## Treatment of electron-electron correlations in electronic structure calculations

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A methodology is introduced for the systematic treatment of electron-electron correlations in solids and other interacting quantum N-particle systems. The method is developed within the framework of electronic structure theory (band theory) but, in contrast to conventional approaches, which are based on the singleparticle picture, it is formulated within a many-particle picture in which n particles in d-dimensional phase space are treated as a single particle in a phase space of nd dimensions. In this phase space, interparticle interactions appear as external potentials allowing the treatment of the system of particles through the use of single-particle methods, while at the same time allowing a systematic, direct, and nonperturbative treatment of interparticle interactions. The method makes use of the invariance of the Hamiltonian describing an interactingparticle system under partitioning into subsystems of n particles. This treatment leads to exact results in the limit  $n \rightarrow N$ . Based on such partitioning, we propose a generalization of density functional theory and an appropriately defined local density approximation to treat the interactions between the *n*-particle units in a system of  $N \ge n$  particles. This approach yields *n*-particle correlated densities and *n*-particle states which can be used in an analysis of the electronic properties of materials, such as total energy, phase stability, electronic transport, and others. We use the formal construct of multiple-scattering theory to develop the method for the calculation of the two-particle electronic structure of a solid and the corresponding total energy of the ground state. We also illustrate some of the properties of the method in terms of a Hubbard model Hamiltonian on a linear ring. Various features of the method and further possible applications are presented in a discussion section. [S0163-1829(97)02240-6]

# I. INTRODUCTION

### A. Preamble

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. In many-particle quantum systems correlation effects can arise either because of the indistinguishability of the particles, i.e., the imposition of Fermi or Bose statistics, because of direct interparticle interactions, e.g., the Coulomb interaction, or because two or more particles interact simultaneously with the same external potential, e.g., in the study of transport in random systems.

The treatment of correlation and exchange effects is a preeminent problem in the study of the electronic structure of solids, as well as that of "small" systems such as atoms and molecules. A number of well-known approximation methods have been developed for the study of fully interacting manyparticle systems. Among the most prominent, the local density approximation (LDA) to density functional theory (DFT),<sup>1,2</sup> various extensions and corrections to the LDA,<sup>2</sup> the various forms of the Hartree-Fock<sup>3</sup> (HF) approximation, and the *GW* approximation<sup>4-6</sup> can be mentioned. These methods, and many improvements introduced to alleviate their various shortcomings, have been discussed in a number of review articles,<sup>1,7</sup> and their numerous applications along with theoretical studies have revealed much of their internal structure as well as their advantages and limitations when compared to one another, or against general criteria of a formal nature.

Although a detailed review of these methods cannot be given here, it may be useful to mention their most outstanding features. The methods based on DFT, such as the LDA, can yield quite accurately ground-state energies and equilibrium volumes of solids in most cases, but they can fail to give the correct structure for the ground state of the system (e.g., Fe where LDA predicts the ground state to be in a face centered instead of body centered cubic structure<sup>8</sup>). The inacuracies that can ensue from using such methods to predict the excitation spectrum of semiconductors and insulators is well known.<sup>9</sup> In spite of a number of attempts at improvement, such as self-interaction corrections<sup>10–12</sup> and gradient corrections,<sup>13,14</sup> the treatment of exchange and correlation and of excited states remains the most serious impediment in numerical applications of DFT.

Hartree-Fock-based methods, on the other hand, do allow a proper treatment of exchange effects and do not require the removal of spurious self-interaction terms. The most common approaches used for solids, however, neglect correlation effects as, for example, the restricted HF method (single determinantal wave functions). Some improvement in the treatment of such effects in the case of solids is achieved on the basis of additional schemes such as the use of a screened exchange interaction with a diagonal dielectric function. Finally, the GW approximation allows indeed the calculation

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All methods briefly outlined above are based directly on the calculation of single-particle properties of the interacting system, such as the density or the Green function. Therefore, they cannot lead directly to correlated two-particle (or higher-order) correlation functions. Furthermore, there seems to be no unique way of improving systematically any of these methods so that correlation effects are taken into account through the treatment of increasingly larger numbers of particles.

Finally, there is an additional reason for pursuing a determination of two-particle states (or density) in a material. It is not clear that materials behavior can be described most efficiently in every case in terms of single-particle states. For example, transport properties can be expressed directly in terms of the two-particle Green function which, in presentday applications, is approximated by the product of two single-particle Green functions. Therefore, it seems worthwhile to attempt the development of a formalism which allows the calculation of two-particle quantities (and by extension n-particle quantities) including a direct treatment of interparticle interactions.

As is shown in this paper, a scheme can be constructed which allows the direct and self-consistent calculation of n-particle densities using *single-particle* methods. The formalism is based on the framework of DFT, which is generalized to apply to n-particle states, leading to a description of the ground state of a system in terms of the n-particle correlated density. Also, the energy is given as a unique functional of that density and assumes its minimum value for the exact density. A preliminary account of the formalism presented in this paper has been given in a previous publication.<sup>16</sup>

For the sake of ease of presenting the formalism, we treat explicitly the case of two-particle states with vanishing total spin, but the extension to n-particle states is straightforward. We also neglect relativistic effects. Thus, the formalism as presented here applies directly to spin-compensated systems. Furthermore, we treat the case of solids with an infinite number of electrons so that no questions arise with regard to partitioning the system into two-particle units.

The remainder of the paper takes the following form. In Sec. II, we develop DFT for the case of two-particle states, and in Sec. III we show how the formal construct of multiple-scattering theory can be used to solve the Schrödinger equation for the solid within a generalized version of the LDA. Section IV contains the results of model calculations for a system of four electrons on a linear ring of four sites described by a Hubbard Hamiltonian with on-site interaction. Some conclusions that can be drawn from this work and some future plans are presented in Sec. V. Finally, an Appendix contains a number of formal results about partialwave expansions in higher-dimensional spaces.

