

Systematic treatment of correlations in a generalized Hartree-Fock approximation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 3535

(<http://iopscience.iop.org/0953-8984/10/16/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 12:59

Please note that [terms and conditions apply](#).

Systematic treatment of correlations in a generalized Hartree–Fock approximation

A Gonis and T C Schulthess†

Department of Chemistry and Materials Science, L-268 Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

Received 16 June 1997

Abstract. The Hartree–Fock (HF) approximation is generalized to the study of n -particle states, taking correlation effects in interacting quantum-mechanical many-particle systems systematically into account. The case of $n = 2$ is developed explicitly. It is shown that the form of the HF equations remains essentially the same as in the usual formulation, but with appropriate interpretations of various parameters in terms of n -particle, rather than single-particle, states. We show results of calculations for model systems that illustrate the power of the method when compared to ordinary versions of the HF treatment.

1. Introduction

The various forms of the Hartree–Fock (HF) approximation, to be referred to as Hartree–Fock theory (HFT), provide one of the best known [1–4] methods for the study of interacting quantum many-particle systems in condensed matter physics, such as the electron cloud in atoms, molecules, or solids.

The most serious and long-standing objection to the Hartree–Fock approximation is its neglect of correlation effects which are, in fact, defined as differences between exact results and the results obtained using the HF method. This difficulty remains in the various forms in which the HFT has been expressed, such as in Dirac’s [5] and Löwdin’s [6] formulations based on the properties of density matrices. In fact, attempts to treat correlations within the HF scheme usually involve additional procedures, such as Jastrow’s construction [3].

In this paper, we show that, contrary to conventional wisdom, the HF method can be generalized within an n -particle framework, n HF, which allows the direct treatment of correlations in a systematic way as n increases. In this generalization, the basic formal construct of the HF method remains unchanged, but this construct is applied to n -particle states rather than to states describing a single particle.

There is an additional motivation for searching for an n -particle description of interacting quantum systems. It is conceivable that there may exist states of such systems which are not accurately described within a single-particle picture [7]. Furthermore, the study of many physical properties of materials, e.g. transport properties, can be expressed most conveniently in terms of two-particle Green functions. It appears that a method which leads directly to the calculation of two-particle quantities such as the wave function (or the Green function) for a system of interacting particles may be of some benefit.

† Present address: Oak Ridge National Laboratory, Oak Ridge, TN 37831-6114, USA.

It should be pointed out that the formalism as presented here bears some formal resemblance to the theory of so-called geminals [8, 9], or two-particle states, that were commanding some interest a few years ago. However, that theory suffers from a severely limiting handicap, namely that it does not lend itself to the construction of a many-particle wave function that has the proper symmetry, i.e., Fermi–Dirac or Bose–Einstein. This difficulty arises because it is not possible to construct properly symmetric (or antisymmetric) N -particle states with respect to individual particle coordinates out of n -particle states ($n < N$) that are determined independently of one another. It is well known that there exists no building-up principle for n -tuples of states because these states cannot be ordered in energy in such a way that their use to construct the final N -particle state is consistent with the requirements of the exclusion principle. A simple illustration of this feature is provided in the body of the paper in connection with a simplified treatment of the four electrons of the Be atom. This feature is completely avoided in the generalization of the HF method presented here. In the present approach, one considers only those n -particle states which can be deduced from the system wave function that is properly antisymmetrized with respect to the indices of individual particles. Thus, only those states which are allowed by the Pauli principle are used throughout the solution process. Furthermore, this approach is not restricted to a particular value of n , but is applicable to any partition of the system into sets of particles, each set containing n_i particles, so that $\sum_i n_i = N$, the total number of particles in the system. On the other hand, we know of no generalization of the theory of geminals to n -tuples of particles with $n > 2$.

It may be useful at this point to summarize the mathematical basis of our method in connection to a system of fermions (the treatment of bosons is similar, with the replacement of determinants in the following discussions by permanents). It rests on the observation that any determinant of order N can be written as a sum of products of determinants of orders n and $N - n$. This is Laplace's [10] theorem for expanding a determinant, which contains as a special application the elementary expansion in terms of individual elements along a row (or column) and their minors. This theorem allows one to write the expanded form of a Slater determinant in terms of determinants associated with specific sets of particles and all possible combinations of states. The idea now is to begin with such a construction for the case of non-interacting electrons, and allow these determinantal states, which are consistent with the exclusion principle, to evolve under the influence of external and/or inter-particle interactions. The equations describing this evolution of states are obtained by minimizing an energy expectation value as in ordinary HFT, but with respect to n -particle states. In fact, the starting point of the iterations for solving these n HF equations can be obtained from the ordinary FH method, since these latter can be thought of as evolving out of a set of non-interacting states under the influence of external and inter-particle fields as treated within the method.

One word on notation before we turn to formal considerations. We indicate non-interacting states (or states that can be described by means of single-particle quantum numbers) by a zero subscript (or superscript as convenient). The states that evolve out of combinations of such single-particle states, and which are no longer describable in terms of single-particle quantum numbers, are indicated by the same symbols but with no zero subscripts or superscripts. We hope that this notation, introduced only to simplify the presentation, will not lead to confusion.

