

Long-Range Behavior of Hartree-Fock Orbitals*

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The widely held belief that Hartree-Fock orbitals φ_i behave asymptotically like $\exp[-(-2 \times \epsilon_i)^{1/2}r]$, where ϵ_i is the orbital energy of φ_i , is shown to be incorrect, with one exception: atomic configurations consisting entirely of *s* orbitals. The correct asymptotic form of φ_i is a sum of terms like $\exp[-(-2\epsilon_j)^{1/2}r]$, in which all ϵ_j appear. The former misconception apparently resulted from too superficial a treatment of the exchange potential at large r .

I. INTRODUCTION

Theoretical treatments of physical processes involving interacting systems, such as intermolecular forces in a gas or energy transfer in a crystal, need wave functions accurate at large distances. It is remarkable that the long-range behavior of a common approximate wave function, the Hartree-Fock wave function, appears to be misunderstood. Many statements in the literature¹ imply that the Hartree-Fock self-consistent field potential goes like $-1/r$ at large r . As a consequence the long-range behavior of a given Hartree-Fock spin orbital φ_i would be given by²

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

where ϵ_i is the orbital energy of φ_i . With certain exceptions which are discussed later, the asymptotic form (1) is incorrect. The correct asymptotic form of φ_i is a sum of terms like the right-hand side of Eq. (1) in which *all* the orbital energies occur. First we show by example how the long-range behavior of the exchange potentials precludes the form (1), and then derive the correct long-range behavior of the Hartree-Fock orbitals.

II. EXAMPLE: $(1s)^2(2p)^6$ ATOMIC CONFIGURATION

This simple hypothetical example demonstrates the incorrectness of the asymptotic form of Eq. (1). [A slightly more complicated example is neon $(1s)^2(2s)^2(2p)^6$.] The Hartree-Fock equation for the 1s orbital may be written

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \int \frac{dV'}{|\vec{r}-\vec{r}'|} \left(\varphi_{1s}^2(\vec{r}') \right. \right. \\ \left. \left. + 2 \sum_{m=-1}^1 |\varphi_{2p_m}(\vec{r}')|^2 \right) - \epsilon_{1s} \right] \varphi_{1s}(\vec{r}) = 0$$

$$- \sum_{m=-1}^1 \varphi_{2p_m}(\vec{r}) \int \frac{dV'}{|\vec{r}-\vec{r}'|} \varphi_{2p_m}^*(\vec{r}') \varphi_{1s}(\vec{r}') = 0. \tag{2}$$

The nuclear attraction term plus the Coulomb terms (which have been written to include the self-exchange term) in Eq. (2) behave asymptotically like $r^{-1}\varphi_{1s}(\vec{r})$, and are therefore negligible compared with $-\epsilon_{1s}\varphi_{1s}(\vec{r})$ at large r . To find the asymptotic form of the exchange term, we make the substitutions

$$\varphi_{1s} = R_{1s}(r)Y_0^0(\theta, \varphi), \tag{3}$$

$$\varphi_{2p_m} = R_{2p_m}(r)Y_1^m(\theta, \varphi), \tag{4}$$

and use the asymptotic expansion for $|\vec{r}-\vec{r}'|^{-1}$ for large r ,

$$|\vec{r}-\vec{r}'|^{-1} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l (2l+1)^{-1} r'^l r^{-l-1} \\ \times Y_l^{m*}(\theta, \varphi) Y_l^m(\theta', \varphi'), \tag{5}$$

where the $Y_l^m(\theta, \varphi)$ denote spherical harmonics. After the angular integrations, the exchange term is

$$-\frac{4\pi}{3} \sum_{m=-1}^1 R_{2p_m}(r) Y_1^m(\theta, \varphi) Y_1^{m*}(\theta, \varphi) \\ \times r^{-2} \int_0^{\infty} dr' r'^3 R_{2p_m}(r') R_{1s}(r')$$

$$= -k_{2p, 1s} R_{2p}(r)/r^2, \tag{7}$$

$$\text{where } k_{2p, 1s} = \int_0^{\infty} dr r^3 R_{2p}(r) R_{1s}(r) \tag{8}$$

