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The n-particle Picture and the Calculation of the Electronic Structure of Atoms, Molecules, and Solids

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1 Introduction

There are several problems in the physics of quantum systems whose importance is attested to by the time and effort that have been expended in search of their solutions. A class of such problems involves the treatment of interparticle correlations with the electron gas in an atom, a molecule (cluster) or a solid having attracted significant attention by quantum chemists and solid-state physicists. This has led to the development of a large number of theoretical frameworks with associated computational procedures for the study of this problem. Among others, one can mention the local-density approximation (LDA) to density functional theory (DFT) [1, 2, 3, 4, 5], the various forms of the Hartree-Fock (HF) approximation[1, 2, 6, 7], the so-called GW approximation[8, 9, 10], and methods based on the direct study of two-particle quantities[11, 12, 13], such as two-particle reduced density matrices[14, 15, 16, 17, 18], and the closely related theory of geminals[17, 18, 19, 20], and configuration interactions (CI's)[21]. These methods, and many of their generalizations and improvements[22, 23, 24] have been discussed in a number of review articles and textbooks[2, 3, 25, 26].

The great formal variety that characterizes these methods provides evidence of the complexity of the problem at hand. This diversity has evolved

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out of attempts to treat specific features of this complex problem, ranging from the electron gas in “small systems”, e.g., atoms and molecules, and atomic clusters, where HF-based methods and CI’s, for example, have been found very useful, or electrons in solids where the LDA has met with considerable success in determining ground-state densities and energies. Even a cursory review of the advantages and limitations of the various methods that have been proposed to study the inhomogeneous electron gas is far beyond the scope of the present work. Suffice it to say that each of these methods have come to be accepted as the most appropriate for a particular aspect of this very complex problem, while having only limited and even questionable applicability in other domains.

However, in spite of much progress along different directions and in different areas, there exists no unified conceptual framework[26] capable of providing systematic improvements to the study of correlations across a broad spectrum of materials types, while possessing well-defined convergence characteristics. Furthermore, the disparity between so-called single-particle methods, such as the LDA, and many-body techniques, e.g, Green-function theory, has led to the perception that these two approaches are irreparably divorced and disjointed from one another in a formal sense.

This perception, however, may be premature. It appears that it is possible to adopt a point of view which provides for a unified approach to the problem of correlations for systems of any size or structure. This viewpoint is the natural outgrowth of work initiated as far back as the 1930’s and which has continued in certain areas to the present.

Initially, Pauling used the concept of a single state (bond state) to describe the behavior of two electrons participating in molecular binding[27]. In the late 1950’s and early 1960’s, Brueckner[11] and collaborators, and Kadanoff and Baym[12, 28] showed, respectively, how the two-particle t -matrix and the two-particle Green function could be used in the study of interacting quantum systems in a straightforward generalization of the methods based on the corresponding single-particle quantities. However, the most telling developments have accrued from a particular approach initiated in the field of atomic and molecular physics. In this methodology, it has proved profitable to study the electronic structure and related properties of atoms by considering *all* the N electrons in the system as forming a single particle in a space of $3N$ dimensions. There is a large body of work on this approach, from which a single representative reference is given here[29].

In this method, the problem of N particles in 3-dimensional space is mapped onto a problem of a single-particle in a hyperspace of $3N$ dimensions, moving under the influence of an external potential. This potential is made up of the external potentials acting on the particles, as well as their

mutual interactions. This reduction to a single-particle in an external field has the formal nicety of allowing the use of single-particle methods in the solution of a many-particle problem. Not to downplay the significance of the computational ramifications of this formalism, we note that applying single-particle methods to hyperspace, e.g., partial-wave analysis of scattering, can be an extremely difficult task. In fact, it becomes quickly intractable when the number of particles increases beyond even some fairly small number, say $N = 4$. This feature has limited the application of this method to fairly small systems such as the He atom and the molecule H_2^+ , (where the two particles combined into one in a space of six dimensions are the nuclei). Applications to extended systems characterized by a large number of centers of force seems to be hopelessly out of reach. (However, for some innovative approaches to atoms with infinite charge and the interpretation of the results, the reader is referred to the literature[29].)

