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N-BODY EXCITED STATES: EXACT EIGENVALUE OF THE STATES AS LOWER BOUND TO ENERGY VALUES

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Abstract: The Hartree-Fock equations for the lowest excited state of a N-body problem are derived, using the orthogonality of the trial function to the approximate ground state and the diagonalization of the Hamiltonian between these states as constraints. It is shown that the exact eigenvalue of the excited states is a lower bound to the approximate energy values. The method is illustrated for the para-state of a two-electron problem in a Coulomb field.

1. Introduction

The calculation of the energies and the wave functions of excited atomic and molecular states is a formidable problem. Not only is the computational labor required much greater than for the ground state, which has to be known with some accuracy, but the mathematical formulation of the Hartree-Fock method for excited states is less satisfactory. It may be helpful to relate the Hartree-Fock formalism to the Rayleigh-Ritz method of the calculus of variations. For a one-dimensional action principle, trial functions depending on one or several parameters are used and the minimum of the action under variation of these parameters is calculated. If one admits infinitely many parameters, i. e. an arbitrary analytic function, one regains the Euler-Lagrange equation of the action principle. For more-dimensional problems, one has the option, as noted by Hartree, of specifying the more-dimensional wave function only to the extent that it be expressed in terms of arbitrary one-dimensional wave functions; instead of either a finite number of parameters or ∞^N parameters as the extreme choices, one leaves $N \cdot \infty$ parameters free. The specification of the many-particle wave function in terms of one-particle wave function is very convenient for the application to quantum physics, since it allows one to incorporate easily the required symmetry property under permutations of the indistinguishable particles. This has been done by Slater and Fock.

Unfortunately, the mathematical foundation for the calculation of excited states, as given by Courant in the Maximum-Minimum Principle[1)] is not easily applicable to the Hartree-Fock equation, and in any case would require an excessive amount of labor. One is therefore content to apply the minimum principle as for the ground state with the additional requirement that the state should be orthogonal to the ground state[2)]. If Φ is the ground state and Ψ the excited state, one assumes

$$E^{(0)} = < \Phi \,|\, H \,|\, \Phi > = \text{Min}, \quad < \Phi \,|\, \Phi > = 1 \tag{1}$$

$$E^{(1)} = < \Psi \,|\, H \,|\, \Psi > = \text{Min}, \quad < \Psi \,|\, \Psi > = 1 \tag{2}$$

$$< \Psi \,|\, \Phi > = 0. \tag{3}$$

Expansion in the exact eigenfunctions U_k

$$H\, U_k = E_k\, U_k \tag{4}$$

$$\Phi = \Sigma\, A_k\, U_k, \quad \Psi = \Sigma\, B_k\, U_k \tag{5}$$

gives, assuming

$$E_0 < E_1 < E_2 \dots$$

$$< \Phi \,|\, H \,|\, \Phi > = \Sigma\, E_k \,|\, A_k \,|^2 \geqq E_0 \tag{6}$$

$$< \Psi \,|\, H \,|\, \Psi > = \Sigma\, E_k \,|\, B_k \,|^2 \geqq E_1 - (E_1 - E_0) \,|\, B_0 \,|^2. \tag{7}$$

The action principle (2) has not the exact eigenvalue as a lower bound. However, the condition (3) ensures that the last term in (7) will have an upper bound, depending on the equality of the ground state approximation. With the help of the condition (3)

$$\Sigma\, A^*_k\, B_k = 0 \tag{8}$$

and, using Schwarz's inequality

$$|\, B_0 \,|^2 \leq \frac{1}{|\, A_0 \,|^2} (1 - |\, A_0 \,|^2)\, (1 - |\, B_0 \,|^2) \tag{9}$$

hence,

$$|\, B_0 \,|^2 < (1 - |\, A_0 \,|^2) \tag{10}$$

but there is no easy method for finding A_0. A generalization of the Rayleigh-Ritz which gives an approximate energy eigenvalue with the exact value as a lower bound, was proposed by Hylleraas and Undheim[5)] and by MacDonald[6)]. We consider the expectation value of H for a state which is a linear combination of two functions f_0 and f_1, with coefficients c_0 and c_1. The roots of the secular equation are