In what follows, we show how the HF method can be formulated in terms of n -particle states, rather than the customary single-particle formulation. To keep the notation simple, we will assume that $n = 2$. The derivation for $n > 2$ follows straightforwardly and will be commented upon thereafter.

2. The Hartree–Fock method for n -particle states

The Hamiltonian describing an N -particle interacting system is taken to have the form (in units of $\hbar^2/2m = 1$)

$$H = \sum_{i=1}^N -\nabla_i^2 + \sum_{i=1}^N v(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j}^N v(\mathbf{r}_i, \mathbf{r}_j) \quad (1)$$

where ∇^2 is the three-dimensional Laplacian, $v(\mathbf{r}_i)$ denotes an external potential acting on the particle at \mathbf{r}_i , and $v(\mathbf{r}_i, \mathbf{r}_j)$ is a pairwise interaction between the particles at \mathbf{r}_i and \mathbf{r}_j . When the latter is zero the system is termed non-interacting, and for this case the solution of the corresponding Schrödinger equation can be constructed out of single-particle states, which we denote by

$$\phi_v(\mathbf{r}) = \begin{bmatrix} v \\ \mathbf{r} \end{bmatrix}_0$$

in terms of a single Slater determinant:

$$\Psi_{v_1 v_2 \dots v_N}^0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \hat{A} \begin{bmatrix} v_1 \\ \mathbf{r}_1 \end{bmatrix}_0 \begin{bmatrix} v_2 \\ \mathbf{r}_2 \end{bmatrix}_0 \dots \begin{bmatrix} v_N \\ \mathbf{r}_N \end{bmatrix}_0 \quad (2)$$

where v_i and \mathbf{r}_i , respectively, represent state and particle coordinates that include the spin degree of freedom. For fermions, \hat{A} is the antisymmetrizing operator with respect to the state indices (symmetrizing in the case of bosons).

This Slater determinant in terms of single-particle states can also be viewed as a linear combination of product states which constitute individual states in $3N$ -dimensional space that can be labelled with the particular permutation of single-particle indices. Retaining the linear coefficients, which are either 1 or -1 depending on the sign of the permutation, we now switch on the interaction between particles and let the individual states in $3N$ -dimensional space evolve under its influence; i.e., in N -particle space this interaction appears as an external potential, which allows a description of the time evolution of the system in terms of scattering off this external potential. This is exactly analogous to the scattering description (the Lippmann–Schwinger equation formulation) of the Schrödinger equation for a single particle moving in an external field. The interacting states in $3N$ -dimensional space can thus be found, at least formally, by solving an associated Lippmann–Schwinger equation in N -particle space. Combining the individual interacting states in $3N$ -dimensional space with the original linear coefficients that we have retained from the non-interacting system yields the correctly symmetrized N -particle wave function

$$\Psi_{v_1 v_2 \dots v_N}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \begin{bmatrix} v_1 & v_2 & \dots & v_N \\ \mathbf{r}_1 & \mathbf{r}_2 & \dots & \mathbf{r}_N \end{bmatrix} \quad (3)$$

that has evolved out of the non-interacting solution, equation (2).

At this point, it is important to clarify the meaning of the indices labelling single-particle states in the many-body wave function for the interacting system that occur in the last expression. In the interacting system, individual particles lose their significance and a description of the system in terms of single-particle states is in general inappropriate. The indices can still be used to label the state of the system in terms of the single-particle states describing a non-interacting system from which the final state evolves under the action of the inter-particle potential. Thus, the set of single-particle indices is to be considered as a single, collective index that labels the final state. This interpretation is also to be used in terms of the two-particle states that occur in the following discussion.

Solving for the fully interacting wave function in $3N$ -dimensional hyperspace is of course a formidable task and an approximate treatment is usually required. The route that we will take here relies on the fact that, from Laplace's theorem [10], the non-interacting solution of equation (2) can be written in terms of n -particle units (to simplify the notation we take $n = 2$ and N to be a multiple of 2), i.e.,

$$\Psi_{\nu_1 \nu_2 \dots \nu_N}^0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \hat{A} \begin{bmatrix} \nu_1 & \nu_2 \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0 \begin{bmatrix} \nu_3 & \nu_4 \\ \mathbf{r}_3 & \mathbf{r}_4 \end{bmatrix}_0 \dots \begin{bmatrix} \nu_{N-1} & \nu_N \\ \mathbf{r}_{N-1} & \mathbf{r}_N \end{bmatrix}_0 \quad (4)$$

with \hat{A} being applied to the state indices. The two-particle units

$$\begin{bmatrix} \nu & \mu \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0$$

used in this last expression are Slater determinants constructed from the two single-particle states

$$\begin{bmatrix} \nu \\ \mathbf{r}_1 \end{bmatrix}_0 \quad \text{and} \quad \begin{bmatrix} \mu \\ \mathbf{r}_2 \end{bmatrix}_0.$$