The works referred to above indicate the usefulness of viewing an N -particle system from a higher-dimensional perspective. In doing so, one should attempt to strike a balance between conceptual clarity and computational efficiency, which mitigates against considering calculations in $3n$ -dimensional space except for rather small values of n . It appears that such a procedure may be profitably employed if a system of N particles were to be considered as consisting of a collection of units or sets, $\{I_k\}$, each containing n_k particles, so that

$$\sum_k n_k = N. \quad (1)$$

The resulting problem associated with these sets of particles that interact with one another is obviously formally identical to the original one (only the meaning of the term particle having been redefined in the present case). However, it possesses the formal advantage of allowing, in principle, the systematic approach to an exact solution by treating the entire system as a single unit (N -particle picture). The operative words here are “in principle”, as practical applications do not seem to be possible but for the smallest number of particles in a unit, say $n = 2$ or $n = 3$. However, in such an implementation, the interparticle correlation is treated directly and explicitly within a unit, resulting in a more accurate treatment of the system the larger the number of particle in a unit. Furthermore, this methodology can be applied to a broad spectrum of systems, such as atoms, molecules, and solids, with fairly strong expectations that it will yield improved results compared to its corresponding use within strictly single-particle methods. For example, one can determine the ground-state two-particle, correlated density and energy in terms of two-particle states by using a generalization of DFT and LDA to the appropriate hyperspace, as is discussed below. Similarly, al-

loy phase stability and transport properties (which can be expressed directly in terms of the two-particle Green function) can also be studied, as can the ground state properties of small clusters, molecules, and atoms, within appropriate generalizations of the HF method. Finally, this method may provide a more realistic description of the electronic structure of a system than can be achieved within a single-particle framework. Even if its computational implementation is only possible for small values of particles in a unit, the method to be developed below has one very important conceptual characteristic: it tends to obscure the sharp boundaries that divide single-particle (band-theory) methods from many-body approaches, leading to a broader viewpoint and providing a possibly deeper insight into the effects of correlations than has been hitherto possible.

2 Basic Notions

We begin with the Hamiltonian for a system of N interacting particles,

$$\begin{aligned} H &= \sum_i -\nabla_i^2 + \sum_i v_i + \frac{1}{2} \sum_{i \neq j} v_{ij} \\ &= \sum_i h_i + \frac{1}{2} \sum_{i \neq j} v_{ij}. \end{aligned} \quad (2)$$

Here, ∇_i^2 is the kinetic energy operator for particle i , (with $\hbar = 1$, $2m_i = 1$, for all i), v_i represents the interaction of particle i with an external potential, such as that associated with nuclei in the system, and v_{ij} represents the mutual interaction between particles i and j . The definition of the single-particle Hamiltonian, h_i , is evident. We are interested in the solutions of the many-particle time-independent Schrödinger equation,

$$H\Psi = E\Psi, \quad (3)$$

where Ψ is the many-particle wave function for the system.

At least two different possible viewpoints present themselves immediately as alternative procedures for solving Eq.(3). One may consider the entire interacting system as a single particle in a configuration space of $3N$ dimensions, or one may consider the system wave function as consisting of certain combinations of wave functions of individual particles. In either case, of course, one is obligated to incorporate into the solution the statistics, either Fermi or Bose, governing the behavior of the system.

The first viewpoint defines the N -particle picture and leads in principle to an exact solution of Eq.(3). Leaving aside the question of whether or

not one could extract useful information from the complicated form that such an exact solution for large values of N would be bound to take, the computational hindrance associated with this approach as N increases has mitigated against widespread use of such a direct procedure. At the same time, where it has been implemented[29], such as in connection with the He atom, this approach has yielded results which agree to great precision with those of exact numerical procedures.

The second viewpoint defines what will be referred to as the single-particle picture, in which one attempts the construction of the many-body solution of Eq.(3) through the use of solutions associated with individual particles. It should be emphasized that in the language used here, the single-particle picture is not synonymous to what has come to be known as single-particle theory, in which the properties of the entire system are studied through judiciously chosen single-particle solutions of an effective Schrödinger equation. In the present terminology, the methods of single-particle theory, as well as canonical many-body theory are developed within the single-particle picture as defined above. Not to belabor the possibly obvious point, we should note that the N -particle picture mentioned above lends itself to computational procedures which are themselves generalizations of methods developed within single-particle theories. In any case, because of relative ease of implementation, the study of interacting quantum systems has proceeded almost exclusively within the single-particle picture.