$$E^{(0)\prime} = H_{00} - \frac{1}{2}(H_{11} - H_{00}) \left[\left(1 + 4\,|H_{01}|^2/(H_{11} - H_{00})^2\right)^{1/2} - 1\right] \tag{11}$$

$$E^{(1)\prime} = H_{11} + \frac{1}{2}(H_{11} - H_{00}) \left[\left(1 + 4\,|H_{01}|^2/(H_{11} - H_{00})^2\right)^{1/2} - 1\right] \tag{12}$$

where $H_{01} = < f_0 \,|\, H \,|\, f_1 >$. The coefficients c_0 and c_1 corresponding to the two eigenvalues can easily be found, and we get for the ground state and the first excited state the wave functions

$$\varphi = N\,[f_0 - f_1\, H_{10}/(H_{11} - E^{(0)\prime})] \tag{13}$$

$$\psi = N\,[f_1 + f_0\, H_{01}/(E^{(1)\prime} - H_{00})]. \tag{14}$$

The approximate ground state energy $E^{(0)\prime}$ will obviously be smaller than H_{00}, i.e. the approximation obtained with f_0 alone. It has been shown by the authors quoted[5,6)] that both (11) and (12) are larger than the corresponding exact eigenvalues E_0 and E_1.

In a more recent paper by Perkins[9)] it was pointed out that the above application of the Rayleigh-Ritz method can be combined with the Hartree-Fock procedure. We may ask for those functions f_0 and f_1 which make the approximate energy values (11) and (12) as small as possible. It will be sufficient in many cases to calculate the best f_1 only, since the energy of the ground state (11) will in any case be an improvement over the lowest approximation. It should be kept in mind, however, that the variation of f_1 has to be performed in (12): it would be incorrect to vary f_1 in the expectation value of H with the coefficients c_0 nad c_1 kept constant, and to insert their appropriate values in the final Hartree-Fock equation. The energy calculated from the Hartree-Fock equation will not have the form (12) if such a procedure is carried out. Unfortunately the variation of f_1 in (12) will in general lead to a very complicated equation. We propose here another approach which also has the exact energy E_1 as a lower bound. We will supplement the principle (2) not only with (3), but will demand additionally

$$< \psi \,|\, H \,|\, \Phi > = 0. \tag{15}$$

We will show that the so-obtained approximate eigenvalue $E^{(1)}$ has also E_1 as a lower bound, if the approximate ground state energy $E^{(0)}$ is smaller than E_1. With the notation of (4) and (5), (15) has the form

$$\Sigma\, E_k\, A_k^*\, B_k = 0 \tag{16}$$

and together with (8)

$$\Sigma\, (E_k - E_1)\, A_k^*\, B_k = 0 \tag{17}$$

or

$$(E_1 - E_0)\, A_0^*\, B_0 = \sum_2 (E_k - E_1)\, A_k^*\, B_k \tag{18}$$

and, using Schwarz's inequality

$$(E_1 - E_0)^2 \mid A_0 \mid^2 \mid B_0 \mid^2 \leqq (\sum_2 (E_k - E_1) \mid A_k \mid^2 (\sum_2 (E_k - E_1) \mid B_k \mid^2). \tag{19}$$

On the other hand, we have assumed

$$0 < E_1 - E^{(0)} = (E_1 - E_0) \mid A_0 \mid^2 - \sum_2 (E_k - E_1) \mid A_k \mid^2 \tag{20}$$

and therefore

$$0 < \sum_2 (E_k - E_1) \mid A_k \mid^2 < (E_1 - E_0) \mid A_0 \mid^2 \tag{21}$$

and we can now rewrite (19)

$$\begin{aligned} (E_1 - E_0)^2 \mid A_0 \mid^2 \mid B_0 \mid^2 &\leqq (E_1 - E_0) \mid A_0 \mid^2 \mid \sum_2 (E_k - E_1) \mid B_k \mid^2 = \\ &= (E_1 - E_0) \mid A_0 \mid^2 [E^{(1)} - E_1 + (E_1 - E_0) \mid B_0 \mid^2] \end{aligned} \tag{22}$$

or

$$E^{(1)} \geqq E_1 \quad \text{if} \quad E^{(0)} < E_1. \tag{23}$$

The latter assumption will usually be satisfied, unless the energy levels are very closely spaced.