# II. DFT FOR *n*-PARTICLE STATES

We consider the Hamiltonian of a fully interacting *N*-particle system,

$$\hat{H} = \sum_{i} -\nabla_{i}^{2} + \sum_{i} v_{i} + \frac{1}{2} \sum_{ij} v_{ij}, \qquad (1)$$

where  $\nabla_i^2$  is the Laplacian operator for particle i,  $v_i = v(\mathbf{r}_i)$  is a single-particle potential for particle i, and  $v_{ij} = v(\mathbf{r}_i, \mathbf{r}_j)$  is the interparticle potential, with  $v_{ii} = 0$ . Ordinarily, we are interested in the solutions of the many-particle wave equation,

$$H\Psi = E\Psi, \tag{2}$$

where  $\Psi$  denotes the many-body wave function for the interacting system.

We consider the density  $n(\mathbf{r})$  for the (nondegenerate) ground state of the system. The usual proof of the uniqueness of the external potential as a functional of the density proceeds by *reductio ad absurdum*. Let there be two external potentials,  $v(\mathbf{r})$  and  $v'(\mathbf{r})$ , differing by more than a constant and each giving the same ground-state density  $n(\mathbf{r})$ . Let also  $\hat{H}$  and  $\hat{H}'$  be the corresponding many-body Hamiltonians, and  $\Psi$  and  $\Psi'$  the associated wave functions. Both  $\hat{H}$  and  $\hat{H}'$  would correspond to the *same* ground-state density, but the wave functions  $\Psi$  and  $\Psi'$  would be different. Take  $\Psi'$ to be a trial wave function for the system described by  $\hat{H}$ [which includes  $v(\mathbf{r})$ ] and use the fact that the expectation value of the energy is a minimum for the correct wave function to obtain the result

$$E_{0} < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle$$
$$= E_{0}' + \int n(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d^{3}r, \qquad (3)$$

where  $E_0$  and  $E'_0$  denote, respectively, the energy of the *N*-electron system (excluding nuclear-nuclear repulsion), under the influence of v and v'. The integral  $\int n(\mathbf{r})v(\mathbf{r})d^3r$ describes the interaction of the charge distribution with the external field. Similarly, taking  $\Psi$  as a trial wave function for the system described by  $\hat{H}'$ , we have

$$E_{0}^{\prime} < \langle \Psi | \hat{H}^{\prime} | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}^{\prime} - \hat{H} | \Psi \rangle$$
$$= E_{0} - \int n(\mathbf{r}) [v(\mathbf{r}) - v^{\prime}(\mathbf{r})] d^{3}r .$$
(4)

Adding the last two equations, we obtain

$$E_0 + E'_0 < E'_0 + E_0. \tag{5}$$

These inequalities constitute a contradiction to the premise that there can be two different v's, differing by more than a constant, that give the same density  $n(\mathbf{r})$  for the ground state of the system. This proves the theorem (the second theorem of Hohenberg and Kohn<sup>17</sup>). We now show that this theorem carries through virtually intact in a hyperspace in which n particles are considered as a single particle. We consider explicitly the case n=2.

Let us consider again the Hamiltonian of Eq. (1) but as a sum of distinct, nonoverlapping pairs of particles (so that a given particle belongs to only one pair), labeled by I, and write the Hamiltonian in the form

$$H = \sum_{I} -\nabla_{I}^{2} + \sum_{I} V_{I} + \frac{1}{2} \sum_{I, J \neq I} \frac{1}{2} V_{IJ}.$$
 (6)

This Hamiltonian is the same as that above, Eq. (1), except that it is expressed in terms of pairs of particles. We consider explicitly systems with infinite numbers of particles (or with finite but even numbers) so that the partition into pairs can be effected exactly. Also, we consider singlet pairs only so that exchange effects on the wave function arise only from the interchange of particles across pairs. This partition does not constitute a restriction for zero-spin systems. Now, we note that for each such pair we can write,

$$\nabla_i^2 + \nabla_j^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} + \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2} = \sum_{\alpha=1}^6 \frac{\partial^2}{\partial x_{I\alpha}^2}$$
$$= \nabla_I^2 = \nabla_{\mathbf{x}}^2, \qquad (7)$$

where the coordinates of the two particle have been combined in a single coordinate in six dimensions

$$\mathbf{x} = (x_i, y_i, z_i, x_j, y_j, z_j) = (x_1, x_2, x_3, x_4, x_5, x_6).$$
(8)

This six-dimensional coordinate forms the direct part of the phase space (hyperspace) of the two particles, in which the pair appears as a single particle. The other terms that appear in Eq. (6) are uniquely defined in terms of the original Hamiltonian. Thus, with  $\mathbf{x} = (\mathbf{r}_i, \mathbf{r}_j)$ , we have

$$V_{I} \equiv V(\mathbf{x}) = V(\mathbf{r}_{i}, \mathbf{r}_{j}) = v(\mathbf{r}_{i}) + v(\mathbf{r}_{j}) + \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}, \qquad (9)$$

and

$$V_{IJ} \equiv V(\mathbf{x}, \mathbf{x}') = V(\mathbf{r}_{i}, \mathbf{r}_{j}; \mathbf{r}_{i}', \mathbf{r}_{j}') = \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{i}'|} + \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}'|} + \frac{1}{|\mathbf{r}_{j} - \mathbf{r}_{i}'|} + \frac{1}{|\mathbf{r}_{j} - \mathbf{r}_{j}'|}.$$
(10)

This completely defines the Hamiltonian in Eq. (6).

The important feature to notice about this Hamiltonian is that it has a form *identical* to that in Eq. (1). Therefore, it suggests a treatment using a single-particle framework, where the particles are in six-dimensional (rather than threedimensional) coordinate space. This form of the Hamiltonian allows one to carry through essentially unchanged the proof of the Hohenberg-Kohn theorem so that it holds in the phasespace of two particles (or n particles). Thus the potential, and hence the energy, is a unique functional of the density, so that we can write for the energy of the electron gas,

$$E[n(\mathbf{x})] = T[n(\mathbf{x})] + U[n(\mathbf{x})], \qquad (11)$$

where the various terms are assigned their familiar meaning from ordinary DFT, but must be interpreted as quantities in an appropriate phase space. For example, for n=2 the term  $U[n(\mathbf{x})]$  contains all electrostatic interactions among and between particles in six-dimensional space, as well as their interaction with the nuclei.

