zeta r}Y_{l_i}^{m_i}(\theta,\phi)\,. \tag{10}$$

The value of ζ is obtained from the orbital energy of the highest occupied orbital, $\epsilon_{\rm ho}$, which we have presumed to be smallest in magnitude:

$$-\tfrac{1}{2}\zeta^2 = \epsilon_{\rm ho}\,. \tag{11}$$

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To determine the values of the β_i, one first substitutes Eq. (10) into Eq. (9) to obtain,

$$\{(-\tfrac{1}{2}\zeta^2-\epsilon_i)k_i+r^{-1}[(\zeta\beta_i-Z+2N-1+\zeta)k_i+(-\tfrac{1}{2}\zeta^2-\epsilon_i)a_i]\}$$

$$\times r^{\beta_i}e^{-\zeta r}Y_{l_i}^{m_i}\sim\sum_{j(\neq i)}\sum_m k_j r^{\beta_j-\lambda-1}e^{-\zeta r}Y_{l_j}^{m_j}Y_\lambda^{m*}d_{ji\lambda m}\,. \quad (12)$$

[Note that by Eqs. (6)–(8), λ depends on i and j, even though in Eq. (12), that dependence is not explicitly indicated.] Let β_p denote the largest of the β_i. For $i=p$, the right-hand side of Eq. (12) is at least $O(r^{\beta_p-2}\times e^{-\zeta r})$. Consequently we obtain from the r^{β_p} and r^{β_p-1} terms of the left-hand side,

$$-\tfrac{1}{2}\zeta^2=\epsilon_p\,, \quad (13)$$

$$\beta_p=[Z-(2N-1)-\zeta]/\zeta\,. \quad (14)$$

Clearly, by Eqs. (11) and (13) ϵ_p and ϵ_{ho} are equal: the highest occupied orbital has the largest β_p! In the RHF method, the other orbitals in the same subshell, which differ from ϕ_p only in the m quantum number, have the same radial dependence and thus the same β_p.

Next consider the second largest β_i, say, β_q. We assume that there is no accidental degeneracy, so that $\epsilon_p\neq\epsilon_q$. For the moment, we also assume that either $l_p\neq0$ or $l_q\neq0$. With $i=q$, all the terms on the right-hand side of Eq. (12) vanish at least as fast as $r^{\beta_q-2}e^{-\zeta r}$, except the term with $j=p$, which vanishes as $r^{\beta_p-\lambda-1}$. If $\beta_q>\beta_p-\lambda-1$, then the right-hand side would vanish more strongly (formally) than the left, $-\frac{1}{2}\zeta^2$ would equal ϵ_q, and ϕ_q and ϕ_p would be degenerate. On the other hand, if $\beta_q<\beta_p-\lambda-1$, then the right-hand side of Eq. (12) would itself have to vanish (or at least its leading terms would). Such a cancellation would be most unlikely. Thus, by elimination,

$$\beta_q=\beta_p-\lambda-1\,. \quad (15)$$

Similarly, it follows in general that

$$\beta_i=\beta_p-\lambda-1\,, \quad (16)$$

or, more precisely, that

$$\beta_i=\beta_p-|l_i-l_p|-1\,, \quad (l_i\neq l_p)\,, \quad (17)$$

$$=\beta_p-3\,, \quad (l_i=l_p\neq0\,,\ i\neq p)\,. \quad (18)$$

The case $l_i=l_p=0$ requires additional comment. The exchange operators do not *directly* couple ϕ_i with ϕ_p; terms with $l_j=0$ are absent from the *asymptotic* Eq. (12) when $l_i=0$. Instead ϕ_i is coupled indirectly to ϕ_p via each ϕ_j with $l_j\neq0$. Equation (17) is then replaced by

$$\beta_i=\max[\beta_j-\lambda(i,j)-1]=\beta_p-2l_{\min}-2\,, \quad (l_i=l_p=0)\,, \quad (19)$$

where $l_{\min}$ is the smallest nonzero l value of the occupied RHF orbitals.

GENERALIZATIONS

By a similar argument, one can show that each subdominant solution is keyed to the orbital whose orbital energy determines its exponential factor. The general result is that

$$f_{jj}(r)\sim k_{jj}r^{\beta^{(j)}}\,, \quad (20)$$

TABLE I. Predicted asymptotic behavior at large r of the atomic orbitals of Ne, Ar, and Ca. Values of ζ are given in atomic units for the common exponential factor $\exp(-\zeta r)$, and the value of β is indicated for the prefactor r^β.

		Ne[a]	Ar[b]	Ca[c]
ζ		1.3041	1.0871	0.6253
β	$1s$	−2.2332	−2.0801	−3.4008
	$2s$	−2.2232	−2.0801	−3.4008
	$3s$		−2.0801	−3.4008
	$4s$			0.5992
	$2p$	−0.2332	−3.0801	−1.4008
	$3p$		−0.0801	−1.4008

[a]Orbital energy of $2p$ orbital is −0.85034 a.u. (Ref. 6).
[b]Orbital energy of $3p$ orbital is −0.59092 a.u. (Ref. 7).
[c]Orbital energy of $4s$ orbital is −0.19552 a.u. (Ref. 6).

$$f_{ij}(r)\sim k_{ij}r^{\beta^{(j)}-\lambda_{ij}-1}\,, \quad (i\neq j)\,, \quad (21)$$

$$\lambda_{ij}=|l_i-l_j|\,, \quad (l_i\neq l_j)\,, \quad (22)$$

$$=2\,, \quad (l_i=l_j\,,\ i\neq j)\,, \quad (23)$$

$$=2l_{\min}+1\,, \quad (l_i=l_j=0\,,\ i\neq j)\,, \quad (24)$$

where $\beta^{(j)}$ is given by

$$\beta^{(j)}=[Z-(2N-1)-\zeta^{(j)}]/\zeta^{(j)}\,, \quad (25)$$

$$\zeta^{(j)}=(-2\epsilon_j)^{1/2}\,. \quad (26)$$

In the case that all shells are only half filled and are S coupled, Eqs. (20)–(26) still hold with $2N$ replaced by the total number of electrons.

In the case of states with s orbitals only, the exchange operators do not asymptotically couple the RHF orbitals. Equations (20), (25), and (26) are still valid, but Eq. (21) is replaced by $f_{ij}=0$, $(i\neq j)$.

In Table I the predicted asymptotic behavior of the RHF orbitals of three atoms is given for the purpose of illustrating the kind of coupling which typically occurs.

DISCUSSION

Because of coupling by the exchange operators, the tails of the RHF orbitals are dominated by a common exponential radial factor, $\exp(-\zeta r)$, where $\zeta=(-2\epsilon_{ho})^{1/2}$, but with a prefactor that depends on the l distance from the highest occupied orbital. The highest occupied orbital has a prefactor r^β, where $\beta=(Z-2N+1-\zeta)/\zeta$. Other RHF orbitals with the same l_{ho} have a prefactor $r^{\beta-3}$ if l_{ho} is nonzero, while all other RHF orbitals with l_i different from l_{ho} have a prefactor $r^{\beta-|l_i-l_{ho}|-1}$. If $l_{ho}=0$, then other s orbitals have a prefactor $r^{\beta-2l_{\min}-2}$, where $l_{\min}$ is the smallest l value of the occupied RHF orbitals. The only exception is a state consisting of only s orbitals, such as $1s^22s^2$ Be. The radial prefactors for the RHF orbitals derived here are similar to the radial prefactors found for the natural orbitals of helium in its ground state.[8]

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