A trial function Ψ for the first excited state must contain at least four free parameters in order to have one parameter free to minimize the energy $E^{(1)}$. The other three parameters will be needed to satisfy the conditions (3), (15) and the normalization. Comparing this with the usual method (11), (12), we observe that the number of free parameters is the same in both cases. We need there two parameters to normalize f_0 and f_1 while the other two parameters c_0 and c_1 could be eliminated. This elimination was possible because the trial function depended linearly on the free parameters and this linear dependence is crucial in the usual method. Our method does not rely on any special functional dependence of the trial function on the free parameters. The main advantage of the usual method lies in the fact that it gives not only an approximation to $E^{(1)}$, but supplies also an improvement of the ground state energy. Since the Rayleigh-Ritz method gives usually a very good approximation to the ground state, this improvement will not be important in many problems. The main advantage of our method becomes clear when we discuss the Hartree-Fock equations for the excited state. We can here minimize linear functionals as distinct from (11) and (12).

2. First excited state

We assume now that the ground state, described by a single Slater determinant Φ formed from N spin-orbitals $\varphi_1, \varphi_2 \ldots$, is known. These orbitals satisfy the Hartree-Fock equations

$$T_1 \varphi_k + \sqrt{2} \sum \int d^3 r_2 \, \varphi_l^* (2) \, V_{12} \{\varphi_k (1), \varphi_l (2)\} = \sum \lambda_{kl}^{(0)} \, \varphi_l (1) \tag{24}$$

where $\{\varphi_k(1), \varphi_l(2)\}$ denotes the two by two determinant formed from $\varphi_k(1)$ and $\varphi_l(2)$ and multiplied with $(2)^{-1/2}$ to preserve normalization. We note that the set of equations (24) remains invariant under transformations

$$\varphi_n = \sum_m c_{nm} \varphi'_m \tag{25}$$

with constant coefficients c_{nm}, which form a unitary matrix. The first excited state Ψ will also be formed from single-particle spin-orbitals $\psi_1, \psi_2 \ldots$, although it will not be possible to use a single Slater-determinant. The requirement that the state corresponds to a definite angular momentum, will lead to a description in terms of a sum of Slater determinants with each term describing a particular distribution of spin and orbital angular momenta over the particles. We will nevertheless use a single determinant for the general formalism, and point out the necessary modifications at the appropriate places.

We may assume of course

$$< \psi_k \,|\, \psi_l > = \delta_{kl}, \tag{26}$$

but we can also satisfy the condition (3) easily if we make one spin-orbital, say ψ_f, orthogonal to all spin-orbitals of the ground state

$$< \psi_f \,|\, \varphi_k > = 0 \, k = 1, 2, 3, \ldots N. \tag{27}$$

This is certainly a sufficient condition for (3) to hold. If Ψ is a single Slater determinant, (27) can be assumed without loss of generality. Since the action principle (2) is invariant under transformations (25) for the set of functions ψ_k, and since the determinant formed of the elements $< \psi_k \,|\, \varphi_l >$ will vanish because of (3), nontrivial solutions c_{nm} will exist, such that a ψ'_f will satisfy (27) even if none of the ψ_k satisfy (27). If the trial function is a sum of determinants, this transformation cannot be carried out in every case and one would have to rely on special symmetry properties of the system to find one and the same ψ_f in each determinant.

