Decomposition Property of the Slater Determinant

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The first step in solving the atomic many-body problem is the independent-particle, or Hartree-Fock method. This leads to the formulation of the system eigenfunction in terms of a single Slater determinant (neglecting correlations). By defining a matrix, the elements of which are the one-particle orbitals occurring in the Slater determinant, a method is developed whereby the wave function is written as a polynomial in the eigenvalues of the matrix. This method, when used in conjunction with the variational principle, reduces the arithmetic tedium usually resulting in the Hartree-Fock method. The numerical results are in agreement with the Hartree-Fock method (to within 1.5 %) and within 1.56 % of the exact values for a seven electron atom.

I. Introduction

The first step in solving the atomic many-body problem is the Hartree-Fock method. Here it is assumed that the electrons of the atom travel in orbits that are independent of the position of the other electrons. We call these one-electron trajectories one-particle orbitals. The Hamiltonian of the electron system is found by summing the Hamiltonians of all electrons, and then summing the Hamiltonians of all pairs of electrons. The potential field acting on each electron is a combination of the Coulomb field of the nucleus and the Coulomb field due to the charge distribution of the other electrons. We thus wish to solve the Schroedinger equation

\[ \left[ -\frac{\hbar^2}{2m} \sum_{i} \left( \frac{p_i^2}{r_i} - \frac{Ze^2}{r_i} \right) + \frac{e^2}{2} \sum_{i \neq j} \int \frac{|\varphi_i(q_i)|^2}{r_{ij}} d\tau \right] \Psi = E \Psi \]  

(1)

where \( \hbar \) is PLANCK’s constant divided by \( 2\pi \), \( m \) is the mass of the electron, \( e \) is its charge, \( Ze \) is the charge of the nucleus, \( p_i^2 \) is the Laplacian of the \( i \)’th electron, \( r_i \) is the distance of the \( i \)’th electron from the nucleus, \( r_{ij} \) the mutual distance between the \( i \)’th and \( j \)’th electrons, \( \varphi_i(q_i) \) the one-particle orbital describing the motion of the \( i \)’th particle, \( q_i \) the spin and space coordinates of the \( i \)’th electron, \( d\tau \) an element of volume, \( \Psi \) the total system wave function, and \( E \) the energy of the system. In virtue of the fact that we are assuming statistical independence between the motions of the electrons, the total wave function is written as the

product of the one-particle orbitals. This does not take into account the symmetry properties of the electrons however, and the wave function must therefore be properly antisymmetrized. To do this, we introduce an antisymmetry operator $A(P) = (-1)^P$, where $P$ is a permutation of the electron coordinates. The total wave function is thus

$$\Psi = C \sum_P (-1)^P \prod_i \phi_i(q_k)$$

where $k$ is one member of a sequence corresponding to the permutation $P$. Equation (2) is recognized as being of determinental form. This determinant is called a Slater determinant\(^2\). By expanding this determinant into the sums and differences of products of one-particle orbitals, we may proceed to solve the Schrödinger equation. Guesses are usually made for the numerical values of the one-particle orbitals. These values are then varied in accordance with the variational principle to produce a minimum expectation value of the many-electron Hamiltonian. From this minimum, the energy eigenvalue associated with the removal of a single electron is obtained. Summing the energies of all electrons, the total energy of the atom is obtained.

Due to the fact that there are $n^2$ one-particle orbitals associated with an $n$-electron atom, and $n!$ permutations of a one-particle orbital coordinates, in using the variational principle there are $n \cdot n!$ variations that must be made to compute the energy of the atom. Clearly, for large systems of electrons, the arithmetic tedium becomes too great to handle. By defining a matrix, the elements of which are the one-particle orbitals, this tedium may be reduced by a large extent. It is the purpose of this paper to present a method whereby the total wave function may be written as a polynomial (in terms of the one-particle orbitals and the eigenvalues of the matrix). This method reduces the mathematical tedium associated with the Hartree-Fock method while retaining a minimum amount of error (relative to the exact values of energy eigenvalues).

**II. Discussion**

We recall that the energy eigenvalues $E$, occurring in the Schrödinger equation

$$H \psi = E \psi$$

may be obtained, if the Hamiltonian $H$ is represented by a matrix, by solving the eigenpolynomial

$$\det [H - E(\delta_{ij})] = 0$$

where $\delta_{ij}$ is the Kronecker delta. The zeroes of the eigenpolynomial (4) are the energy eigenvalues associated with the Hamiltonian $H$. Written

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