This generalization of the Hohenberg-Kohn theorem is a straightforward consequence of the observation that the original proof is not dependent on dimensionality. In other words, the theorem holds intact in a configurational space of 3N dimensions for systems described by the Hamiltonian of Eq. (6). As is the case with respect to its canonical form, *n*DFT yields an energy functional which is stationary with respect to variations in the density and assumes its lowest value for the correct density of the ground state.

# A. The Kohn-Sham equations

In order to make DFT a usefull tool, explicit expressions for the energy functional E[n] are needed. The Kohn-Sham (KS) formalism<sup>19</sup> provides such an expression for ordinary DFT by writing the kinetic energy in terms of single-particle states, which can be determined in a straightforward selfconsistent scheme, and casting the rest of the kinetic energy as well as the nonlocal part of the potential energy into the so-called exchange and correlation functional, for which suitable approximations such as LDA can be found. The KS formalism is reviewed in a number of texts and review articles<sup>13,14</sup> and only some of its more salient features will be mentioned here.

We will now attempt to make clear which formal results of the KS formalism hold irrespective of dimensionality and which must be justified when applied to a space with a dimension larger than three. With this in mind, we introduce single-particle orbitals, generalized KS functions, such that

$$n(\mathbf{x}) = \sum_{I} |\Psi_{I}(\mathbf{x})|^{2}.$$
 (12)

The meaning of these functions as well as the extent of the sum over I is commented upon below. For the moment, we consider these functions as the solutions of an effective "single-particle" Schrödinger equation obtained as follows.

We define a single-body potential by the relation,

$$V(\mathbf{x}) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \int d^6 x' V(\mathbf{x}, \mathbf{x}') n(\mathbf{x}')$$
$$- \sum_n Z_n \left[ \frac{1}{|\mathbf{r}_i - \mathbf{R}_n|} + \frac{1}{|\mathbf{r}_j - \mathbf{R}_n|} \right], \quad (13)$$

where  $\mathbf{x} = (\mathbf{r}_i, \mathbf{r}_j)$ , and  $V(\mathbf{x}, \mathbf{x}')$  is given by Eq. (10). For a given density, the energy is evaluated in the usual manner,

$$E[n(\mathbf{x})] = T_s[n(\mathbf{x})] + \int d^6 x V(\mathbf{x}) n(\mathbf{x}) + J[n(\mathbf{x})]$$
  
+  $E_{\mathbf{x}c}[n(\mathbf{x})], \qquad (14)$ 

where

$$T_{s}[n(\mathbf{x})] = \sum_{I} \int d^{6}x \Psi_{I}^{*}(\mathbf{x}) \nabla_{\mathbf{x}} \Psi_{I}(\mathbf{x}), \qquad (15)$$

represents the kinetic energy functional of a noninteracting gas,

$$J[n(\mathbf{x})] = \frac{1}{2} \int d^6x \int d^6x' n(\mathbf{x}) n(\mathbf{x}') V(\mathbf{x}, \mathbf{x}'), \quad (16)$$

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<sup>18</sup> and is given by the expression

$$E_{\mathrm{xc}}[n(\mathbf{x})] = T[n(\mathbf{x})] - T_s[n(\mathbf{x})] + \int d^6 x_1 \int d^6 x_2 V(\mathbf{x}_1, \mathbf{x}_2)$$
$$\times [n(\mathbf{x}_1, \mathbf{x}_2) - n(\mathbf{x}_1)n(\mathbf{x}_2)]. \tag{17}$$

Now, the single-particle Schrödinger equation yielding the solutions  $\Psi_l(\mathbf{x})$  takes the form,

$$\left[-\nabla_{\mathbf{x}}^{2}+V(\mathbf{x})+\mu_{\mathrm{xc}}(\mathbf{x})\right]\Psi_{I}(\mathbf{x})=E_{I}\Psi_{I}(\mathbf{x}),\qquad(18)$$

where the *exchange-correlation* potential is given by the expression,

$$\mu_{\rm xc}(\mathbf{x}) = \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{x})}.$$
(19)

Up to this point, the KS scheme is formally identical to that originally proposed for the case of three-dimensional systems. Most importantly, the wave functions (orbitals)  $\Psi_I(\mathbf{x})$  are to be interpreted only as an "aid to the calculation," their function being to reproduce the density by means of Eq. (12).

The proper implementation of the variatonal principle to the energy functional of Eq. (11) is carried out by restricting the set of trial densities to those which are v representable, i.e., to densities for which a corresponding local external potential can be found for the interacting Hamiltonian. The assumption that underlies the derivation of the KS scheme is that each of these v-representable densities can also be represented by a noninteracting Hamiltonian which leads to the single-particle Schrödinger equation of the form of Eq. (18). Such densities are said to be interacting as well as noninteracting v representable. For ordinary particles the assumption is justified when the ground state is nondegenerate,<sup>19</sup> but even for degenerate ground states a rigorous extension of the Kohn-Sham theorem can be formulated. This is done by assuming forms for the kinetic energy functional which include a fully antisymmetric wave function rather than the product states used for Eq. (15). In order to generalize the formalism to *n*-particle states and construct the kinetic energy functional in *n*-particle space, one therefore has to ascertain that the proper symmetry of the wave function with respect to individual particles is retained when the system wave function is written in terms of n-particle states. In the remainder of this section, we will outline how this can be done.

We begin by noting that any noninteracting state in conventional three-dimensional space can be constructed from a linear combination of Slater determinants. Using Laplace's theorem<sup>20</sup> the expanded form of a determinant of order *N* can be expressed as the sum of products of determinants of lower orders,  $n_i$ , such that in *each* product  $\sum_i n_i = N$ . Furthermore, applied to a Slater determinant, this means that each n-order determinant can be associated with the coordinates of a given set of n particles distributed over all possible combinations of N states for the noninteracting system taken n at a time. This is consistent with the partition of the Hamiltonian into distinct sets of particles while preserving the symmetry of the wave function required by the exclusion principle.

Now, allow the interaction between particles *within* each unit to set in which results in an external potential acting on the particles described by the Hamiltonian of Eq. (6). The various determinantal states now evolve under the action of this potential resulting in a system which is "partially" interacting in the context of ordinary particles but strictly *noninteracting* in terms of *n*-particle units. However, the wave function written in terms of the final *n*-particle states, and corresponding to a noninteracting system in hyperspace, leads to a density in that space which is by construction noninteracting v representable in hyperspace. Furthermore, this wave function is fully antisymmetric with respect to the coordinates of individual (three-dimensional) particles.