In any typical calculation, this integral will not be zero. The asymptotic form of Eq. (2) therefore is

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} - \epsilon_{1s}\right)R_{1s}(r) = k_{2p,1s} \frac{R_{2p}(r)}{r^2} . \quad (9)$$

If $|\epsilon_{1s}| > |\epsilon_{2p}|$, which is usual, Eq. (9) is clearly not satisfied by the asymptotic forms given in Eq. (1). Hence those forms cannot represent the correct asymptotic behavior. The "rub" is that the effective local exchange potential acting on φ_{1s} is

$$-(k_{2p,1s}/r^2)R_{2p}(r)/R_{1s}(r) , \quad (10)$$

which, if Eq. (1) held, would behave like

$$-\exp[(-2\epsilon_{1s})^{1/2}r - (-2\epsilon_{2p})^{1/2}r] \rightarrow -\infty \text{ as } r \rightarrow \infty ,$$

i. e., an exponential hole at ∞ ! It is apparent that Eq. (2) could not be solved for a bound-state orbital if the resultant local exchange potential has this exponential dependence.

III. THE ASYMPTOTIC HARTREE-FOCK EQUATIONS FOR CLOSED-SHELL SYSTEMS

Consider a closed-shell system with N doubly occupied orthonormal Hartree-Fock orbitals φ_i , $i=1, 2, \dots, N$. The Hartree-Fock equations are

$$\begin{aligned} & \left[-\frac{1}{2}\nabla^2 - \sum_a \frac{Z_a}{r_a} + \int \frac{dV'}{|\vec{r} - \vec{r}'|} \right. \\ & \quad \left. \times \left(2 \sum_{j=1}^N |\varphi_j(\vec{r}')|^2 + |\varphi_i(\vec{r}')|^2 - \epsilon_i \right) \right] \varphi_i(\vec{r}) \\ & = \sum_{j=1}^N \varphi_j(\vec{r}) \int \frac{dV'}{|\vec{r} - \vec{r}'|} \varphi_j^*(\vec{r}') \varphi_i(\vec{r}') , \\ & \quad (i=1, 2, \dots, N) . \quad (11) \end{aligned}$$

The angular parts of the kinetic energy, the nuclear attraction potential, and the Coulomb operators are all negligible compared with ϵ_i at large r . The $|\vec{r} - \vec{r}'|^{-1}$ expansion [Eq. (5)] can be used to obtain the asymptotic form of the exchange term,

$$\begin{aligned} \varphi_j(\vec{r}) \int dV' |\vec{r} - \vec{r}'|^{-1} \varphi_j^*(\vec{r}') \varphi_i(\vec{r}') \\ = r^{-3} \vec{k}_{ji} \cdot \vec{r} \varphi_j(\vec{r}) + O[r^{-3} \varphi_j(\vec{r})] , \quad (12) \end{aligned}$$

$$= K_{ji}(\vec{r}) \varphi_j(\vec{r}) , \quad (13)$$

$$\text{where } \vec{k}_{ji} = \int dV' \varphi_j^*(\vec{r}') \vec{r}' \varphi_i(\vec{r}') \quad (14)$$

$$\text{and } K_{ji} = r^{-3} \vec{k}_{ji} \cdot \vec{r} + O(r^{-3}) . \quad (15)$$

The orthogonality of the orbitals precludes the $l=0$ term in Eq. (5), i. e., the charge distribu-

tion $\varphi_j^* \varphi_i$ is neutral. If the system is an atom, then the \vec{k}_{ji} can be zero because of symmetry, and the K_{ji} in (15) can be of order r^{-l-1} with $l > 1$. For example $j \rightarrow 3d$ and $i \rightarrow 1s$ gives $l=2$. For the case in which both i and j are s -type orbitals in an atom, the exchange terms vanish much more strongly than $O(r^{-3} \varphi_j)$. We discuss this case in Sec. IV.