Unlike the N -particle picture, which in principle leads naturally to the exact solution of the many-particle Schrödinger equation, the single-particle picture has led to the development of a number of different approximation schemes designed to address particular issues in the physics of interacting quantum systems. A particularly pointed example of this state of affairs is the strict dichotomy that has set in between so-called single-particle theories and canonical many-body theory[30, 31]. Each of the two methodologies can claim a number of successful applications, which tends to reinforce the perceived formal gap between them.

Under these conditions, one is moved to ask if indeed this gap is real or perhaps could be bridged in a way that may reveal the unified features of the problem and possibly lead to a deeper understanding of the behavior of interacting quantum systems. The work described here is an attempt to bridge this gap in a computationally viable way. It is based on a point of view bounded by the single-particle picture at one end and the N -particle picture at the other. In this point of view an interacting quantum system of N particles is taken to consist of non-overlapping units or sets of particles, $I_k = \{\mathbf{r}_1^{I_k}, \mathbf{r}_2^{I_k}, \dots, \mathbf{r}_k^{I_k}\}$, so that a particle belongs to only one such unit, and the particles in all these sets equal N , the total number of particles in

the system. Denoting the number of particles in a set I_i by n_i , leads to Eq.(1). At this point, there is no restriction as to the number of sets chosen or the numbers of particles in each set. This seems to raise the danger of possibly mishandling the statistics of the system by treating some particles in a preferential way. It will be shown below that, even though this is a "real" danger, it can be avoided.

With these considerations in mind, we return to the Hamiltonian of Eq.(2). If we denote the Hamiltonian describing the particles in a unit or subsystem I_k by H_{I_k} ,

$$H_{I_k} = \sum_{i \in I_k} \nabla_i^2 + \sum_{i \in I_k} v_i + \sum_{i \in I_k, j \in I_k} v_{ij}, \quad (4)$$

we can write the Hamiltonian of the original system in the form,

$$H = \sum_k H_{I_k} + \frac{1}{2} \sum_{k \neq l} v_{I_k, I_l}, \quad (5)$$

where

$$v_{I_k, I_l} = \frac{1}{2} \sum_{i \in I_k, j \in I_l} v_{ij}, \quad I_k \neq I_l, \quad (6)$$

where $i \in I$ indicates that i belongs to the set I and the last expression defines the mutual interaction of particles across two different units.

Now, the Hamiltonian in the form of Eq.(5) looks formally identical to that in Eq.(2), with the sets of particles I_k in the new description playing the role of individual particles in the original (single-particle) picture. We will refer to this point of view as the n -particle picture. It is seen that the traditional single-particle picture corresponds to $n = 1$, while the N -particle picture is obtained when $n = N$, the total number of particles in the system. Therefore, if we treat the Hamiltonian of Eq.(5) as consisting of individual "particles" in appropriately defined higher-dimensional spaces, we go a long way toward obtaining the unifying viewpoint alluded to above. In fact, however the Hamiltonian of Eq.(5) may be treated, and two different ways are presented below, one is assured of an exact limit as the number of units or subsystems approaches one and, correspondingly, $n \rightarrow N$.

There are, however, some very important issues still to be addressed before specific techniques are introduced for solving the Schrödinger equation in connection with the form of the Hamiltonian of Eq.(5). These have to do with retaining the proper symmetry in the wave function for the system as a whole when written in terms of wave functions of the higher-dimensional particles on which the n -particle picture is based. In the following, we shall use

the generic term “particle” to refer either to an ordinary particle in three dimensions, or to single point in a space of $3n$ dimensions, $\mathbf{x}_n = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$, describing n ordinary particles. It is hoped that the context of the discussion will provide sufficient indication as to what is meant to avoid confusion.

Let us first consider the case of distinguishable particles and take the wave function of the system, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, to be a product of single-particle states. Denoting these states by $\Phi_{I_k}(\{\mathbf{r}\}_{I_k})$, where $\{\mathbf{r}\}_{I_k}$ denotes the set of coordinates of the ordinary particles assigned to I_k , we have

$$\begin{aligned}\Psi &= \prod_k \Phi_{\alpha_k}(\{\mathbf{r}\}_{I_k}) \\ &= \prod_k \Phi_{\alpha_k}(\mathbf{x}_{I_k}),\end{aligned}\tag{7}$$

where α_k is a state of the particle I_k . These states can be chosen to be both orthonormal and complete in the usual sense. These states can be found by the usual procedure of minimizing the quantity,