This discussion has also revealed the extent of the summation over I in Eq. (12). This index runs over all possible combinations of fully interacting n-particle states which evolve out of combinations of the states of an N-particle system considered n at a time.

### B. A simple example: the Be atom

It may be useful to illustrate some of the previous discussion through a simple example. Even though we are interested specifically in the case of solid materials, describing a system with a small number of electrons within a twoparticle formalism can reveal a number of important features. It illustrates the structure of the two-particle states, shows how the two-particle density is to be evaluated, how the single-particle density can be obtained from it, and how it is possible for a spin-compensated system to construct a fully antisymmetrized wave function from the knowledge of only product states.

Beryllium has four electrons and its ground-state configuration is  $1s^22s^2$ . 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  $\sigma$ . Labeling the electrons 1, 2, 3, and 4, we can construct a wave function for the entire noninteracting 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, which leads to a single Slater determinant. This determinantal wave function has 4!=24 terms, each consisting of products of single-particle states.

Now, it follows from Laplace's theorem<sup>20</sup> 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 overall 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 the Be atom in the form,

$$\Psi = |\chi_{1s\uparrow}(1)\chi_{1s\downarrow}(2)\chi_{2s\uparrow}(3)\chi_{2s\downarrow}(4)|$$

$$= |\chi_{1s\uparrow}(1)\chi_{1s\downarrow}(2)||\chi_{2s\uparrow}(3)\chi_{2s\downarrow}(4)|$$

$$- |\chi_{1s\uparrow}(1)\chi_{2s\uparrow}(2)||\chi_{1s\downarrow}(3)\chi_{2s\downarrow}(4)|$$

$$+ |\chi_{1s\uparrow}(1)\chi_{2s\downarrow}(2)||\chi_{1s\downarrow}(3)\chi_{2s\uparrow}(4)|$$

$$- |\chi_{1s\downarrow}(1)\chi_{2s\uparrow}(2)||\chi_{1s\uparrow}(3)\chi_{2s\downarrow}(4)|$$

$$+ |\chi_{1s\downarrow}(1)\chi_{2s\downarrow}(2)||\chi_{1s\uparrow}(3)\chi_{2s\uparrow}(4)|$$

$$+ |\chi_{2s\uparrow}(1)\chi_{2s\downarrow}(2)||\chi_{1s\uparrow}(3)\chi_{1s\downarrow}(4)|. (20)$$

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

Now, it is easily shown that the single-particle density obtained from integrating out of the modulus of the total wave function the coordinates of three of the particles has the form of Eq. (12) as a sum of moduli of single-particle states. It is equally easily shown that the two-particle density obtained by integrating out of the modulus of the system wave function the coordinates of two of the particles has a similar form,

$$n(\mathbf{x}) = |\chi_{1s\uparrow}(1)\chi_{1s\downarrow}(2)|^{2} + |\chi_{1s\uparrow}(1)\chi_{2s\uparrow}(2)|^{2} + |\chi_{1s\uparrow}(1)\chi_{2s\downarrow}(2)|^{2} + |\chi_{1s\downarrow}(1)\chi_{2s\uparrow}(1)|^{2} + |\chi_{1s\downarrow}(1)\chi_{2s\downarrow}(2)|^{2} + |\chi_{2s\uparrow}(1)\chi_{2s\downarrow}(2)|^{2}, (21)$$

in which various simplifications through a collection of terms that contribute equally to the final result is evident. This expression is indeed a sum over two-particle states, with each such state consisting of all possible pairs of indices of single-particle states that entered the construction of the original wave function. Also, we note in this expression the presence only of states that are consistent with the exclusion principle for the entire system. Furthermore, the states entering the expression for the density can indeed be ordered in terms of increasing energy, with the possibility of degeneracy associating different states with the same level. These states, such as  $\chi_{1s\downarrow}(1)\chi_{2s\downarrow}(2)$  and  $\chi_{1s\downarrow}(2)\chi_{2s\downarrow}(1)$ , would be distinguished by the distribution of their other quantum numbers, such as those of angular momentum or spin.

The expression for the density in terms of two-particle states, Eq. (12), must be interpreted in the light of the last expression. It consists of a sum of the moduli of two-particle states (*n* particle in general) which yields the exact twoparticle (*n*-particle) density of the ground state of the system (which is still noninteracting). Which states are to be used is to be decided by the exchange-correlation potential function leading to them. For example, in the case of the Be atom with zero interaction, that function would incorporate the proper conditions imposed by the Pauli principle so that the only functions that would derive from it are those in the last expression. In the more general case of nonvanishing correlation, the exact potential function of DFT will yield only those solutions which have the property of reproducing the energy of the system, avoiding nonphysical solutions that do not satisfy the Pauli principle. These states will not, in general, subscribe to a description in terms of single-particle states, but then there is no reason that they should. Finally, these states can be used to construct the system wave function through their combination into a sum of products which in the zero interaction limit passes over into Eq. (20).

It follows from the last expression for the two-particle density that the single-particle density can be obtained by first summing over (integrating out) one of the state indices that characterize a two-particle state in the noninteracting limit, and integrating over the coordinates of one of the particles. When this procedure is applied to the Green function, it leads to the down-folding process discussed in the section on numerical results.

It is also interesting to note that a fully antisymmetrized wave function for the system can be obtained from a simple product of *n*-particle states. To accomplish this, we form a product of states which in the noninteracting limit reduces to a product entering a single determinant, and antisymmetrize with respect to particle coordinates which are taken to *include* spin. In fact, one can begin with a simple product, such as that involving the states appearing in the first term on the expansion of the wave function given above, and antisymmetrize with respect to particle coordinates, provided these also include the spin. Because of this feature, it is only necessary to consider product states in coordinate space, which is the basis for developing the formalism of two-particle scattering theory in subsequent sections.

