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ENERGY MINIMUM PRINCIPLE FOR HARTREE-FOCK CALCULATIONS OF CERTAIN EXCITED ATOMIC STATES

J. F. Perkins, Redstone Arsenal, Alabama

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The Hartree-Fock method is of course based on the requirement that the expectation energy shall be stationary with respect to variations of the one-electron orbital functions of which the trial function is composed. The trial function is made antisymmetric to the interchange of the space and spin variables of each pair of electrons in order to correspond to the physical solutions of the nonrelativistic Schrodinger equation. The present discussion will be limited to cases where the trial function is of a definite symmetry, i.e., is an eigenfunction of L^2, L_z, S^2, S_z, and parity. This implies that one makes stationary the expectation energy of a particular multiplet rather than the average energy of all multiplets arising from a given configuration, as is sometimes done. The stationary-energy requirement seems appropriate for excited states as well as for ground states since the exact wave functions of excited states have the stationary-energy property.

Since states of different symmetries are orthogonal, the well-known energy minimum principle guarantees that the Hartree-Fock energy for a state of a given symmetry lies above the exact energy of the lowest state of this symmetry. Thus in dealing with the lowest-lying multiplet of a given type, the stationary-energy requirement is equivalent to the requirement that the expectation energy be the best possible approximation to the exact energy for a trial function of the general Hartree-Fock form. Similar conclusions would apply to higher-lying states of a given symmetry if the trial function were constrained to be orthogonal to the

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exact wave functions of lower-lying states of the same symmetry, but this is not really very helpful since the exact wavefunctions are not known.

The principal purpose of this paper is to point out that the energy-minimum principle of equation 1 applies to Hartree-Fock calculations of a large number of optical states without the necessity of requiring the trial function to be orthogonal to the exact wave functions of lower states of the same symmetry. This property follows from the stationary-energy requirement of the Hartree-Fock method, as may be shown by applying a theorem of MacDonald and Hylleraas and Undheim to an expansion-type Hartree-Fock calculation.

The one-electron radial functions of which a Hartree-Fock function is built can be formally expanded in a countable, complete set of basis functions, as shown in equation 2. Any variation of $u_a(r)$ can then be expressed as a variation of the expansion coefficients $C_{a,j}$. The requirement that expectation energy be stationary with respect to variation of $u_a(r)$ can thus be expressed as the usual Hartree-Fock integrodifferential equations in the function $u_a(r)$ or, alternatively, as an infinite-order secular equation. In actual expansion-type (or analytic) Hartree-Fock calculations the basis set is, of course, finite. We make the highly plausible assumption that as $N \to \infty$ the roots of a finite-order secular equation approach the solutions of the equation which is formally equivalent to the infinite-order secular equation.

Now in many cases, an optical state which is not the lowest of a given symmetry, arises from a configuration which differs from those of lower states of the same symmetry only by the principal quantum number of a single, series electron. In many such cases, the Hartree-Fock wave function is linear in the expansion coefficients of the radial function of this electron, i.e., we have equation 3, and the lower-lying states of this symmetry frequently have a one-to-one correspondence to the lower-lying roots of the secular equation for this electron. As a simple example we consider lithium $1s^2 3p\ ^2P^o$, for which we would have, for example, equation 4. Now equation 3 is a special case of a more general form of expansion of the Rayleigh-Ritz type, as given in equation 5.

From a theorem of MacDonald and Hylleraas and Undheim it is known that equations 6 and 7 hold. That is (6) the kth lowest root of the secular equation for an expansion of length N lies above (or equals) the kth lowest root associated with an expansion obtained by adding one or more terms to the original N, and (7) the kth lowest root of the secular equation lies above the exact energy of the kth lowest state which is not orthogonal to the trial function by symmetry. The energy minimum principle, equation 1, for an expansion-type Hartree-Fock calculation, follows directly from MacDonald's theorem for the type of state considered. If it is assumed that the results of an expansion-type calculations approach solutions of the corresponding integrodifferential equations as N → ∞ it follows that the principle also holds for the numerical Hartree-Fock method.