In a similar way, we also partition the Hamiltonian of the interacting system into distinct sets of particles, so that a given particle is a member of only one pair, and choose the pairing to correspond to the partition of particles in the wave function (the lower row in equation (3)). Denoting the pair formed by particles i_1 and i_2 by I , and the points of the corresponding two-particle space by $\mathbf{x}_I = (\mathbf{r}_{i_1}, \mathbf{r}_{i_2})$, we have

$$H = \sum_I (-\nabla_I^2 + V(\mathbf{x}_I)) + \frac{1}{2} \sum_{I, J \neq I} V(\mathbf{x}_I, \mathbf{x}_J) \quad (5)$$

where ∇_I^2 is the six-dimensional Laplacian operating in the space \mathbf{x} , the quantity $V(\mathbf{x}_I)$ is an *external* potential acting on a pair of particles,

$$V(\mathbf{x}_I) = v(\mathbf{r}_{i_1}) + v(\mathbf{r}_{i_2}) + v(\mathbf{r}_{i_1}, \mathbf{r}_{i_2}) \quad (6)$$

and $V(\mathbf{x}_I, \mathbf{x}_J)$ is the interaction between pairs I and J ,

$$V(\mathbf{x}_I, \mathbf{x}_J) = v(\mathbf{r}_{i_1}, \mathbf{r}_{j_1}) + v(\mathbf{r}_{i_1}, \mathbf{r}_{j_2}) + v(\mathbf{r}_{i_2}, \mathbf{r}_{j_1}) + v(\mathbf{r}_{i_2}, \mathbf{r}_{j_2}). \quad (7)$$

We note that the inter-particle interaction between the members of a given pair appears as an external local potential acting on the pair at point \mathbf{x} . Thus, similarly to the N -particle treatment that led to equation (3) we can determine interacting two-particle wave functions

$$\begin{bmatrix} \nu & \mu \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_p$$

which evolve out of the non-interacting two-particle determinants

$$\begin{bmatrix} \nu & \mu \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0.$$

The subscript p was introduced to distinguish the two-particle wave function of the partially interacting system, for which inter-pair interactions of equation (7) are neglected, from two-particle wave functions of the fully interacting system which will be introduced below. The full wave function of the partially interacting N -particle system can be found from the same linear combination as was used to construct the determinant in equation (4). We denote this procedure by the following expression:

$$\begin{bmatrix} \nu_1 \nu_2 | & \nu_3 \nu_4 | & \cdots | & \nu_{N-1} \nu_N \\ \mathbf{r}_1 \mathbf{r}_2 | & \mathbf{r}_3 \mathbf{r}_4 | & \cdots | & \mathbf{r}_{N-1} \mathbf{r}_N \end{bmatrix}_p = \hat{A} \begin{bmatrix} \nu_1 & \nu_2 \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_p \begin{bmatrix} \nu_3 & \nu_4 \\ \mathbf{r}_3 & \mathbf{r}_4 \end{bmatrix}_p \dots \begin{bmatrix} \nu_{N-1} & \nu_N \\ \mathbf{r}_{N-1} & \mathbf{r}_N \end{bmatrix}_p \quad (8)$$

where the vertical bars indicate the two-particle nature of the states that the full wave function in this construction consists of.

The interaction between pairs, equation (7), can now be included in an approximate way similar to that in which the inter-particle interaction is included in the ordinary HF approximation. To facilitate the derivation of the n HF equations, we briefly recall the essence of the canonical HF theory.

2.1. The canonical HF equations

We start by recalling that in ordinary HF theory the non-interacting and the interacting single-particle states which form the Slater determinant are taken to satisfy the conditions of orthonormality:

$$\int d^3r \begin{bmatrix} \nu \\ \mathbf{r} \end{bmatrix}_0^* \begin{bmatrix} \mu \\ \mathbf{r} \end{bmatrix}_0 = \int d^3r \begin{bmatrix} \nu \\ \mathbf{r} \end{bmatrix}^* \begin{bmatrix} \mu \\ \mathbf{r} \end{bmatrix} = \delta_{\nu\mu} \quad (9)$$

and completeness:

$$\sum_{\nu} \begin{bmatrix} \nu \\ \mathbf{r} \end{bmatrix}_0^* \begin{bmatrix} \nu \\ \mathbf{r}' \end{bmatrix}_0 = \sum_{\nu} \begin{bmatrix} \nu \\ \mathbf{r} \end{bmatrix}^* \begin{bmatrix} \nu \\ \mathbf{r}' \end{bmatrix} = \delta(\mathbf{r} - \mathbf{r}'). \quad (10)$$

The (single-particle) HF equations are derived by taking expectation values of the Hamiltonian with respect to the determinantal wave function, incorporating the orthonormality condition by means of a Lagrange multiplier, and minimizing the expression

$$\left\{ \langle \Psi | H | \Psi \rangle - \sum_{\nu} \epsilon_{\nu} \int d^3r \begin{bmatrix} \nu \\ \mathbf{r} \end{bmatrix}^* \begin{bmatrix} \nu \\ \mathbf{r} \end{bmatrix} \right\}$$

with respect to

$$\begin{bmatrix} \nu \\ \mathbf{r} \end{bmatrix}^*.$$

This yields the ‘eigenvalue’ equation

$$F \begin{bmatrix} \nu \\ \mathbf{r} \end{bmatrix} = \epsilon_{\nu} \begin{bmatrix} \nu \\ \mathbf{r} \end{bmatrix} \quad (11)$$

in terms of the well-known Fock operator [2].