$$I = \langle \Psi | H | \Psi \rangle - \sum_k \epsilon_{\alpha_k} \int d^{3n} x_{I_k} |\Phi_{\alpha_k}(\mathbf{x}_{I_k})|^2,\tag{8}$$

with respect to $\Phi_{\alpha_k}^*(\mathbf{x}_{I_k})$, where an asterisk denotes a complex conjugate. This leads to an eigenvalue equation determining the levels ϵ_{α_k} ,

$$[H_{I_k} + v^{\text{eff}}] \Phi_{\alpha_k} = \epsilon_{\alpha_k} \Phi_{\alpha_k},\tag{9}$$

where v^{eff} denotes the interaction of the particles in I_k with an external field, (e.g., the nuclei in the system), as well as their interactions with the particles in other units, $I_l \neq I_k$. This term takes the form of a Hartree-like expression involving the density of the particle I_k , and reduces to the conventional Hartree expression in the canonical single-particle description.

We now consider the case of indistinguishable particles, treating explicitly a system of Fermions. It is convenient to write the wave function for a system of *free* Fermions in the form,

$$\Psi_{i_1 i_2 \dots i_N}^0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \begin{bmatrix} i_1 & i_2 & \dots & i_N \\ \mathbf{r}_1 & \mathbf{r}_2 & \dots & \mathbf{r}_N \end{bmatrix},\tag{10}$$

In this notation, we designate a single-particle state by the symbol $\phi_i(\mathbf{r}) = \begin{bmatrix} i \\ \mathbf{r} \end{bmatrix}$. This notation is meant to emphasize the fact that a fully antisymmetrized wave function for non-interacting particles may be obtained by distributing individual particles over all possible states written in some order or, alternatively, by distributing all possible states over *particles* which

have been labeled in a permanent way. Thus, a fully antisymmetrized wave function is obtained from the last expression as a sum of terms resulting from keeping the particle labels in the order given in the lower row, and performing all possible permutations on the state indices in the top row. From now on, we take this expression to denote this fully antisymmetrized wave function.

Let us now partition the particles in the system according to some scheme which assigns n_i particles to distinct sets I_i in accordance with Eq.(1). As this partitioning depends only on the number of particles in each unit, it can be effected by dividing the lower row in the expression for the wave function, Eq.(10), into sets of n_i particles beginning from the left. Thus, particles 1, 2, ..., n_1 are taken to form the first set, particles $n_1 + 1, n_1 + 2, \dots, n_1 + n_2$, to form the second set, and so on. Each set is marked off by means of vertical lines as given in the following expression written explicitly for the case of pairs, (assuming that the total number of particles is divisible by two),

$$\begin{aligned} & \left[\begin{array}{cc|cc|ccc} i_1 i_2 & i_3 i_4 & \cdots & i_{N-1} i_N \\ \mathbf{r}_1 \mathbf{r}_2 & \mathbf{r}_3 \mathbf{r}_4 & \cdots & \mathbf{r}_{N-1} \mathbf{r}_N \end{array} \right] = \hat{A} \left[\begin{array}{cc} i_1 & i_2 \\ \mathbf{r}_1 & \mathbf{r}_2 \end{array} \right] \\ & \times \left[\begin{array}{cc} i_3 & i_4 \\ \mathbf{r}_3 & \mathbf{r}_4 \end{array} \right] \cdots \left[\begin{array}{cc} i_{N-1} & i_N \\ \mathbf{r}_{N-1} & \mathbf{r}_N \end{array} \right], \end{aligned} \quad (11)$$

where the antisymmetrizing operator, $\hat{A}$, acts on the state indices, and the vertical lines indicate the partitioning of the system into pairs of particles and their corresponding pair states. In this expression, we can use the combined notation $\mathbf{x}_k$ to denote the particles in I_k as a single point in a space of $3n_k$ dimensions. In the present case, we have $\mathbf{x}_1 = (\mathbf{r}_1, \mathbf{r}_2)$, $\mathbf{x}_2 = (\mathbf{r}_3, \mathbf{r}_4)$, and so on. It is, therefore, seen that because of the equivalence of distributing states over particles to distributing particles over states, the wave function of a system of free Fermions is not affected by a partitioning into sets of specific particles.