#### C. The LDA in phase space

We have seen that the Hamiltonian of a fully interacting N-particle system (with  $N \rightarrow \infty$ ) can be written in the forms of Eqs. (6)–(10), with the ground-state energy given by Eq. (14).

In these expressions, the exchange and correlation part,  $E_{\rm xc}[n({\bf x})]$ , can be evaluated numerically for a homogeneous system of interacting particles in hyperspace and then used in the LDA sense in terms of the local density,  $n({\bf x})$ . Although no explicit reference to spin is made here, the functions  $\Psi_l({\bf x})$  are extensions of the familiar Kohn-Sham spin functions and satisfy the effective single-particle Eq. (18),

$$\left[-\nabla_{\mathbf{x}}^{2}-V(\mathbf{x})-\boldsymbol{\mu}_{\mathrm{xc}}(\mathbf{x})\right]\Psi_{I}(\mathbf{x})=E_{I}\Psi_{I}(\mathbf{x}),\qquad(22)$$

where the exchange-correlation potential is given by the usual relation of DFT, Eq. (19),

$$\mu_{\rm xc} = \frac{\delta E_{\rm xc}[n]}{\delta[n(\mathbf{x})]}.$$
(23)

In terms of these functions, the single-particle Green function in hyperspace takes the form

$$G(\mathbf{x}, \mathbf{x}'; E) = \sum_{I} \frac{\Psi_{I}^{*}(\mathbf{x})\Psi_{I}(\mathbf{x}')}{E - E_{I}},$$
(24)

so that consistent with the usual definition of a single-particle density we have

$$n(\mathbf{x}) = \sum_{I} |\Psi(\mathbf{x})|^2, \qquad (25)$$

where *I* denotes a set of single-particle states in two-particle phase space, as described in the previous section. We note that the density can also be obtained in terms of the imaginary part of the appropriate Green function,  $G(\mathbf{x}, \mathbf{x}'; E)$ , in the form,

$$n(\mathbf{x}) = -\frac{1}{\pi} \int dE \operatorname{Im} G(\mathbf{x}, \mathbf{x}; E).$$
 (26)

The single-particle density is now obtained by means of the relation,

$$n(\mathbf{r}) = \int d^3 r' n(\mathbf{r}, \mathbf{r}')$$
$$= \frac{1}{\pi} \int d^3 r' \int_{F}^{E_F^{(2)}} dE \operatorname{Im} G(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}'; E), \quad (27)$$

where  $E_F^{(2)}$  is the highest energy of an occupied two-particle state.

As in its ordinary three-dimensional applications, 2LDA consists of the determination of the two-particle levels of a system and the subsequent determination of the density by occupying the states lowest in energy. In this procedure, the prevailing statistics can be taken explicitly into account by occupying the states lowest in energy according to the presence or absence of the exclusion principle.

An application of the LDA would require the knowledge of  $E_{\rm xc}[n({\bf x})]$ , and consequently of  $\mu_{\rm xc}$ , for interacting but otherwise uniformly distributed electrons as a function of the pair density. In principle, this quantity must be obtained through numerical studies of the six-dimensional uniform, interacting gas (jellium). It is to be noted that this procedure is not equivalent to a six-dimensional treatment of threedimensional jellium. Such a treatment would result in a nonuniform density because of the presence of the interparticle potential between the members of a pair, whereas application of the LDA requires the treatment of system that is uniform in six-dimensional phase space. Such a system can be obtained by zeroing the intrapair interaction and considering six-dimensional particles interacting by means of the potential  $V(\mathbf{x}, \mathbf{x}')$ . We refer to applications of DFT and LDA to *n*-particle states and *n*DFT and *n*LDA, respectively.

Furthermore, the exchange-correlation functional must be constructed so as to account in principle for the effects of symmtery that are not taken into account within the *n*-particle states. For example, if determinantal wave functions are used, then  $\mu_{xc}$  must contain the effects of symmetry across *n*-particle units. On the other hand, simple product states can be used in which case the exchange-correlation potential must describe the effects of interchanging the coordinates of any two particles. Thus, the exchange-correlation functional guarantees that the Kohn-Sham equations yield only those solutions which enter the construction of the ground-state density.

This completes the description of the LDA in the phase space of two particles for the systems under consideration here. We now turn our attention to the solution of the "single-particle" effective Schrödinger equation given by Eq. (22), using the formalism of multiple scattering theory (MST). The first step in that direction is the characterization of the geometry of hyperspace in the presence of interparticle interactions. For the sake of simplicity, and also because in the case of solids we are only interested in the construction of the density rather than the wave functions, we develop the formalism in terms of product states rather than determinantal states. This makes the formal aspects of the development considerably clearer without affecting its viabilty. Fully antisymmetrized two-particle (or *n*-particle) states can be used if necessary. On the other hand, only product states can be employed provided that the exchange-correlation functional is constructed to include the effects of symmetry among all particles in the system.

#### **D.** The structure of hyperspace

We consider a three-dimensional single-particle space<sup>21</sup> defined by a set of N points and positions  $\mathbf{R}_n$ . The corresponding two-particle space, also to be referred to as correlated space or hyperspace, consists of  $N^2$  points and positions  $\mathbf{R}_N = (\mathbf{R}_n, \mathbf{R}_m)$ . In the case of a three-dimensional periodic lattice generated by the primitive vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$ , the two-particle space is generated by the six primitive vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  are orthogonal to the set  $\mathbf{a}_4$ ,  $\mathbf{a}_5$ ,  $\mathbf{a}_6$ , where the vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  are orthogonal to the set  $\mathbf{a}_4$ ,  $\mathbf{a}_5$ ,  $\mathbf{a}_6$ , although the two sets are identical within each subspace. Now, we have

$$\mathbf{R}_N = \sum_{i=1}^6 N_i \mathbf{a}_i.$$
(28)

We confine our discussion to the periodic case.

