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Z Expansion of Hartree-Fock Wave Functions

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Let a many-electron Hartree-Fock radial function

$$\Phi^{\mathrm{HF}}(nl;r)=\prod_{i=1}^{N} P^{\mathrm{HF}}(n^i l^i;r_i)$$

and the corresponding nonseparable variational function $\Phi(nl;r)$ be expanded in hydrogenic product functions $\Phi^{\mathrm{H}}(nl;r)$. The expansion coefficients $\langle \mathrm{H}n'l|nl\rangle$ of Φ are $O(Z^{-1})$ for $n'\not\equiv n$; they vanish when the sets n,n' differ by more than two one-electron quantum numbers. It is shown that the expansion coefficients $\langle \mathrm{H}n'l|\mathrm{HF}n\rangle$ are $O(Z^{-2})$ when

$$\nu(n,n')=N-\sum_{i=1}^{N}\delta(n^i n^{i\prime})=2,$$

i.e., when n and n' differ in two places, and are $O(Z^{-1})$ when $\nu(n,n')=1$. In the second case $\langle \mathrm{H}n'l|\mathrm{HF}nl\rangle=\langle \mathrm{H}n'l|nl\rangle+O(Z^{-2})$; the Hartree-Fock and the nonseparable expansion coefficients coincide to first order. This result holds only if the one-electron Hartree-Fock functions P^{HF} are not restricted by auxiliary conditions other than normalization. It does not hold, for example, if one requires the P^{HF} to satisfy the orthogonality condition $\langle P^{\mathrm{HF}}(nl;r)P^{\mathrm{HF}}(n'l;r)\rangle=\delta(n,n')$. From the result just stated, it follows that many-electron Hartree-Fock functions characterized by distinct sets of principal quantum numbers but the same set of azimuthal quantum numbers are orthogonal to first order in Z^{-1} (but not to higher orders). It also follows from the stated result that the coefficient W_0 in the Z expansion $W^{\mathrm{HF}}=W_2Z^2+W_1Z+W_0+O(Z^{-1})$ of a Hartree-Fock energy is given (in atomic units) by the formula

$$W_0=\mathop{\mathbf{S}}_{\nu(n,n')=1}\frac{|\langle \mathrm{H}n|V|\mathrm{H}n'\rangle|^2}{W_2-W_2'},\quad W_2=-\sum_{i=1}^{N}\frac{1}{2n^{i2}},$$

where V is the mutual electrostatic interaction of the electrons.

I. INTRODUCTION

THE Z expansions of Hartree-Fock wave functions and atomic parameters evaluated from them have been studied by Hartree,[1] Froese,[2] Dalgarno and his co-workers,[3] and others.[4] The first term in the expansion of a Hartree-Fock wave function is a hydrogenic wave function; the second term satisfies an inhomogeneous second-order differential equation whose solution can be obtained in closed form.[5] The two leading terms contain enough information about the wave function for many practical purposes. For example, they enable one to calculate the four leading coefficients in a Z expansion of the Hartree-Fock energy [see Eq. (1) below]; this is usually sufficient. Moreover, the first-order calculations yield explicitly Z-dependent results; exact Hartree-Fock calculations can be carried out only for specific values of Z. This advantage of the Z-dependent first-order calculations often compensates for the (usually small) loss of accuracy.

The Z expansions of many-electron state vectors and energies have another use: They provide the key to a useful classification of configuration mixing.[6] In a nonrelativistic approximation the energy of a many-electron atom may be expanded in the form

$$W=W_2Z^2+W_1Z+W_0+O(Z^{-1}),\quad W_2=-\sum_{i=1}^{N}\frac{1}{2n^{i2}}. \tag{1}$$

In order to evaluate the coefficient W_1 one must use a correct first-order description of the mixing of configurations belonging to the same complex (i.e., the same principal quantum numbers and the same parity). The correct zero-order state vector is a linear combination with constant coefficients of hydrogenic-state vectors pertaining to configurations in the same complex. A finite calculation employing hydrogenic wave functions suffices for the evaluation of these coefficients and of the coefficient W_1 in the Z expansion [Eq. (1)] of the energy.[7]

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[1] D. R. Hartree, Proc. Cambridge Phil. Soc. **51**, 684 (1955); *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), p. 118.