To proceed with formal developments, we now associate with each particle I_k in hyperspace a coordinate $\mathbf{x}_k$, and a state α_k , which in the form employed here is such as to correspond to all possible independent combinations of the free particle states into the units I_k . *As long as the particles remain free*, a fully antisymmetrized wave function can be obtained by antisymmetrizing with respect to *particle* indices a product of the type given in Eq.(7).

It is tempting to think that this procedure can be used when the states α_k are obtained directly through the solution of an appropriate Schrödinger equation in $3n_k$ -dimensional space. This, however, is not the case. As a specific example, let us consider the Be atom whose ground state configuration is $1s^2 2s^2$. The states involved are (in a hopefully obvious notation), $\chi_1 = 1s \uparrow$,

$\chi_2 = 1s \downarrow$, $\chi_3 = 2s \uparrow$, and $\chi_4 = 2s \downarrow$. Using these wave functions, an approximate wave function for the system in the form of a Slater determinant can be obtained by antisymmetrizing the product $\chi_1(1)\chi_2(2)\chi_3(3)\chi_4(4)$ *either* with respect to state or particle indices. However, suppose that we are given states of pairs of particles, (each fully antisymmetrized and consistent with the Pauli principle), and choose the two of the lowest energies to construct the ground-state wave function of the system. In this case these would be determinantal wave functions denoted by $(\chi_1(1)\chi_2(2))$ and $(\chi_1(3)\chi_4(4))$, since the state of immediately higher energy than the ground state of two particles is obtained by exciting *one* of them to the next level. Now, forming the product of these two states and antisymmetrizing with respect to particle indices *does not* cause the final wave function to vanish for violating the exclusion principle, and thus this incorrect state is not excluded from the final wave function as it should be. This feature is obviously retained when the pair states are obtained directly, rather than as products of single-particle states. Because of it, the ordinary theory of geminals, depending on the determination of two-particle states, does not allow the construction of a properly antisymmetrized wave function that is consistent with the Pauli exclusion principle. Hence, the well-known absence of an *aufbau prinzip* (building-up principle) in terms of *independently* determined n -particle states. Of course, antisymmetrization with respect to single-particle-state indices would take care of the problem, and eliminate inappropriate wave functions, but this procedure is not viable when n -particle states are determined directly and independently of one another.

One of the applications of the n -particle picture made below involves the generalization of the Hatree-Fock approximation to n -particle states. If one attempted to determine n -particle states directly from the equations, coupled with an antisymmetrization procedure with respect to particle indices, one would encounter precisely the same difficulty as noted above. Instead, the problem must be approached from a different perspective.

In this approach, we consider the evolution of a system of particles described by means of the generalized HF equations as the interparticle interaction is turned on, starting from a single Slater determinant. The determinantal state corresponding to the zero-interaction limit provides an “initial condition” for solving the generalized HF equations within the n -particle picture. The states which evolve out of this procedure are known to satisfy the Pauli principle in the zero-interaction limit, and the generalized HF procedure to be described below maintains the correct symmetry as well as the requirements of the exclusion principle.

We also discuss the generalization of density-functional theory to n -partical states, n DFT, and the possible extension of the local density ap-

proximation, n LDA. We will see there that the difficulty of describing the state of a system properly in terms of n -particle states presents no formal difficulties since DFT is directed only at the determination of the particle density rather than individual-particle wave functions. The extent to which practical applications of n DFT within a generalized Kohn-Sham scheme will provide a viable procedure is commented upon below.

3 Generalization of the Hartree-Fock Approximation

The equations of the HF approximation are derived by taking expectation values of the Hamiltonian with respect to a determinantal wave function written in terms single-particle states, incorporating the orthonormality condition by means of a Lagrange multiplier, and minimizing the expression $\left\{ \langle \Psi | H | \Psi \rangle - \sum_i \epsilon_i \int d^3r \begin{bmatrix} i \\ \mathbf{r} \end{bmatrix}^* \begin{bmatrix} i \\ \mathbf{r} \end{bmatrix} \right\}$ with respect to $\begin{bmatrix} i \\ \mathbf{r} \end{bmatrix}^*$. In the coordinate representation, this yields the "eigenvalue" equation

$$\begin{aligned} & \left[-\nabla^2 + v(\mathbf{r}) + \sum_{j \neq i}^{N/2} \int d^3r' \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \phi_i(\mathbf{r}) \\ & - \sum_{j \neq i}^N \int d^3r' \frac{\phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}) = \epsilon_i \phi_i^*(\mathbf{r}). \end{aligned} \quad (12)$$

We note the presence of the direct or Hartree term and the exchange term, third term inside the brackets and first term outside, respectively. The term $i = j$ can be included in the direct term since it is canceled 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.