We consider systems in which the single-particle potential,  $V(\mathbf{r})$ , is a sum of contributions from nonoverlapping cell potentials,

$$V(\mathbf{r}) = \sum_{n} V(\mathbf{r} - \mathbf{R}_{n}), \qquad (29)$$

centered at the lattice sites,  $\mathbf{R}_n$ . Because of translational symmetry, we have  $V(\mathbf{r} + \mathbf{R}_n) = V(\mathbf{r})$ . These cell potentials give rise to a potential in two-particle space which has the form,

$$v(\mathbf{x}) = \sum_{n} V(\mathbf{x} - \mathbf{R}_{N}), \qquad (30)$$

associated with cells in two-particle space. The cell potential,  $V(\mathbf{x}-\mathbf{R}_N)$ , is given by Eq. (9), so that for the cell in hyperspace corresponding to the single-particle cells at  $\mathbf{R}_N = (\mathbf{R}_n, \mathbf{R}_m)$ , we have

$$V(\mathbf{x}-\mathbf{R}_N) = V(\mathbf{r}_1) + V(\mathbf{r}_2) + U[|\mathbf{r}_1+\mathbf{R}_n-(\mathbf{r}_2+\mathbf{R}_m)|],$$
(31)

where the periodicity of the single-particle potentials has been used. It follows from this expression that the potential in hyperspace is periodic only when U=0. In the presence of the interaction, the potential retains only a partial periodicity of the form,

$$V(\mathbf{x} - \mathbf{R}_N^N) = V(\mathbf{x}), \qquad (32)$$

where  $\mathbf{R}_N^N = (\mathbf{R}_N, \mathbf{R}_N)$ . Thus, in the presence of the Coulomb interaction, the potential is partitioned into a collection of N

three-dimensional periodic potentials associated with each interlattice distance and having the form,

$$V_n(\mathbf{x}) = V(\mathbf{r}_1) + V(\mathbf{r}_2) + U(|\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{R}_n|).$$
(33)

Clearly, this potential contains the interparticle interaction between two particles located inside two cells separated by a vector distance  $\mathbf{R}_n$  apart. Therefore, because of the form that the potential takes, the hyperspace separates naturally into N"parallel" three-dimensional surfaces, each characterized by the cell potential given in the last expression. This construction is quite analogous to that encountered in the treatment of layered materials, such as surfaces and interfaces of threedimensional systems, which often are characterized by parallel layers inside each of which the potential is periodic in two dimensions. The treatment of the present sixdimensional structure within MST can be effected by a direct extension of methods derived for the treatment of layered materials in three dimensions.

## **III. MULTIPLE-SCATTERING THEORY**

The cell structure of the potential in hyperspace is well suited for treatment within the framework of MST. Since the basic formalism of the theory remains the same in any dimensionality, we quote only those results that are relevant to our immediate discussion, and refer the reader to the literature<sup>22-24</sup> for more details.

## A. Basic elements of MST

We seek a determination of the single-particle Green function in two-particle phase space characterized by the potential of Eq. (31). The corresponding Lippmann-Schwinger equation takes the form

$$G(\mathbf{x},\mathbf{x}') = G_0(\mathbf{x},\mathbf{x}') + \int d^3 x'' G_0(\mathbf{x},\mathbf{x}'') V(\mathbf{x}'') G(\mathbf{x}'',\mathbf{x}').$$
(34)

It is easy to verify that solutions to this equation are also solutions of the corresponding Schrödinger equation for the Green function. Iteration of Eq. (34) yields the expression

$$G(\mathbf{x}, \mathbf{x}') = G_0(\mathbf{x}, \mathbf{x}') + \int d^6 x_1 \int d^6 x_2 G_0(\mathbf{x}, \mathbf{x}_1)$$
$$\times T(\mathbf{x}_1, \mathbf{x}_2) G_0(\mathbf{x}_2, \mathbf{x}'), \qquad (35)$$

where the T matrix is given by

$$T(\mathbf{x}_{1},\mathbf{x}_{2}) = V(\mathbf{x}_{1}) \,\delta(\mathbf{x}_{1} - \mathbf{x}_{2}) + V(\mathbf{x}_{1}) \int d^{6}x_{3}G_{0}(\mathbf{x}_{1},\mathbf{x}_{3})T(\mathbf{x}_{3},\mathbf{x}_{2}).$$
(36)

In the case in which the potential is given as a sum of cell contributions, the T matrix can be written in the form

$$T(\mathbf{x},\mathbf{x}') = \sum_{MN} \mathcal{T}^{MN}(\mathbf{x},\mathbf{x}'), \qquad (37)$$

where (suppressing the arguments and the integrals),

$$\mathcal{T}^{MN} = V_m \delta_{MN} + V_m G_0 \sum_P \mathcal{T}^{PN}.$$
(38)

In order to express  $\mathcal{T}^{MN}$  in terms of the *t* matrices associated with individual cells we write this equation in the form,

$$\mathcal{T}^{MN} - V_M G_0 \mathcal{T}^{MN} = V_M \delta_{MN} + v_M G_0 \sum_{P \neq M} \mathcal{T}^{PN}.$$
 (39)

This, in turn, can be written as (with integral signs restored),

$$\mathcal{T}^{MN}(\mathbf{x},\mathbf{x}') = t^{M}(\mathbf{x},\mathbf{x}')\,\delta_{MN} + \int d^{6}x_{1}t^{M}(\mathbf{x},\mathbf{x}_{1})$$
$$\times \int d^{6}x_{2}G_{0}(\mathbf{x}_{1},\mathbf{x}_{2})\sum_{P\neq M}\mathcal{T}^{PN}(\mathbf{x}_{2},\mathbf{x}')\,,$$
(40)

where  $t^M = V_M + V_M G_0 t^M$  is the *t* matrix for potential in cell  $\mathbf{R}_M$ . This can be verified by operating on both sides of Eq. (40) with  $1 - V_M G_0$ .