The general asymptotic form of the Hartree-Fock equations (11) then becomes

$$\begin{aligned} \left(-\frac{1}{2}\frac{d^2}{dr^2} - \epsilon_i\right)\varphi_i(\vec{r}) \sim \sum_{j=1}^N K_{ji}(\vec{r}) \varphi_j(r) , \\ (j \neq i) \\ (i=1, 2, \dots, N) . \quad (16) \end{aligned}$$

The exchange terms on the right-hand side of Eq. (16) cannot be dropped at this stage because we have no way of comparing $\varphi_i(\vec{r})$ with $\varphi_j(\vec{r})$ for large r .

IV. SINGLE ASYMPTOTIC EQUATIONS FOR HARTREE-FOCK ORBITALS

Equations (16) are not transparently solvable because the φ_i are coupled together. The $N=2$ case indicates how to uncouple them and yields a single asymptotic equation for the φ_i .

Define, for convenience,

$$\Delta_i = -\frac{1}{2} d^2/dr^2 - \epsilon_i . \quad (17)$$

When $N=2$, Eqs. (16) become

$$\Delta_1 \varphi_1 \sim K_{21} \varphi_2 , \quad (18)$$

$$\Delta_2 \varphi_2 \sim K_{12} \varphi_1 . \quad (19)$$

Operate on Eq. (18) with Δ_2 ,

$$\Delta_2 \Delta_1 \varphi_1 \sim K_{21} \Delta_2 \varphi_2 + (\Delta_2 K_{21} - K_{21} \Delta_2) \varphi_2 . \quad (20)$$

Since

$$\begin{aligned} (\Delta_2 K_{21} - K_{21} \Delta_2) \varphi_2 \\ = \varphi_2 \left(-\frac{1}{2} d^2/dr^2 K_{21} \right) - (d/dr) \varphi_2 (d/dr) K_{21} , \quad (21) \end{aligned}$$

$$= O(r^{-1} K_{21} \Delta_2 \varphi_2) , \quad (22)$$

the last term in Eq. (20) can be dropped to obtain

$$\Delta_1 \Delta_2 \varphi_1 \sim K_{21} \Delta_2 \varphi_2 . \quad (23)$$

With Eq. (19), Eq. (23) becomes

$$\Delta_1 \Delta_2 \varphi_1 \sim K_{21} K_{12} \varphi_1 . \quad (24)$$

$$\text{But } K_{21} K_{12} \varphi_1 = O(r^{-4} \varphi_1) , \quad (25)$$

$$\text{while } \Delta_1 \Delta_2 \varphi_1 = O(\varphi_1) , \quad (26)$$

$$\text{so that } \Delta_1 \Delta_2 \varphi_1 \sim 0 . \quad (27)$$

From the symmetry of Eqs. (18) and (19), φ_2 must satisfy the same equation. The solution of

Eq. (27) is postponed until the next section.

The generalization of Eq. (27) to the N orbital case is that each of the N Hartree-Fock orbitals φ_i satisfies the asymptotic equation

$$\begin{aligned} & \left(-\frac{1}{2}d^2/dr^2 - \epsilon_1\right)\left(-\frac{1}{2}d^2/dr^2 - \epsilon_2\right) \\ & \times \dots \left(-\frac{1}{2}d^2/dr^2 - \epsilon_N\right)\varphi_i \sim 0, \\ & (i=1, 2, \dots, N). \end{aligned} \quad (28)$$