We now extend the formalism just summarized to two-particle states. We begin by writing the wave function of the system of N particles as the sum of products of two-particle states each of which possesses the proper symmetry under exchange of ordinary particles, and with the total wave function being fully symmetrized or antisymmetrized with respect to exchange of individual particles. Denoting such a two-particle state by the symbol $\begin{bmatrix} i & j \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}$ we have for the full wave function the expression given in Eq.(11).

We now envision these pair states to evolve out of free and non-interacting plane-wave states as the interaction with the nuclei and between the particles are introduced. This is a natural way of viewing the evolution of a set of

initially free particles under the action of an external field (e.g. nuclear attraction) and their mutual interaction. Under the action of the external field the particles form a bound system, described approximately through the solutions of the HF equations. The n -particle picture allows an approximate description of the way in which the interaction among the particles now modifies these HF states. Clearly, this description becomes exact as $n \rightarrow N$. At the same time, the solutions for the n -particle states should yield a lowering of the total energy of the system compared to the HF method because of the more accurate treatment in the former of correlation effects that would tend to keep the particles apart thus lowering their potential energy.

In the procedure just outlined, the final wave function retains the proper symmetry under exchange of state indices or particle exchange. This wave function, described in more detail below, corresponds to a particular partition of the particles into pairs, and each of the pairs is associated with every possible two-particle state that can be formed by and evolves out of an original set of single-particle free and non-interacting states. Denoting by a zero subscript two-particle states in free space, we have the following orthonormality

$$\begin{aligned} & \int d^3r_1 d^3r_2 \begin{bmatrix} i & j \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0^* \begin{bmatrix} k & l \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0 \\ &= \int d^3r_1 d^3r_2 \begin{bmatrix} i & j \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0^* \begin{bmatrix} k & l \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}_0 = \delta_{ik} \delta_{jl} \end{aligned} \quad (13)$$

and completeness

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

relations.

In order to generalize the HF equations to n -particle states, 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 $\begin{bmatrix} i & j \\ \mathbf{r}_1 & \mathbf{r}_2 \end{bmatrix}$ by following the same formal

procedure as in the single-particle case. From the variational condition

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

with respect to $\begin{bmatrix} i & j \\ \mathbf{x} \end{bmatrix}^*$ we obtain the equation in the coordinate representation

$$\begin{aligned} & \left[-\nabla_{\mathbf{x}}^2 + V(\mathbf{x}) + \int d^6x' V(\mathbf{x}, \mathbf{x}') \rho_{(ij)}(\mathbf{x}') \right] \begin{bmatrix} i & j \\ \mathbf{x} \end{bmatrix} \\ & + \sum_{nm} \int d^6x' \begin{bmatrix} n & m \\ \mathbf{x}' \end{bmatrix}^* V(\mathbf{x}, \mathbf{x}') \\ & \times \left\{ \begin{bmatrix} i & j & | & n & m \\ \mathbf{x} & | & \mathbf{x}' \end{bmatrix} - \begin{bmatrix} i & j \\ \mathbf{x} \end{bmatrix} \begin{bmatrix} n & m \\ \mathbf{x}' \end{bmatrix} \right\} = \epsilon_{ij} \begin{bmatrix} i & j \\ \mathbf{x} \end{bmatrix}, \end{aligned} \quad (16)$$

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

$$\rho_{(ij)}(\mathbf{x}) = \sum_{nm \neq ij} \begin{bmatrix} n & m \\ \mathbf{x} \end{bmatrix}^* \begin{bmatrix} n & m \\ \mathbf{x} \end{bmatrix}. \quad (17)$$

It should be emphasized that the combinations of “single-particle” indices, such as i, j , are to be viewed as a single combined index denoting the pair state that has evolved out of the individual particle states, i and j , under the interparticle interaction (and the interaction with an external potential).

The generalized two-particle HF equations are seen to have a structure equivalent to their single-particle counterparts, exhibiting the presence of a direct term, written in terms of the density, and an “exchange” term. As 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 fully correlated two-particle states removing to this extent the most basic objection to the HF method.