[2] C. Froese, Proc. Roy. Soc. (London) **A239**, 311 (1957); **A244**, 390 (1958); Phys. Rev. **116**, 900 (1959); Can. J. Phys. **41**, 50 (1963).

[3] A. Dalgarno, Proc. Phys. Soc. (London) **75**, 439 (1960); M. Cohen and A. Dalgarno, Proc. Roy. Soc. (London) **A261**, 565 (1961); M. Cohen, A. Dalgarno, and J. M. McNamee, *ibid.*, **A269**, 550 (1962).

[4] J. Linderberg, Phys. Rev. **121**, 816 (1961); C. S. Sharma and C. A. Coulson, Proc. Phys. Soc. (London) **80**, 81 (1962); C. S. Sharma, *ibid.* **80**, 839 (1962).

[5] E. Constantinides, Thesis, Harvard University, 1963 (unpublished); see also M. Cohen and A. Dalgarno, Proc. Phys. Soc. (London) **77**, 165 (1961).

[6] D. Layzer, Astron. J. **56**, 43 (1951); Monthly Notices Roy. Astron. Soc. **114**, 692 (1954); Ann. Phys. (N. Y.) **8**, 271 (1959); D. Layzer and J. Bahcall, Ann. Phys. (N. Y.) **17**, 177 (1962).

[7] W_1 is given for all terms belonging to complexes of the type $(1^2 2^q)$ and $(1^2 2^q)^0$ by D. Layzer, Ann. Phys. (N. Y.) **8**, 271 (1959). Godfredsen [Thesis, Harvard University, 1963 (unpublished)] has extended these calculations to complexes of the type $(1^2 2^q 3^r)$ and $(1^2 2^q 3^r)^0$.

The Z-independent energy contribution W_0, as well as subsequent terms in the energy expansion, may be split up into three parts, representing the effects of: (a) screening in its broadest sense (departures of the one-electron radial functions from the hydrogenic form); (b) radial correlation; and (c) configuration mixing in its narrowest sense (mixing of configurations labeled by distinct sets of azimuthal quantum numbers). The Hartree-Fock approximation accounts for the entire screening contribution but for none of the remaining contributions.

Successive terms in the energy expansion [Eq. (1)] correspond to successive orders of a perturbation expansion based on hydrogenic-state vectors. The purpose of the present note is to point out that the Hartree-Fock contribution to W_0 corresponds exactly to the part of the second-order perturbation energy involving energy matrix elements that connect configurations which differ through a single principal quantum number. Similarly, in the Z expansion of a Hartree-Fock function the expansion functions whose coefficients are of order Z^{-1} differ from the zero-order function through one-electron substitutions.

This way of characterizing the Hartree-Fock approximation is advantageous for certain problems. For example, it enables one to give a short and simple proof of an orthogonality property of many-electron Hartree-Fock functions, a special case of which was recently established by Sharma and Coulson.[4]

II. DERIVATION

An antisymmetric N-electron ket characterized by N pairs of one-electron quantum numbers n^il^i and by additional quantum numbers Γ can be written in the form

$$|n^1l^1\cdots n^Nl^N\Gamma\rangle \qquad \mathcal{A}\Phi(n^1l^1\cdots n^Nl^N;r_1\cdots r_N))\rangle|l^1\cdots l^N\Gamma\rangle_{1\ldots N}, \tag{2}$$

where the antisymmetrizing operator $\mathcal{A}$ acts on the subscripts that distinguish the electron coordinates and spins. The radial function Φ need not be separable in the radial coordinates r_i. The best radial function Φ in the sense of the variation principle satisfies a linear, second-order, partial differential equation. In the following discussion Φ represents this optimum radial function.