The explicit expressions of the HF equations in the coordinate representation take the form

$$\left[-\nabla^2 + v(\mathbf{r}) + \sum_{\mu \neq \nu}^N \int d^3r' v(\mathbf{r}, \mathbf{r}') \right] \phi_{\nu}(\mathbf{r}) - \sum_{\mu \neq \nu}^N \int d^3r' v(\mathbf{r}, \mathbf{r}') \phi_{\mu}(\mathbf{r}) = \epsilon_{\nu} \phi_{\nu}^*(\mathbf{r}). \quad (12)$$

We note the presence of the direct or Hartree term and the exchange term, the third term inside the brackets and the first term outside, respectively. The term $\nu = \mu$ can be included in the direct term since it is cancelled by the corresponding inclusion into the exchange term. Therefore, we have the well-known result that the HF approximation does not include self-interaction terms.

2.2. Generalization to two-particle states

We now extend the formalism just summarized to two-particle states. Similarly to their single-particle counterparts, the two-particle states have the following orthonormality

$$\begin{aligned} \int d^3r_1 d^3r_2 \begin{bmatrix} \nu & \mu \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0^* \begin{bmatrix} \nu' & \mu' \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0 \\ = \int d^3r_1 d^3r_2 \begin{bmatrix} \nu & \mu \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0^* \begin{bmatrix} \nu' & \mu' \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0 = \delta_{\nu\nu'}\delta_{\mu\mu'} - \delta_{\mu\nu'}\delta_{\nu\mu'} \end{aligned} \quad (13)$$

and completeness

$$\begin{aligned} \sum_{\nu\mu} \begin{bmatrix} \nu & \mu \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0^* \begin{bmatrix} \nu & \mu \\ \mathbf{r}'_1 & \mathbf{r}'_2 \end{bmatrix}_0 \\ = \sum_{ij} \begin{bmatrix} \nu & \mu \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0^* \begin{bmatrix} \nu & \mu \\ \mathbf{r}'_1 & \mathbf{r}'_2 \end{bmatrix}_0 = \delta(\mathbf{r}_1 - \mathbf{r}'_1)\delta(\mathbf{r}_2 - \mathbf{r}'_2) - \delta(\mathbf{r}_1 - \mathbf{r}'_2)\delta(\mathbf{r}_2 - \mathbf{r}'_1) \end{aligned} \quad (14)$$

relations. In order to derive the HF equations in a manner analogous to that given above, we perform a variational procedure. In this procedure it is convenient to identify clearly and uniquely the particle space in which the two-particle wave functions are acting. This identification is considerably easier when the particle pairings are uniquely and distinctly defined, as is done in constructing the wave function or in partitioning the Hamiltonian. We can now obtain an eigenvalue-like equation for the two-particle states

$$\begin{bmatrix} \nu & \mu \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}$$

by following the same formal procedure as in the single-particle case. From the variational condition

$$\delta \left[\langle \Psi | H | \Psi \rangle - \sum_{\nu\mu} \epsilon_{\nu\mu} \int d^6x \begin{bmatrix} \nu\mu \\ \mathbf{x} \end{bmatrix}_0^* \begin{bmatrix} \nu\mu \\ \mathbf{x} \end{bmatrix}_0 \right] = 0 \quad (15)$$

with respect to

$$\begin{bmatrix} \nu\mu \\ \mathbf{x} \end{bmatrix}_0^*.$$

This variational condition is unambiguously defined since the coordinate \mathbf{x} is unique and remains intact throughout the process. This is the result of constructing the wave function by applying the statistics to the state indices (for the initial state), which keeps the association of particles into units the same throughout. In the coordinate representation, the 2HF equation can be written in the form

$$\begin{aligned} \left[-\nabla_{\mathbf{x}}^2 + V(\mathbf{x}) + \int d^6x' V(\mathbf{x}, \mathbf{x}') \rho_{(\nu\mu)}(\mathbf{x}') \right] \begin{bmatrix} \nu\mu \\ \mathbf{x} \end{bmatrix}_0 + \sum_{(\nu',\mu') \neq (\nu,\mu)} \int d^6x' \begin{bmatrix} \nu'\mu' \\ \mathbf{x}' \end{bmatrix}_0^* V(\mathbf{x}, \mathbf{x}') \\ \times \left\{ \begin{bmatrix} \nu\mu | & \nu'\mu' \\ \mathbf{x} | & \mathbf{x}' \end{bmatrix} - \begin{bmatrix} \nu\mu \\ \mathbf{x} \end{bmatrix}_0 \begin{bmatrix} \nu'\mu' \\ \mathbf{x}' \end{bmatrix}_0 \right\} = \epsilon_{\nu\mu} \begin{bmatrix} \nu\mu \\ \mathbf{x} \end{bmatrix}_0 \end{aligned} \quad (16)$$