The specific conditions for applicability of the principle are shown on the next slide. Condition (a) is fairly restrictive. Condition (b) rules out a few states where three or more electrons outside closed shells couple differently, i.e., cases of different parentage. Condition (c) could always be met by use of an "open-configuration" scheme, but is not very restrictive, anyway, since multiple occupancy of the outer shell is usually associated with violation of condition (a).

Clearly orbital orthogonality constraints which do not affect the radial function of the series electron have no effect on the previous arguments. It can be shown that an orthogonality constraint on the series electron has the effect of reducing by unity the order of a finite basis set in which this function is expanded. The argument leading to equation 1 then goes through except insofar as the one-to-one correspondence of physical states to the roots of the secular equation may be upset. In a case such as He 1s2s ^1S, a requirement of orthogonality between the radial function of the series electron and that of a lower-lying shell of the same ℓ cannot be consistently imposed in treating lower states of the same symmetry. Thus the lowest-lying solution of the Hartree-Fock equations with such an orthogonality constraint imposed gives an upper limit (probably poor) to the ground-state energy, rather than an approximation to the 1s2s ^1S state as might have been hoped. We have investigated the amount by which the energy of the one-radial-node solution is shifted when orbital orthogonality is required and find it is substantial and results in a value below the experimental 1s2s ^1S energy.

The method employed to guarantee orbital orthogonality is shown on the last slide. It is very simple to apply and is essentially equivalent to a more complex scheme suggested by Huzinaga. The idea is that orthogonality at each state of iteration in an expansion-type method merely results in a single linear condition on the expansion coefficients of the orbital being varied. It is easily shown that this is a necessary but not sufficient condition that the energy be stationary with respect to variation of all expansion coefficients except for a single constraint of mutual orthogonality. Thus the self-consistent solution obtained depends on the form of the trial 1s orbital used to start the solution.

$$< E > \geq E^{exact} \qquad (1)$$

$$u_2 \ (r) = \sum_{j=1}^{\infty} C_{2,j} \ u_j(r) \qquad (2)$$

$$\psi^{HF} = \sum_{j=1}^{N} C_{2,j} \ \psi_j^{HF} \qquad (3)$$

Li $1s^2np \ ^2P^o$:

$$\psi_j^{HF} = \{ \ u_1\alpha, \ u_1\beta, \ u_{2,j} \ Y_{1,0}\alpha \ \}. \qquad (4)$$

$$\psi = \sum_{j=1}^{N} C_j \ \psi_j \qquad (5)$$

$$\lambda_k^N \geq \lambda_k^{N+1} \qquad (6)$$

$$\lambda_k^N \geq E_k^{exact} \qquad (7)$$

Conditions for applicability of energy minimum principle $< E > \geq E^{exact}$:

(a) State must be formed from configuration which differs from those of lower-lying states of the same symmetry only by the excitation of a single electron into a higher shell of same ℓ.

(b) Vector coupling must be the same as for lower states of the same symmetry.

(c) HF wave function of excited state must be linear in the radial function of the excited electron.

(d) Orbital orthogonality constraints must be limited to those which can be consistently applied in treating lower states of the same symmetry.

$$u_1(r) = \sum_{i=1}^{M} C_{1,i}\, u_{1,i}(r), \tag{14}$$

$$u_2(r) = \sum_{j=1}^{N} C_{2,j}\, u_{2,j}(r). \tag{15}$$

$$S_{12} = \sum_{j=1}^{N} A_j\, C_{2,j} = 0, \text{ where} \tag{16}$$

$$A_j = \int u_1(r)\, u_{2,j}(r)\, d\tau = \sum_{i=1}^{M} C_{1,i} \int u_{1,i}(r)\, u_{2,j}(r)\, d\tau. \tag{17}$$

Variation of $u_2(r)$ subject to (16) is equivalent to variation of

$$u_2'(r) = \sum_{j=1}^{N-1} C_{2,j}'\, u_{2,j}'(r), \text{ where} \tag{18}$$

$$u_{2,j}'(r) = u_{2,j}(r) - \frac{A_j}{A_n}\, u_{2,N}(r) \tag{19}$$

$$D_{i,j}' = D_{ij} - \frac{A_j}{A_N} D_{i,N} - \frac{A_i}{A_N} D_{j,N} + \frac{A_i\, A_j}{A_N\, A_N} D_{N,N}. \tag{20}$$