3.1 Numerical illustration

We present the resulting calculations of single-particle spectra for four electrons (2 of 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,

$$H_{ij}^{(1)} = \epsilon_i \delta_{ij} + t_{ij}, \quad (18)$$

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 neighbor 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 interparticle 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 $n_i n_j$ 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, Eq.(18), 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,

$$H_{ij;kl}^{(2)} = [\epsilon_i + \epsilon_j] \delta_{ik} \delta_{jl} + t [(1 - \delta_{ik}) \delta_{jl} + (1 - \delta_{jl}) \delta_{ik}]. \quad (19)$$

This describes a single particle on a torus with site energies $\epsilon_i + \epsilon_j$ (corresponding to two particles on the linear ring being on sites i and j), and nearest-neighbor 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 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 $U\langle n_i n_i \rangle = \frac{U}{4}$. 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 shows, for $U = 10.0$, the single-particle spectra for four electrons on a ring of four sites (half-filled band) obtained in the ordinary version of HF treatment (restricted HF) (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

Figure 1: Single-particle spectra for a ring with four sites with $U = 10.0$. The solid line is the spectrum calculated from the restricted HF while the dashed line is the spectrum obtained with the 2HF, and the dotted line is the exact spectrum.

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. Also, for the sake of ease of comparisons, we do not display the shift in the on-site energies since they do not affect the structure of the spectra.

As the present results indicate, the single-particle HF approximation is completely insensitive to the presence of interparticle interactions. On the other hand, the use of 2HF, the present method, which essentially consists of the treatment of two-particles, provides a much improved representation of the exact spectra.

4 Generalization of DFT

Given the formal similarity between the Hamiltonians defined in Eqs.(2) and (5), it follows that the ground-state energy, E , is given in terms of a universal functional of the pair (or n -particle) density, $n(\mathbf{x})$, which attains its minimum value for the exact pair density. Furthermore, within a Kohn-Sham scheme, the form of this functional is identical to the functional of ordinary DFT but is given in terms of the correlated pair density. The details of this derivation

are identical to those of ordinary DFT and we confine ourselves to the final result. The energy functional which determines the density in two-particle phase space can be written in the form,

$$E[n(\mathbf{x})] = T_s[n(\mathbf{x})] + U[n(\mathbf{x})] + E_{xc}[n(\mathbf{x})], \quad (20)$$

where $T_s[n(\mathbf{x})]$ represents the kinetic energy of a system of non-interacting particles at the density $[n(\mathbf{x})]$, the quantity $U[n(\mathbf{x})]$ is defined by

$$\begin{aligned} U[n(\mathbf{x})] &= \int d^6x V(\mathbf{x})n(\mathbf{x}) \\ &+ \int d^6x_1 \int d^6x_2 n(\mathbf{x}_1)V(\mathbf{x}_1, \mathbf{x}_2)n(\mathbf{x}_2), \end{aligned} \quad (21)$$

and $E_{xc}[n(\mathbf{x})]$ contains the difference between the exact kinetic energy $T[n(\mathbf{x})]$ and that represented by $T_s[n(\mathbf{x})]$, as well as the difference between the exact interparticle interaction and its “classical” approximation given by Eq.(21),

$$\begin{aligned} E_{xc}[n(\mathbf{x})] &= T[n(\mathbf{x})] - T_s[n(\mathbf{x})] + \int d^6x_1 \int d^6x_2 \\ &\times V(\mathbf{x}_1, \mathbf{x}_2) [n(\mathbf{x}_1, \mathbf{x}_2) - n(\mathbf{x}_1)n(\mathbf{x}_2)]. \end{aligned} \quad (22)$$

Here, $n(\mathbf{x}_1, \mathbf{x}_2)$ represents the two-particle correlated density in two-particle space or, equivalently, the correlated density of four ordinary particles. As in ordinary DFT, the exchange-correlation functional is not known but can be used in a local density approximation (LDA) sense through, for example, the study of 6-dimensional jellium.

Both formal analysis and computational developments associated with DFT can be carried over intact to n DFT. For example, the exact two-particle ground-state density, $n_0(\mathbf{x})$, can be determined through a constrained search[32] for that many-particle, properly symmetrized or antisymmetrized wave function, with symmetry imposed with respect to ordinary particles, which yields n_0 and also minimizes the many-particle energy, $T + V_{pp}$, where V_{pp} denotes the interparticle interaction in two-particle space. Essentially any method developed within a single-particle application of DFT for the study of electronic structure can, with appropriate technical modifications, be extended to two-, or n -particle states. The use of multiple-scattering theory to calculate fully correlated two-particle densities in solids will be given in a future publication.