where the two-particle density, $\rho_{(\nu\mu)}(\mathbf{x})$, is given by the expression

$$\rho_{(\nu\mu)}(\mathbf{x}) = \sum_{(\nu',\mu') \neq (\nu,\mu)} \begin{bmatrix} \nu'\mu' \\ \mathbf{x} \end{bmatrix}_0^* \begin{bmatrix} \nu'\mu' \\ \mathbf{x} \end{bmatrix}_0. \quad (17)$$

Here, the indices ν', μ' run over all state indices associated with the initial state of the system. As derived above, the two-particle state solutions of equation (16) are properly antisymmetrized with respect to individual particle coordinates, but are no longer expressible as determinants of single-particle states. This is a direct consequence of approximating the many-particle wave function by means of two-particle states, equation (8). In the non-interacting limit these are indeed second-order determinants. Under the inter-particle interaction, the latter evolve into two-particle states which have been treated as interactions with other such states in a manner analogous to that in which single particles interact with one another in ordinary HF theory. From these solutions, an approximate many-particle wave function can be constructed, e.g., equation (8). This wave function can then be used to compute expectation values of operators such as the Hamiltonian to obtain the corresponding observables.

The generalized two-particle HF equations are seen to have structure equivalent to their single-particle counterparts, exhibiting the presence of a direct term, written in terms of the density, and an ‘exchange’ term. Like the canonical HF equations, the present expressions do not contain spurious self-interaction terms. However, unlike the single-particle equations, they allow the determination of correlated two-particle states, removing to this extent the most basic objection to the HF method.

Finally we note that Laplace’s theorem [10] applies to any subdivision of the N particle system and not just to the two-particle units chosen in equation (4). It is thus a matter of simple algebra to become convinced that the generalized HF equations preserve their form under arbitrary partitions of the system of N particles into separate sets containing n_ν particles each, such that $\sum_\nu n_\nu = N$.

2.3. The system wave function

It is clear from what has been said above that the n HF equations lead to states that consist of all possible combinations of N particles (or states) taken n at a time, and their corresponding energy levels. In that sense, they seem to contain more information than necessary to construct the wave function of the system out of these n -tuple states.

The system wave function can be constructed in a straightforward way by starting from a product of n -tuple sates which evolves out of a product of non-interacting states, and symmetrize (or antisymmetrize) with respect to particle indices (since state indices are no longer discernible in the interacting states). The energy of the system is given by adding the energies corresponding to the states entering the initial product just mentioned. Because there may be several ways of identifying such a product, a search should be conducted to determine that product which yields the lowest energy.

3. An illustrative case: Be

In this section, we provide explicit expressions for the pair wave functions that are determined within a simple application of the 2HF method in the case of a four-particle system such as the Be atom. Although the following discussion is inadequate for a realistic description of the Be atom, which would require a linear combination of determinants, it is sufficient for illustrating some basic elements of our formalism.

Beryllium has four electrons and its ground-state configuration is $1s^2 2s^2$. Let $\chi_{nl\sigma}(m)$ denote that particle m is in state $|nl\sigma\rangle$, characterized by principal quantum n , orbital quantum number l , and spin σ (we will use a bar to denote opposite spin directions). (The extent to which such a description in terms of single-particle states is meaningful in the case of

an interacting system poses a very relevant question, but one which is somewhat beside the point for the present discussion.) Labelling the electrons 1, 2, 3 and 4, we can construct an (approximate) wave function for the entire system by antisymmetrizing the product $\chi_{1s\uparrow}(1)\chi_{1s\downarrow}(2)\chi_{2s\uparrow}(3)\chi_{2s\downarrow}(4)$ with respect to particle indices. Furthermore, the solutions of a single-particle (effective) Schrödinger equation, $\chi_{nl\sigma}$, can be arranged uniquely in order of ascending energy in a way in which each level can be occupied by two electrons so that the final wave function satisfies the Pauli principle. This way of building up the electron occupation of energy levels is unique and leads to the well-known *aufbau prinzip* (building-up principle) originally formulated by Bohr. This principle is, however, apparently confined to single-particle states and has no counterpart in terms of states of n particles determined independently from one another.

To see this, consider first a non-interacting system described by hydrogen-like wave functions. We note that any pair state of the form $\chi_{1s\sigma}\chi_{nl\sigma'}$ has an energy lower than $\chi_{2s\sigma}\chi_{2s\bar{\sigma}}$, and that there are an infinity of such states between $\chi_{1s\sigma}\chi_{1s\bar{\sigma}}$ and $\chi_{2s\sigma}\chi_{2s\bar{\sigma}}$. It is, therefore, impossible to describe the ground state of Be by selecting only those combinations forming pair states that minimize the energy while being consistent with the exclusion principle. The same difficulty persists when correlated pair states, e.g., geminals, are considered. It remains, obviously, for any value of n in determining correlated n -particle states. (We know of no attempt to extend the theory of geminals beyond $n = 2$.) For this reason, the theory of geminals has not met with much success and is more or less abandoned at present.