An inductive derivation of Eq. (28) is obtained both from the $N=2$ solution above and by reducing the N equations (16) to $(N-1)$ equations having the same form. Operate on the first $(N-1)$ of Eqs. (16) with Δ_N . For reasons like those used to obtain Eq. (22), ignore $(\Delta_N K_{ji} - K_{ji} \Delta_N)\varphi_j$ relative to $K_{ji} \Delta_N \varphi_j$, to obtain

$$\Delta_i \Delta_N \varphi_i \sim \sum_{j=1}^{N-1} K_{ji} \Delta_N \varphi_j + K_{Ni} \Delta_N \varphi_N. \quad (29)$$

$(j \neq i)$

Substitute into Eq. (29) the last of Eqs. (16) for $\Delta_N \varphi_N$, to obtain

$$\Delta_i \Delta_N \varphi_i \sim \sum_{j=1}^{N-1} K_{ji} \Delta_N \varphi_j + K_{Ni} \sum_{j=1}^{N-1} K_{jN} \varphi_j. \quad (30)$$

$(j \neq i)$

Since $K_{Ni} K_{iN} \varphi_i$ vanishes more strongly than $\Delta_i \Delta_N \varphi_i$, and $K_{Ni} K_{jN} \varphi_j$ vanishes more strongly than $K_{ji} \Delta_N \varphi_j$, the last set of terms in Eq. (30) can be dropped:

$$\Delta_i \Delta_N \varphi_i \sim \sum_{j=1}^{N-1} K_{ji} \Delta_N \varphi_j, \quad (i=1, 2, \dots, N-1). \quad (31)$$

$(j \neq i)$

But Eqs. (31) are just Eqs. (16) with N replaced by $(N-1)$ and φ_i by $\Delta_N \varphi_i$. Equations (28) then follow by induction for $i=1, 2, \dots, (N-1)$, and by symmetry for $i=N$.

V. ASYMPTOTIC BEHAVIOR OF THE ORBITALS

Equation (28) is easily solved. The general solution which vanishes at ∞ , and which gives the asymptotic form of the Hartree-Fock orbitals, is

$$\varphi_i = \sum_{j=1}^N f_{ji}(\vec{r}) \exp[-(-2\epsilon_j)^{1/2}r], \quad (32)$$

where the $f_{ji}(\vec{r})$ are functions of \vec{r} which behave less strongly than the exponentials at ∞ . As a rule, none of the $f_{ji}(\vec{r})$ will be identically zero. The "tail" of φ_i thus consists of a sum of N exponentials, one for each orbital energy ϵ_j . The one case for which the f_{ji} vanish identically when $i \neq j$ is an atomic configuration consisting entirely of s-type orbitals, e. g., the ground state of Be. For s orbitals, the exchange operators $K_{ji}(\vec{r})$ [Eq. (13)] vanish exponentially, because all multipole moments of a localized, spherically symmetric charge distribution, which is overall neutral, vanish identically. Equation (16) then permits the simpler solution given by Eq. (1).

VI. DISCUSSION

We have shown that the Hartree-Fock orbitals φ_i do not go asymptotically like $\exp[-(-2\epsilon_i)^{1/2}r]$, where ϵ_i is the orbital energy, as is the common belief, except in the case of an atomic configuration having only s-type orbitals. The correct asymptotic behavior is given by a sum of terms like $\exp[-(-2\epsilon_j)^{1/2}r]$, where every orbital energy enters each orbital. As a consequence, the ultimate long-range behavior of all Hartree-Fock orbitals, independently of the symmetry type, is the same, dominated by the smallest (in magnitude) orbital energy, i. e., $\exp[-(-2 \times \epsilon_{\text{smallest}})^{1/2}r]$. These results have obvious implications for the process of calculating the Hartree-Fock orbitals, numerically or analytically. In particular, the practice³ of neglecting exchange when r is very large seems suspect. We are unsure whether this unexpected long-range behavior has physical significance or is just an artifact of the Hartree-Fock method. The uniform behavior is a consequence of the long range of the exchange potentials, and any modification of the Hartree-Fock equations which alters these, can alter the long-range behavior of the orbitals. For instance, if all the exchange potentials are computed with $r_{12}^{-1} \exp[-|\alpha|(r_1^2 + r_2^2)]$ instead of with r_{12}^{-1} , or alternatively with the use of Slater's average exchange potential,⁴ then each Hartree-Fock orbital has the long-range behavior specified by its own orbital energy. A method to force this behavior in an analytical basis has been devised and will be published elsewhere.⁵