The canonical development of MST now proceeds via the introduction of the angular momentum representation in twoparticle phase space. In correlated space, this is accomplished in the same way as in three-dimensional space with the obvious difference that in performing a partial-wave expansion the angular momentum states corresponding to the dimensionality of the space are to be used. A summary of some basic relations of hyperspherical harmonics- the generalizations of three-dimensional spherical harmonics to higher-dimensional spaces— is given in the Appendix, while a full exposition can be found in the book by Avery<sup>25</sup>. As is shown there, the spherical harmonics,  $Y_L$ , along with the spherical Bessel, j, Neumann, n, and Hankel,  $h^+$ ,  $h^-$ , functions have immediate generalizations to higher-dimensional spaces. For the sake of easy reference, we use the same symbols as commonly employed in denoting these functions, but use the capital Greek letter  $\Lambda$  instead of L, and  $\lambda$  instead of *l* to denote angular momentum indices in hyperspace. We also define the combinations

$$J_{\Lambda}(\mathbf{x}) = j_{\lambda}(x) Y_{\Lambda}(\hat{x}), \quad N_{\Lambda}(\mathbf{x}) = n_{\lambda}(x) Y_{\Lambda}(\hat{x}),$$
$$H_{\Lambda}^{\pm}(\mathbf{x}) = h_{\lambda}^{\pm}(x) Y_{\Lambda}(\hat{x}), \quad (41)$$

which are the regular  $(J_{\Lambda})$  and irregular solutions of the free-particle Schrödinger equation (Helmholtz equation) in hyperspace.

We also need the expansion of the free-particle propagator in phase space in terms of the hyperspherical functions defined in the last expressions. It can be shown that when x < x', we have

$$G_0(\mathbf{x} - \mathbf{x}') = -ik \sum_{\Lambda} J_{\Lambda}(\mathbf{x}) H_{\Lambda}(\mathbf{x}'), \qquad (42)$$

with  $H=H^+$  and  $E=k^2$ . The condition placed on the magnitudes of the vectors in this expansion is crucial because its failure can result in serious divergences of the sum over  $\Lambda$ . Consistent with this restriction, it can also be shown that when **x** and **x'** are confined inside nonoverlapping spheres (the so-called muffin-tin condition), whose centers are separated by a vector  $\mathbf{R}_N$ , we can write

$$G_0(\mathbf{x} - \mathbf{x}' + \mathbf{R}_N) = \sum_{\Lambda} \sum_{\Lambda'} J_{\Lambda}(\mathbf{x}) G_{\Lambda\Lambda'}(\mathbf{R}_N) J_{\Lambda}(\mathbf{x}').$$
(43)

In applications to three-dimensional systems based on a periodic lattice, the quantities  $G_{\Lambda\Lambda'}(\mathbf{R}_N)$  are commonly referred to as the real-space structure constants of the lattice. Their lattice Fourier transforms are the well-known Korringa-Kohn-Rostoker structure constants of electronic structure calculations. Explicit expressions for the structure constants are given in the Appendix.

At this point it is necessary to comment on the applicability of angular momentum expansions of  $G_0$  when its spatial arguments are not confined inside nonoverlapping spheres. For example, in the case of adjoining, space-filling cells, the expansion in Eq. (43) may diverge for some values of the cell vectors  $\mathbf{x}$  and  $\mathbf{x}'$ . This apparent difficulty in applying MST to non-muffin-tin geometries can be effectively circumvented<sup>24,26</sup> through the replacement of divergent sums with conditionally convergent double sums. The final expressions so obtained are *formally* identical in most cases to the corresponding muffin tin results, with care taken to achieve convergence of the angular momentum expansions. In all cases, MST allows a complete separation of the structure of a system from its potential, and leads to matrix equations in angular momentum space. Because of these properties and for ease of presentation, we will assume that the muffin-tin expansions are applicable to all geometries and proceed in the knowledge that rigorous final expansions can be obtained through appropriately defined summation procedures.<sup>27</sup>

We now pass over to the angular momentum representation. We define the scattering-path operator,  $\mathcal{T}_{\Lambda\Lambda'}^{NM}$ , by

$$\mathcal{T}_{\Lambda\Lambda'}^{NM} = \int d^6x \int d^6x' J_{\Lambda}(\mathbf{x}_M) \mathcal{T}^{MN}(\mathbf{x},\mathbf{x}') J_{\Lambda'}(\mathbf{x}_N'),$$
(44)

where  $\mathbf{x}_M = \mathbf{x} - \mathbf{R}_M$  is a vector confined inside the cell at  $\mathbf{R}_M$ . Using the expansion of the free-particle propagator in Eq. (43), we obtain the following *equation of motion* for the scattering-path operator,<sup>28</sup>  $\mathcal{T}_{\Lambda\Lambda'}^{NM}$ ,

$$\mathcal{T}_{\Lambda\Lambda'}^{NM} = t_{\Lambda}^{M} \left[ \delta_{\Lambda\Lambda'} \delta_{MN} + \sum_{P \neq M} \sum_{\Lambda''} G_{\Lambda\Lambda''}^{NP} \mathcal{T}_{\Lambda''\Lambda'}^{PM} \right].$$
(45)

Considered as a matrix in a combined site and angular momentum representation, the scattering-path operator may be written as

$$\mathcal{T}_{\Lambda\Lambda'}^{MN} = [t(1-Gt)^{-1}]_{\Lambda\Lambda'}^{MN} = [t^{-1}-G]_{\Lambda\Lambda'}^{MN}.$$
(46)

In systems with translational symmetry, the equation of motion can be solved by means of lattice Fourier transforms leading to well-known expressions for the electronic band structure of a material.<sup>28</sup>

Once the scattering path operator has been determined, the Green function follows. For vectors  $\mathbf{x}$  and  $\mathbf{x}'$  confined inside no other cells than those centered at  $\mathbf{R}_N$  and  $\mathbf{R}_M$  in two-particle space, the Green function takes the form,<sup>22–24</sup>

$$G(\mathbf{x}, \mathbf{x}'; E) = \sum_{\Lambda} \sum_{\Lambda'} Z_{\Lambda}^{N}(\mathbf{x}) \mathcal{T}_{\Lambda\Lambda'}^{MN}(E) Z_{\Lambda}^{M}(\mathbf{x}')$$
$$-\sum_{\Lambda} Z_{\Lambda}^{N}(\mathbf{x}) S_{\Lambda}^{M}(\mathbf{x}') \delta_{NM}.$$
(47)

Here, the functions  $Z_{\Lambda}^{N}(\mathbf{x})$  are those regular solutions of the Schrödinger equation for the potential in cell N which outside a sphere bounding this potential joins smoothly onto the function  $\Sigma_{\Lambda'}J_{\Lambda'}(\mathbf{x})t^{M-1}_{\Lambda'\lambda} - ikH_{\lambda}(\mathbf{x})$ . The functions  $S_{\Lambda}^{N}(\mathbf{x})$  are the corresponding irregular solutions which join smoothly onto  $J_{\Lambda}(\mathbf{x})$ . From the Green function, the spatial particle density in the space and the density of states follow by means of well-known expressions, Eq. (26).