Given this state of affairs, one wonders whether similar difficulties can arise in the case of the pair states (or n -particle states) in the present extension of the HF method. This however is not the case: the formal element which distinguishes n HF theory from the theory of geminals and leads to acceptable and viable procedures in the former where the latter has failed is the incorporation of the correct statistics throughout the solution process.

Consider again the case of atomic Be approximated by a single Slater determinant made up of the wave functions of the ground state of the atom. We will treat this ground state as being exact (as it is for a fictitious system of non-interacting electrons) to illustrate the behaviour of the results expected within the n HF theory. This determinantal wave function has $4! = 24$ terms, each consisting of products of single-particle states. It follows from Laplace's theorem [10] on the expansion of determinants that the expanded form of the determinant can be rearranged in terms of a sum of products of determinants of order n and $4 - n$, $n < 4$. Furthermore, in each such product, particle indices can be made to appear in the same order, e.g., 1, 2, 3, 4, but with each particle index associated with all possible states. Clearly each product that enters the construction of the system wave function is consistent with the Pauli principle. Choosing $n = 2$, and denoting by the symbol $|\alpha_1(1)\alpha_2(2)\cdots\alpha_n(n)|$ a determinantal wave function of n particles, we can express the wave function for the ground state of a Be atom in the form

$$\begin{aligned}\Psi^0 &= |\chi_{1s\uparrow}(1)\chi_{1s\downarrow}(2)\chi_{2s\uparrow}(3)\chi_{2s\downarrow}(4)| \\ &= |\chi_{1s\uparrow}(1)\chi_{1s\downarrow}(2)||\chi_{2s\uparrow}(3)\chi_{2s\downarrow}(4)| \\ &\quad - |\chi_{1s\uparrow}(1)\chi_{2s\uparrow}(2)||\chi_{1s\downarrow}(3)\chi_{2s\downarrow}(4)| + |\chi_{1s\uparrow}(1)\chi_{2s\downarrow}(2)||\chi_{1s\downarrow}(3)\chi_{2s\uparrow}(4)| \\ &\quad - |\chi_{1s\downarrow}(1)\chi_{2s\uparrow}(2)||\chi_{1s\uparrow}(3)\chi_{2s\downarrow}(4)| + |\chi_{1s\downarrow}(1)\chi_{2s\downarrow}(2)||\chi_{1s\uparrow}(3)\chi_{2s\uparrow}(4)| \\ &\quad + |\chi_{2s\uparrow}(1)\chi_{2s\downarrow}(2)||\chi_{1s\uparrow}(3)\chi_{1s\downarrow}(4)|.\end{aligned}\tag{18}$$

The various determinantal wave functions shown here can be orthonormalized and are complete in their respective spaces in the usual sense.

We note that each distinct pair of particles, say 1 and 2, occurs as the argument of

all possible combinations of four single-particle states taken two at a time. Each such combination leads to an interacting two-particle state with the corresponding energy. For example, there is an energy associated with the two-particle state which evolves out of the initial state $\chi_{1s\uparrow}(1)\chi_{2s\uparrow}(2)$ (although this final, interacting state does not necessarily allow a description in terms of the single-particle states from which it has evolved). There are clearly degeneracies in the various energy levels, and the wave functions associated with them can be distinguished in terms of the partial symmetries under rotations in the separate space of each particle (much in the way in which single-particle degenerate states in an atom can be classified according to angular momentum symmetry (p_x , p_y , etc)).

It is a straightforward exercise to substitute the expression for the wave function given above into the HF equation to obtain the general expression of equation (16). The resulting expression makes clear the nature of the exchange terms, as a collection of terms as dictated by the form of the wave function, rather than as a single term as in the traditional treatment.

4. Numerical illustration

We have carried out numerical calculations to illustrate some of the simpler aspects of our method. In what follows, the formalism of 2HF theory is implemented in a manner analogous to the so-called restricted HF approximation within the single-particle picture. In that case, products of two single-particle number operators are decoupled into a number operator and an averaged number operator. This procedure clearly disregards the effects of symmetry. In the present case, a similar decoupling is implemented in terms of products of two-particle number operators, and it also neglects symmetry effects. At the same time, the method allows an improved treatment of correlation, which is the main thrust of the formalism.