We reduce now the expectation value (2) to matrix elements for the individual particles

$$\sum_k < \psi_k \,|\, T \,|\, \psi_k > + \sum_{i<k}\sum < \{\psi_i, \psi_k\} \,|\, V_{12} \,|\, \{\psi_i, \psi_k\} > \tag{28}$$

and the variation of ψ_k^* will give a contribution identical with the left hand side of (24), the usual Hartree-Fock operator. However, for $k = f$, we have to add $-\eta_k \varphi_k$ because of (27). The new quantities η_k are Lagrange multipliers. According to the general discussion in the first section, we must include the subsidiary condition (15). The reduction of (11) in terms of one-particle functions requires some well known expansions of determinants, e.g.

$$\Psi = \frac{1}{\sqrt{N}} \sum_k \psi_k(1)\, M_{k,1} \tag{29}$$

and

$$\Psi = \sqrt{\frac{2}{N(N-1)}} \sum_{i<k}\sum \{\psi_i(1), \psi_k(2)\} N_{ik,12} \tag{30}$$

where the subscripts of N and M indicate the rows and columns of the original determinants which are omitted. Similar expansion hold for Φ and the corresponding subdeterminants will be denoted with $\mathcal{M}$ and $\mathcal{N}$. The kinetic energy matrix element in (15) is then

$$< \Psi | \sum_{\alpha=1}^{N} T_\alpha | \Phi > = \sum < \psi_f | T_1 | \varphi_l > < M_{f,1} | \mathcal{M}_{l,1} > \tag{31}$$

and the potential energy is

$$< \Psi | \sum_{a<\beta}\sum | \Phi > = \sum_{i<kl}\sum\sum < \{\varphi_f, \varphi_l\} | V_{12} | \{\varphi_l, \varphi_k\} > < N_{fl,12} | \mathcal{N}_{lk,12} >. \tag{32}$$

We can now derive the equation for ψ_f and we use (24) to eliminate the kinetic energy in (31)

$$T_1 \psi_f + \sqrt{2} \sum_l \int d^3 r_2 \psi_l^*(2) V_{12} \{\psi_f, \psi_l\} = \sum_l \lambda_{fl}^{(1)} \psi_l + \sum_k \eta_k \varphi_k +$$

$$+ \sqrt{2} \Lambda \Big[\sum_{i<k}\sum \sum_l \int d^3 r_2 \psi_l^* V_{12} \{\varphi_l, \varphi_k\} < N_{fl,12} | \mathcal{N}_{lk,12} > -$$

$$- \sum_i \sum_k \int d^3 r_2 \varphi_k^* V_{12} \{\varphi_l, \varphi_k\} < M_{f,1} | \mathcal{M}_{l,1} > +$$

$$+ \sum_k \sum_l \lambda_{kl}^{(0)} \varphi_l < M_{f,1} | \mathcal{M}_{k,1} > \Big]. \tag{33}$$

The equations for ψ_a with $a \neq f$ is more complicated because the scalar products of subdeterminants will also contribute. We need the additional expansion

$$M_{f,1} = \frac{1}{\sqrt{N-1}} \sum_{a=2}^{N} \psi_a(\alpha) N_{fa,1\alpha} \tag{34}$$

and get from (15):

$$< \Psi | \sum_a T_a | \Phi > = \sum_l < \psi_f | T | \varphi_l > \sum_p < \psi_a | \varphi_p > < N_{fa,12} | \mathcal{N}_{lp,12} > \tag{35}$$

which allows us to find the coefficient of $\delta \psi_a^*$. The contributions from the potential energy (32) consist of two parts. First, for $l = a$ we get

$$- \sqrt{2} \sum_{i<k}\sum \int d^3 r_2 \psi_f^*(2) V_{12} \{\varphi_l, \varphi_k\} < N_{fa,12} | \mathcal{N}_{lk,12} > \tag{36}$$

but there is an additional contribution from $N_{fl,12}$ which requires the expansion

$$N_{fl,12} = \frac{1}{\sqrt{N-2}} \sum_{a=3}^{n} \psi_a(a)\, P_{afl,12a} \tag{37}$$