For the sake of brevity we shall represent the set $(l^1\cdots l^N)$ by the single letter l, the set $(r^1\cdots r^N)$ by the single letter r, and so on. The short form of Eq. (2) is then

$$|nl\Gamma\rangle=\mathcal{A}\Phi(nl;r))|l\Gamma\rangle. \tag{3}$$

We may expand Φ in terms of hydrogenic radial functions:

$$\Phi(n;r)=\mathop{\mathsf{S}}\limits_{n'}\langle n|\mathrm{H}n'\rangle\Phi^{\mathrm{H}}(n'l;r), \tag{4}$$

$$\Phi^{\mathrm{H}}(n'l;r)=\prod_{i=1}^{N}P^{\mathrm{H}}(n^{i\prime}l^i;r_i), \tag{5}$$

where P^{H} is a hydrogenic radial function and the generalized sum in (4) extends over all configurations—including those for which the principal quantum numbers take on continuous, pure imaginary values—that have the same azimuthal quantum numbers as the initial configuration nl. The coefficients in the expansion (4) satisfy the condition

$$\langle n|\mathrm{H}n'\rangle=\delta(n,n')+O(Z^{-1}), \tag{6}$$

where

$$\delta(n,n')=\prod_{i=1}^{N}\delta(n^i,n^{i\prime}). \tag{7}$$

In the Hartree-Fock approximation Φ is given by

$$\Phi\approx\Phi^{\mathrm{HF}}=\prod_{i=1}^{N}P^{\mathrm{HF}}(n^il^i;r_i). \tag{8}$$

The one-electron Hartree-Fock functions P^{HF} may be expanded in hydrogenic functions

$$P^{\mathrm{HF}}(n^il^i;r_i)=\mathop{\mathsf{S}}\limits_{nl'}\langle n^i|\mathrm{H}n^{i\prime}\rangle P^{\mathrm{H}}(n^{i\prime}l^i;r_i), \tag{9}$$

where

$$\langle n^i|\mathrm{H}n^{i\prime}\rangle=\delta(n^i,n^{i\prime})+O(Z^{-1}). \tag{10}$$

The many-electron Hartree-Fock function can now be written in a form analogous to Eq. (4):

$$\Phi^{\mathrm{HF}}(nl;r)=\mathop{\mathsf{S}}\limits_{n'}\langle \mathrm{HF}n|\mathrm{H}n'\rangle\Phi^{\mathrm{H}}(n'l;r), \tag{11}$$

where

$$\langle \mathrm{HF}n|\mathrm{H}n'\rangle=\prod_{i=1}^{N}\langle n^i|\mathrm{H}n^{i\prime}\rangle=O(Z^{-\nu}), \tag{12}$$

the integer ν being given by

$$\nu=\nu(n,n')=N-\sum_{i=1}^{N}\delta(n^i,n^{i\prime}). \tag{13}$$

$\langle \mathrm{HF}n|\mathrm{H}n'\rangle$ vanishes unless $\nu=0$, 1, or 2.

We are now in a position to prove the following two statements:

$$\begin{aligned}\langle \mathrm{HF}n|n'\rangle&=\langle n|\mathrm{H}n'\rangle+O(Z^{-2}), \quad (\nu=1)\\ &=O(Z^{-2}), \qquad\qquad\qquad (\nu=2)\end{aligned} \tag{14}$$

and

$$\langle \mathrm{HF}n^i|\mathrm{H}n^{i\prime}\rangle =\langle n^1\cdots n^i\cdots n^N|n^1\cdots n^{i\prime}\cdots n^N\rangle+O(Z^{-2}). \tag{15}$$

Equation (14) states that the first-order contributions to the Hartree-Fock expansion coefficients coincide with those of the corresponding expansion coefficients of the exact many-electron radial function when $\nu=1$, and vanish when $\nu=2$. Equation (15) relates the expansion of the one-electron Hartree-Fock functions to the expansion of the exact many-electron radial function.