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¹A definite statement that the Hartree-Fock potential goes like $(-1/r)$ at large r may be found in D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961), p. 18. There are, moreover, many papers which note this " $(-1/r)$ asymptotic behavior" while discussing approxi-

mate ways of treating exchange. See, e.g., F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood, New Jersey, 1963), p. 1-8.

²We use atomic units. The unit of length is the Bohr radius, $a_0 \sim 0.53 \text{ \AA}$, and the unit of energy is $e^2/a_0 \sim 27.2 \text{ eV}$.

³C. Froese, *Can. J. Phys.* **41**, 1895 (1963). The choice of slope of the wave function at the outermost point in Froese's "tail procedure" seems to involve the neglect of exchange. See especially her Eq. (6).

⁴J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

⁵M. T. Marron, N. C. Handy, R. G. Parr, and H. J. Silverstone, to be published.

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Multiplet Pattern and Assignments of $\text{Li } 1^b$ Transitions*

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The experimental values of the fine and hyperfine energies of the metastable autoionizing $(1s2s2p)^4P^o$ states of Li are used to definitively identify the transitions responsible for the multiplets at 2934 and 3714 \AA in the optical spectrum of Li. It is found that the optical lines are due to the radiative decay to the $^4P^o$ state of the lowest-lying states with symmetries $^4S^e$ and $^4P^e$. The intervals between the quartet states and the fine and hyperfine splittings of these states are derived from an analysis of the multiplet structures.

I. INTRODUCTION

On the basis of our recent determination¹ of the fine and hyperfine structure of the metastable autoionizing $(1s2s2p)^4P^o$ state of Li, we have identified as 1^b lines² the 2934 and 3714 \AA multiplets observed in the course of studies³⁻⁵ on the $\text{Li}^7 \text{ II}$ spectrum. These lines cannot be classified in the spectrum of the singly excited atom or ion. Our work confirms the tentative assignments⁶ of these lines which are based solely on calculations of the energies of the quartet levels of Li. In the present paper we discuss the calculations of the multiplet structures and intensity profiles for these lines and the effect of hfs in markedly altering the relative line intensities in the case of Li^7 . The fine structure of the $(1s2p^2)^4P^e$ state is determined from an analysis of the 3714 \AA multiplet.

II. METASTABLE LEVELS AND THE Li QUARTET SPECTRUM

The first direct observation of doubly excited states in lithium, which are metastable against

both autoionization and radiative decay, was made by Feldman and Novick in 1963.⁷ The metastability results from the spin selection rule $\Delta S = 0$ for Coulomb autoionization since there are no quartet states in the continuum adjacent to the lowest-lying discrete quartet states. The lowest excitation threshold observed was at $57.3 \pm 0.3 \text{ eV}$, which was identified as corresponding to the $(1s2s2p)^4P_{5/2}$ level. Several secondary thresholds were also observed and were assumed to result from the radiative cascade to the $^4P^o$ state from other quartet states which are metastable against autoionization.

The configuration $(1s2s2p)$ has the lowest energy of those odd-parity quartet states which do not couple via the Coulomb interaction to adjacent continuum states. Holgøien and Geltman⁸ have shown that the lowest lying of such $^4P^o$ states can be classified as

$$|1s, 2n \pm\rangle = 2^{-1/2}(|1s, 2snp\rangle \pm |1s, 2pns\rangle),$$

since the configurations $(1s2snp)$ and $(1s2pns)$ are nearly degenerate (for small n) when the interaction between configurations is neglected. This