and we get then the equation

$$\begin{aligned} T\psi_a + \sqrt{2}\sum_k \int d^3 r_2\, \psi_k^* V_{12}\{\psi_a, \psi_k\} &= \sum_l \lambda_{al}^{(1)} \psi_l + \\ &+ \Lambda\,[\sum_l \langle \psi_f \,|\, T \,|\, \varphi_l > \sum_p \varphi_p < N_{fa,12} \,|\, \mathcal{N}_{lp,12} > - \\ &- \sqrt{2}\sum_{i<k}\sum \int d^3 r_2\, \psi_f^* V_{12}\{\Phi_i, \Phi_k\} < N_{fa,12} \,|\, \mathcal{N}_{ik,12} > + \\ &+ \sum_{i<k}\sum_l\sum < \{\psi_f, \psi_l\} \,|\, V_{12} \,|\, \{\varphi_l, \varphi_k\} > \sum_p \varphi_p < P_{afl,123} \,|\, \mathcal{P}_{pik,123} >]. \end{aligned} \tag{38}$$

It may be desirable to have the Lagrange parameters eliminated. This can be done in the following way, but we will show in the next section that this method fails for a two-body problem. We multiply now (38) with φ_n^* and integrate over r, and subtract from the ensueing equation the conjugate complex of (24) after contraction with ψ_a. We multiply then with $\langle \psi_a \,|\, \varphi_n \rangle$ and sum over a, with $a \neq f$, and n, noting

$$\sum_a \sum_n \langle N_{fa,12} \,|\, \mathcal{N}_{ln,12} \rangle \langle \psi_a \,|\, \varphi_n \rangle = \langle M_{f,1} \,|\, \mathcal{M}_{l,1} \rangle (N-1) \tag{39}$$

and

$$\sum_a \sum_n \langle P_{afl,123} \,|\, \mathcal{P}_{nlk,123} \rangle \langle \psi_a \,|\, \varphi_n \rangle = \langle N_{fl,12} \,|\, \mathcal{N}_{ik,12} \rangle (N-2). \tag{40}$$

Now we use (11) in the reduced form (31) and (32) and obtain

$$\begin{aligned} &\sum_k \sum_a \sum_n [\langle \{\varphi_n, \psi_k\} \,|\, V_{12} \,|\, \{\psi_a, \psi_k\} \rangle - \langle \{\varphi_n, \varphi_k\} \,|\, V_{12} \,|\, \{\psi_a, \varphi_k\} \rangle] < \psi_a \,|\, \varphi_n \rangle = \\ &= \sum_l \sum_a \sum_n [\lambda_{al}^{(1)} \langle \varphi_n \,|\, \varphi_l \rangle \langle \psi_a \,|\, \varphi_n \rangle - \lambda_{ln}^{(0)} < \varphi_l \,|\, \psi_a \rangle \langle \psi_a \,|\, \varphi_n \rangle] - \\ &- \Lambda\,[\sum_{i<k} \sum \sum_n \sum_a \langle \{\psi_n, \psi_f\} \,|\, V_{12} \,|\, \{\varphi_l, \varphi_k\} \rangle \langle N_{fa,12} \,|\, \mathcal{N}_{ik,12} \rangle \langle \varphi_a \,|\, \varphi_n \rangle - \\ &- \sum_{i<k} \sum_l \sum \langle \{\psi_f, \psi_l\} \,|\, V_{12} \,|\, \{\varphi_l, \varphi_k\} \rangle \langle N_{fl,12} \,|\, \mathcal{N}_{ik,12} \rangle] \end{aligned} \tag{41}$$

which is the desired equation for Λ. The same procedure can be carried out starting from the equation for ψ_f. We will get then equations for the η_k.

The total energy of the excited state is given by (2) and (28). With the help of (33) and (38), we find

$$\sum_i \langle \psi_i \mid T \mid \psi_i \rangle + \frac{1}{2} \sum_{i<k}\sum \langle \{\psi_i, \psi_k\} \mid V_{12} \mid \{\psi_i, \psi_k\} \rangle = \sum_i \lambda_{ii}^{(1)}, \tag{42}$$

and hence

$$E^{(1)} = \sum_i \lambda_{ii}^{(1)} + \frac{1}{2} \sum_{i<k}\sum \langle \{\psi_i, \psi_k\} \mid V_{12} \mid \{\psi_i, \psi_k\} \rangle \tag{43}$$

or

$$E^{(1)} = -2 \sum_i \lambda_{ii}^{(1)} - \sum_i \langle \psi_i \mid T \mid \psi_i \rangle .$$