The following three figures show single-particle spectra for four electrons (two with each spin direction) on a linear ring of four sites. The single-particle single-band Hamiltonian describing the *non-interacting* system is defined by its matrix elements in a tight-binding representation:

$$H_{ij}^{(1)} = \epsilon_i \delta_{ij} + t_{ij} \quad (19)$$

where ϵ_i is an on-site energy, and t_{ij} represents electron hopping from site i to site j and is taken to connect only nearest-neighbour sites. In the calculations reported here, we set $\epsilon_i = 0$ and $t = 1.0$. Also, the energies were assigned an imaginary part of $t/4.0$ for ease of presenting the spectra. Within this picture, a description of inter-particle interactions is often given by means of a term $U_{ij}n_i n_j$ being added to the Hamiltonian of non-interacting particles, where U_{ij} represents the Coulomb repulsion between two electrons on sites i and j , and n_i is the number operator for an electron on site i . Usually, U is taken to be site diagonal and we will also take this to be the case. In a (restricted) HF treatment of this model Hubbard Hamiltonian, the pair of number operators $n_i n_i$ is decoupled by replacing one of the two operators by its expectation value. This in turn leads to a Hamiltonian of the non-interacting type, equation (19), but with all on-site energies displaced by an amount $U\langle n_i \rangle$. In this description the structure of the single-particle spectrum remains identical to that for non-interacting particles.

We now generalize the HF treatment just described to two-particle space. The two-particle space associated with a ring of four sites is a torus of 16 sites and the Hamiltonian describing two non-interacting particles has the form

$$H_{ij;kl}^{(2)} = [\epsilon_i + \epsilon_j] \delta_{ik} \delta_{jl} + t [(1 - \delta_{ik}) \delta_{jl} + (1 - \delta_{jl}) \delta_{ik}]. \quad (20)$$

This describes a single particle on a torus with site energies $\epsilon_i + \epsilon_j$ (corresponding to two particles on the linear ring being at sites i and j), and nearest-neighbour hopping t . The

interaction between the particles is described by the operator $f(U)n_i n_j n_k n_l$, where $f(U)$ is a function of the configuration. Thus, when the indices i, j, k, l are all different from one another, $f(U) = 0.0$. When only two of the indices are identical, $f(U) = U$, and in the case of two different pairs of identical indices, $f(U) = 2U$. In the present version of the HF approximation, we decouple the four number operators by replacing two of them by their expectation value (average). In this case, we find that the sites along the main diagonal of the torus have their on-site energies shifted by an amount $2U\langle n_k n_k \rangle + U\langle n_k n_l \rangle = \frac{5}{4}U$, while the energies on sites off the diagonal are shifted by $U\langle n_i n_i \rangle = U/4$. Thus, the two-particle interacting Hamiltonian, which would contain a term U along the main diagonal of the torus, has all on-site energies shifted by the average energy of a pair of opposite-spin electrons on a site.

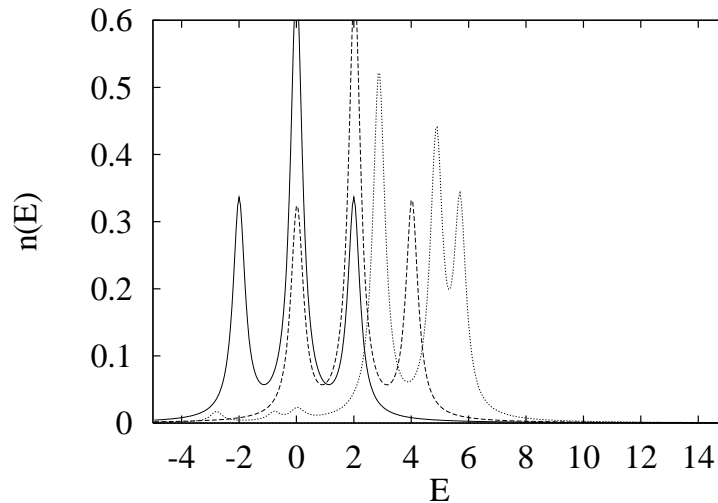


Figure 1. Single-particle spectra for a ring with four sites with $U = 0.1$. The solid line is the spectrum calculated from the restricted HF treatment while the dashed line is the spectrum obtained with the 2HF treatment, and the dotted line is the exact spectrum.

Figures 1, 2 and 3 show the single-particle spectra for four electrons on a ring of four sites (a half-filled band) obtained in the ordinary version of the HF treatment (restricted HF treatment) (solid lines) and in the two-particle generalization of this approach described above (dashed lines), compared to the exact results (dotted line). The exact results were obtained from the exact Green function of the four-electron system by inverting the full configurational matrix in four-particle space, and integrating out (summing over) the coordinates of three of the particles [11]. The three figures correspond to the cases $U = 0.1$, $U = 1.0$ and $U = 10.0$. Also, for the sake of ease of comparison, we do not display the shift in the on-site energies since they do not affect the structure of the spectra.

As the results presented above indicate, the single-particle restricted HF approximation is completely insensitive to the presence of inter-particle interactions. On the other hand, the use of the 2HF treatment, the present method, which essentially consists of the treatment of two-particles within a restricted scheme, provides a much improved representation of the exact spectra. It is, of course, not exact, since it misses the exchange interaction which is expected to be more important for small U (figure 1). However, for large U (figure 3), i.e. for strong correlations, the 2HF treatment gives a fairly accurate description of the band.