4.1 Numerical illustration

In order to illustrate the role played by the two-particle density in the determination of the electronic structure, we study the single-particle spectrum of

four electrons of total spin zero on a four site single-band linear ring described by a Hubbard Hamiltonian

$$H = \sum_i \epsilon_i c_i^\dagger c_i + \frac{1}{2} \sum_{i>j} t_{ij} c_i^\dagger c_j + U \sum_i n_{i\sigma} n_{i\bar{\sigma}}, \quad (23)$$

where $c_i^\dagger$ and c_i are creation and annihilation operators for an electron on site i , the site energies ϵ_i are chosen equal to zero, the hopping term t_{ij} is confined to near neighbors and set equal to 1.0, and the on-site Coulomb interaction felt by electrons of opposite spin is taken to have the values 1.0 and 10.0, with the respective results shown in Figs. 2 and 3. Exact two-particle and single-particle Green functions and spectra are obtained in down-folding procedure by summing over (integrating out) the coordinates of one and three of the particles, respectively, in the four-particle Green function. This, in turn, is obtained through the usual procedure as a “single-particle” Green function in a four-particle phase space which in the present case leads to a 256-dimensional matrix. We also include results obtained within a version of the GW approximation in which the self-energy,

$$\Sigma_{ij}(E) = \lim_{\eta \rightarrow 0} \frac{1}{2\pi} \int e^{-i\omega\eta} W_{ij}(\omega) G_{ij}(E - \omega) d\omega. \quad (24)$$

is given in terms of the exact single-particle Green function and the exact screened interaction which is determined in terms of the non-interacting, zero superscript, and exact two-particle Green functions, $W_{ij;kl}(E) = \{G_{ij;kl}^{(0)}\}^{-1} - G_{ij;kl}^{-1}\}$.

Finally, we also show the single-particle spectra derived through down-folding from an averaged two-particle Green function in which two-particle states are obtained in the presence of another pair of particles. These states are consistent with the Pauli exclusion principle but neglect the interactions among configurations of two-particle spaces. In all cases the energy was assigned an imaginary part of $0.25t$ for presentation purposes.

As is seen in these figures, these averaged results are in considerably better agreement with the exact spectra than those obtained in the present version of the GW approximation, particularly for large values of U . One also sees that the averaged results overestimate the gap in the strong U limit as may be expected in a non-self-consistent procedure of this type. Even for $U/t = 1.0$, a region in which the GW approximation has been found to give accurate results for real systems, the averaging of the two-particle Green function in the presence of a finite density resolves the band structure much more accurately. We note the resonance at $U = 1.0$ which is missed in the GW results, and that both approximate results are displaced somewhat with

Figure 2: Exact single-particle spectrum (solid line) for four electrons on a four-site ring compared with the results of a GW approximation (dash-dotted line) and those obtained from an effective two-particle Green-function (dashed line) for $U = 1.0$.

Figure 3: Results analogous to those of the previous figure but for $U = 10.0$.

respect to the exact ones. Much of this effect, along with the wider gap in the strong U limit mentioned above can be traced back to the incomplete treatment of the Pauli principle, i.e., the neglect of configuration interactions. Both of these approximations can be expected to improve with increased dimensionality and lattice connectivity. More detailed discussions of these and other similar numerical results than can be presented here will be given in a future publication.

5 Discussion

The formalism presented here indicates the unifying power of the n -particle picture and provides an extension of the HF and density functional theories to the treatment of fully correlated two-particle states, (and by a straightforward extension of n -particle states). In the case of the HF method, it allows the study of correlation effects in a systematic way in terms of increasing the unit size, becoming exact as $n \rightarrow N$. In the case of DFT, it leads to a general minimum principle governing correlated densities in quantum systems which is analogous to the principle governing single-particle densities. This formalism also becomes exact in the limit in which the entire system of particles is treated as a single unit. Thus, within an n -particle picture, HF theory and DFT are seen to be two different methods leading to exact results in the same limiting procedure.

Although its computational implementation of the method, say within a partial-wave analysis, increases in difficulty rapidly with increasing dimensionality of the n -particle phase space, its application to two-particle states is well within the domain of present computational technology.

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