To prove Eqs. (14) and (15) we first show that the many-electron Hartree-Fock functions lie asymptotically (i.e., in the limit $Z\rightarrow\infty$) in the product-function space spanned by the functions $\Phi^{\mathrm{H}}(n'l; r)$ with $\nu(n,n')=1$. This function space, of course, is a subspace of the function space spanned by the complete set of functions Φ^{H}. Now, the trial-function space associated with the variational function Φ is the space spanned by the functions Φ^{H}, while the trial-function space associated with Φ^{HF} coincides asymptotically with the subspace spanned by functions Φ^{H} with $\nu=1$. It follows that Φ^{HF} coincides asymptotically with the projection of Φ in the subspace spanned by the Φ^{H} with $\nu=1$. This establishes Eq. (14); Eq. (15) then follows from Eqs. (10) and (12).

The preceding proof breaks down if one imposes the usual orthogonality restrictions on the one-electron Hartree-Fock functions.[8] The space of separable trial functions then no longer coincides asymptotically with the space spanned by the functions $\Phi^{\mathrm{H}}\delta(\nu,1)$, but with a proper subspace of it.

III. APPLICATIONS

Orthogonality

The functions Φ are eigenfunctions of the same linear operator. They accordingly satisfy the orthogonality relations

$$\langle\Phi(n';r)\Phi(n;r)\rangle=\mathop{\mathbf{S}}_{n''}\langle n|\mathrm{H}n''\rangle\langle\mathrm{H}n''|n'\rangle=\delta(n,n'). \quad (16)$$

Equating to zero the contributions to the sum of order Z^{-1} we have

$$\delta[\nu(n,n'),1][\langle n|\mathrm{H}n\rangle\langle\mathrm{H}n|n'\rangle+\langle n|\mathrm{H}n'\rangle\langle\mathrm{H}n'|n'\rangle]=0, \quad (17)$$

whence, using Eqs. (12) and (14) and the fact that $\langle n|\mathrm{H}n\rangle=O(1)$, we obtain

$$\langle\Phi^{\mathrm{HF}}(n';r)\Phi^{\mathrm{HF}}(n;r)\rangle=\delta(n,n')+O(Z^{-2}). \quad (18)$$

That is, many-electron Hartree-Fock functions labeled by the same set of azimuthal quantum numbers are orthogonal to first order in Z^{-1}. Sharma and Coulson[4] gave a direct proof of a particular instance of this theorem (orthogonality of the Hartree-Fock functions for the two lowest ^1S states of helium-like ions). They pointed out that imposing the usual orthogonality requirement on the one-electron Hartree-Fock functions would spoil the first-order orthogonality of the many-electron functions.

The preceding derivation makes it apparent that many-electron Hartree-Fock functions are orthogonal *only* to first order. This, of course, is to be expected on general grounds: distinct Hartree-Fock functions are eigenfunctions of distinct nonlinear operators.

W_0^{HF} and W_0

The Hartree-Fock energy has the Z expansion

$$\langle\Phi^{\mathrm{HF}}\mathrm{H}\Phi^{\mathrm{HF}}\rangle\equiv W^{\mathrm{HF}}=W_2^{\mathrm{HF}}Z^2+W_1^{\mathrm{HF}}Z+W_0^{\mathrm{HF}}+O(Z^{-1}). \quad (19)$$

From Eq. (14) and the complete expression for W_0 given by ordinary second-order perturbation theory, we obtain the following formula for W_0 in the Hartree-Fock approximation:

$$W_0^{\mathrm{HF}}=\mathop{\mathbf{S}}_{\nu(n,n')=1}\frac{|\langle\mathrm{H}n|V|\mathrm{H}n'\rangle|^2}{W_2-W_2'}, \quad (20)$$

where

$$V=\sum_{i<j}\frac{1}{r_{ij}},\quad W_2=W_2^{\mathrm{HF}}=-\sum_{i=1}^{N}\frac{1}{2n^{i2}}. \quad (21)$$

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[8] If one does not impose the usual orthogonality conditions, the Hartree-Fock energy will contain an extra term which is $O(1)$ and is usually very small.