3. *Application to helium*

We will sketch the method presented in the preceding section for the two-electron problem in helium, when both electrons are in a para-states and we write now

$$\Psi = \frac{1}{\sqrt{2}} [\psi_a(1)\, \psi_f(2) + \psi_a(2)\, \psi_f(1)] = \{\psi_a, \psi_f\}$$

and similarly for the ground state with φ_1 and φ_2. The equations for ψ_a and ψ_f are simply

$$\begin{aligned} T\psi_a - \frac{2e^2}{r}\psi_a + \sqrt{2} \int d^3 r_2\, \psi_f^* V_{12} \{\psi_a, \psi_f\} &= \lambda_{aa}\psi_a + \lambda_{af}\psi_f + \\ + \Lambda\, [\varphi_2 \langle \{\psi_f, \varphi_2\} \mid V_{12} \mid \{\varphi_1, \varphi_2\}\rangle + \varphi_1 \langle \{\psi_f, \varphi_1\} \mid V_{12} \mid \{\varphi_1, \varphi_2\}\rangle & - \\ - \sqrt{2} \int d^3 r_2\, \psi_f^* V_{12} \{\varphi_1, \varphi_2\}], & \end{aligned} \tag{44}$$

$$\begin{aligned} T\psi_f - \frac{2e^2}{r}\psi_f + \sqrt{2} \int d^3 r_2\, \psi_a^* V_{12} \{\psi_a, \psi_f\} &= \lambda_{fa}\psi_a + \lambda_{ff}\psi_f + \eta_1\varphi_1 + \\ + \eta_2\varphi_2 + \Lambda\, [\langle \psi_a \mid \varphi_2\rangle \left(\int d^3 r_2\, \varphi_2^* V_{12}\{\varphi_1, \varphi_2\} - \lambda_{11}^{(0)}\varphi_1 - \lambda_{12}^{(0)}\varphi_2\right) & + \\ + \langle \psi_a \mid \varphi_1\rangle \left(\int d^3 r_2\, \varphi_1^* V_{12}\{\varphi_1, \varphi_2\} - \lambda_{21}^{(0)}\varphi_1 - \lambda_{22}^{(0)}\varphi_2\right)] & \end{aligned} \tag{45}$$

while (15) can be written in the form

$$\begin{aligned} \langle \Psi \mid H \mid \Phi \rangle = - \sum_{k=1}^{2} \langle \psi_a \mid \varphi_k \rangle \langle \{\psi_f, \varphi_k\} \mid V_{12} \mid \{\varphi_1, \varphi_2\}\rangle & + \\ + \langle \{\psi_a, \psi_f\} \mid V_{12} \mid \{\varphi_1, \varphi_2\}\rangle = 0. & \end{aligned} \tag{46}$$

We see at once that the process of elimination of Λ which we discussed in the last section will not work here, because (46) is bi-linear in the only two functions ψ_a and ψ_f. We can, however, modify the process and get explicite forms for Λ and the two multipliers η_k. The equations (44) and (45), which should be compared to the approximate theory presented in ref. 2, p. 226, will be discussed in a paper in preparation.

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N-ČESTIČNA POBUĐENA STANJA: EGZAKTNE SVOJSTVENE VRIJEDNOSTI STANJA KAO DONJA GRANICA ENERGETSKIH VRIJEDNOSTI

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Sadržaj

Izvedene su Hartree-Fockove jednadžbe za najniže pobuđeno stanje N-čestičnog problema upotrebljavajući kao uvjet ortogonalnost probne funkcije na aproksimativno osnovno stanje sistema i dijagonalizaciju hamiltonijana između tih stanja. Pokazano je da je točna vlastita vrijednost pobuđenih stanja donja granica aproksimativnim vrijednostima energije. Metoda je ilustrirana primjenom na para-stanje dvoelektronskog problema u Coulombovom polju.