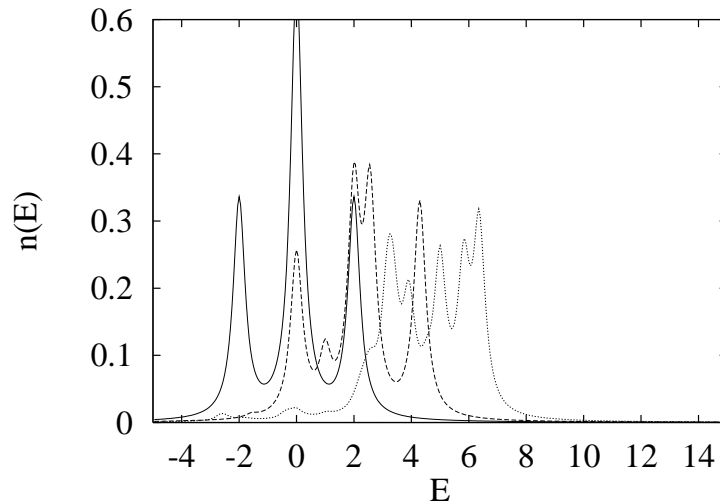


Figure 2. Results analogous to those of figure 1 but for $U = 1.0$.

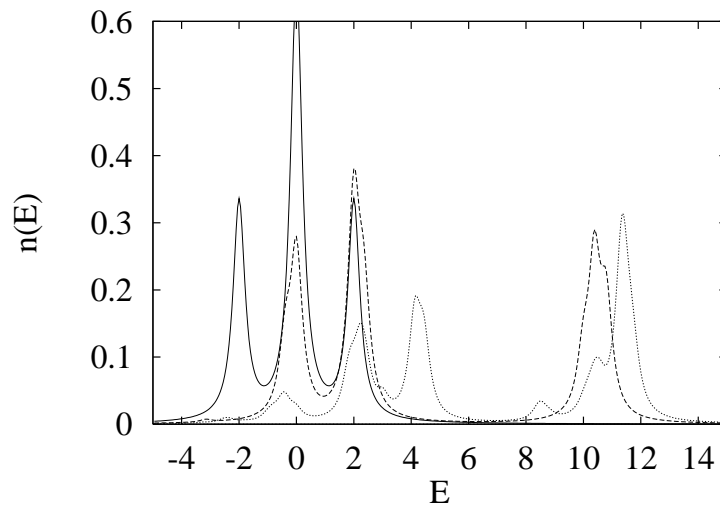


Figure 3. Results analogous to those of figure 1 but for $U = 10.0$.

5. Discussion and conclusions

The method presented above provides a generalization of the traditional Hartree–Fock treatment of interacting quantum systems, carried out within a single-particle picture, to the case of n -particle states, in which n three-dimensional particles are treated as a single unit (a point particle) in a space of $3n$ dimensions. The method is undoubtedly computationally more difficult than the traditional Hartree–Fock one, but allows the direct treatment of the effects of correlation between the members of an n -tuple of particles. It also leads directly to n -particle correlated states. In a previous publication [11] an alternative approach to the calculation of n -particle states was presented that was based on a generalization of density functional theory.

In the present formalism, n -particle states evolve out of a non-interacting many-particle

state whose wave function possesses the proper symmetry under exchange of particle coordinates. That initial state can also be taken to be the state determined as a result of a HF treatment. It is clear that n HF treatment will yield lower energies than m HF treatment for $m < n$, since the larger the number of particles forming a unit, the more the particles will be kept away from one another, thus lowering their potential energy.

Acknowledgments

We wish to acknowledge comments by Helmut Eschrig on one of our previous publications which were relevant to some of the discussion in the present paper. Support for this work was provided by Lawrence Livermore National Laboratory under the auspices of the US Department of Energy under Contract No W-7405-ENG-48.

References

- [1] Dreitzler R M and Gross E K U 1990 *Density Functional Theory* (Berlin: Springer)
- [2] Par R G and Yang Weitao 1989 *Density Functional Theory of Atoms and Molecules* (Oxford: Oxford University Press)
- [3] Fulde P 1995 *Electron Correlations in Molecules and Solids* (New York: Springer)
- [4] Massidda S, Posternak M and Baldereschi A 1993 *Phys. Rev. B* **48** 5058
- [5] Dirac P A M 1930 *Proc. Camb. Phil. Soc.* **26** 376
- [6] Löwdin P-O 1955 *Phys. Rev.* **97** 1474
- [7] Recent work has emphasized the importance of three-particle scattering in determining the electronic structure of solids; see
Manghi F, Bellini V and Arcangeli C 1997 *Phys. Rev. B* **56** 7149
- [8] Hurley A C 1976 *Electron Correlation in Small Molecules* (New York: Academic)
- [9] Kutzelnigg W 1994 *Einführung in die Theoretische Chemie* 2nd edn (Weinheim: VCH) p 2
- [10] Muir T 1960 *Treatise on the Theory of Determinants* (New York: Dover)
- [11] Gonis A, Schulthess T C, van Ek J and Turchi P E A 1996 *Phys. Rev. Lett.* **77** 2981