## B. The scattering-path operator in hyperspace

The structure of two-particle space described above leads immediately to the form of the scattering-path operator. The equation of motion, Eq. (45), for the entire space separates into parts associated with the three-dimensional subspaces characterized by a particular value of the potential. Each site in such a subspace is associated with a *t*-matrix  $t^n$  corresponding to an interparticle interaction,  $U(\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_n)$ . Since such a subspace is generated by the translations  $(\mathbf{R}_n, \mathbf{R}_n)$ , the corresponding part of  $\mathcal{T}$  can be Fourier transformed to yield the formal expression

$$\underline{\mathcal{T}}^{(n)}(\mathbf{q}) = [[\underline{t}^n]^{-1} - \underline{G}(\mathbf{q})]^{-1}, \qquad (48)$$

where  $\underline{G}(\mathbf{q})$  is the Fourier transform of the six-dimensional structure constants over the three-dimensional space generated by all vectors of the form  $(\mathbf{R}_n, \mathbf{R}_n)$ , and an underbar denotes a matrix in angular momentum indices in hyperspace. Now, the equation of motion takes the form,

$$\left[\underline{\mathcal{T}}\right]^{nm}(\mathbf{q}) = \underline{\mathcal{T}}^{(n)}(\mathbf{q}) \left[ \delta_{mn} + \sum_{k \neq m} \underline{G}^{nk}(\mathbf{q}) [\underline{\mathcal{T}}]^{kn}(\mathbf{q}) \right].$$
(49)

In this mixed direct-reciprocal space representation, each site  $\mathbf{R}_n$  of a three-dimensional lattice is associated with a *t* matrix  $\mathcal{T}^{(n)}(\mathbf{q})$ . The resulting structure is reminiscent of the structure of the scattering-path operator arising in the study of layered systems<sup>29</sup> where each site of a "linear" lattice perpendicular to the layered structure is associated with the *t* matrix representing a "plane" in the material passing through that point.

The last form of the equation of motion can be solved either by direct inversion in real space, or through an adaptation of more elaborate but more rigorous techniques<sup>29</sup> familiar from the study of layered systems. Direct inversion may be facilitated through the use of the so-called screened structure constants<sup>30</sup> which will have to be set up in the hyperspace of two particles. Or, screening effects may result in the reduction of the system to a single cluster of "impurity" sites embedded in a translationally invariant effective medium. This system can be solved rigorously using wellknown methods.<sup>29</sup> Once the scattering-path operator has been determined within an adequate approximation, the Green function is obtained from Eq. (47). Related quantities, such as the charge density now follow from the usual expressions.

## C. Energy integrals and charge self-consistency

An application of the formalism presented above hinges crucially on the performance of energy integrations in determining such quantities as the density and the total energy. Such energy integrals extend to the maximum energy of occupied pair states, a level which we will denote as  $E_F^{(2)}$ . However, given that two-particle space (*n*-particle space) is not periodic, the method for the determination of the Fermi level for pairs or higher-order particles is not immediately apparent. It is to be kept in mind that the normalization to be used in determining the "Fermi level" for *n* tuples of states is that given in terms of combinations of states described previously.

To determine  $E_F^{(2)}$ , we exploit the analogy of the twoparticle space to that of a cluster of impurities embedded in a host material mentioned above. As in that case, the Fermi level is determined on the basis of the unperturbed system, each cell of which in the present case is characterized by the two-particle effective potential (and charge density) corresponding to the members of the pair being sufficiently far apart that the pair potential has reached its asymptotic value. The Fermi level is determined as that energy for which an integral over the density of pair states gives the total number of combinations of states consistent with the number of particles needed to balance the nuclear charge.

Charge self-consistency in two-particle space can be achieved through iterative methods such as used in the corresponding case of single-particle electronic structure calculations. At each iteration, the two-particle Green function yields a (two-particle) charge density, a potential, and a total energy. The iterations terminate when the charge density and/or the potential reach preassigned levels of convergence.

This approach allows the study of essentially all properties commonly treated within band-theoretical methods, such as structural stability, phase stability, transport, and others, while taking direct account of the interparticle interaction within the calculation of the electronic structure. Further work, currently in progress, is aimed at understanding in more detail the correspondence between two-particle spectra and observable properties of materials.

### **IV. NUMERICAL ILLUSTRATION**

The full implementation of the formalism described above within *ab initio* methods is certainly an arduous computational task. Certain elements of the formalism, however, can be implemented with relative ease and serve to illustrate the basis elements of the method.

In this section, we illustrate some of the formal aspects introduced in previous sections by the results of numerical calculations. These calculations are carried out in connection with a model system consisting of four sites on a linear ring. We choose the total spin of the system to be equal to zero, and we consider the case of two and four electrons (forming two pairs each of which has zero spin). We calculate the exact two- and four-particle Green functions under the constraint of vanishing total spin and from this we obtain the exact single-particle Green function. In the case of four particles, this Green function is compared to results of approximate procedures obtained within a two-particle formalism.

We consider a single-band, Hubbard model Hamiltonian



FIG. 1. A square lattice representing the correlated space of a linear chain. Sites (i,i) along the main diagonal correspond to two particles on the line occupying the same site and characterized by a pair energy  $2\epsilon_i + U$ , as described in the text. Off the main diagonal, site (i,j) corresponds to two particles on different sites on the line, and is characterized by an energy  $\epsilon_i + \epsilon_j$ .

for a periodic linear chain given by the expression

$$H = \sum_{i} \epsilon_{i} a_{i}^{\dagger} a_{i} + \frac{1}{2} \sum_{i,j \neq i} W_{ij} + \sum_{i} U n_{i,\sigma} n_{i,\overline{\sigma}}.$$
 (50)

Here,  $n_{i,\sigma} = a_{i,\sigma}^{\dagger} a_{i,\sigma}$  is the number operator for a particle with spin  $\sigma$  on site *i*, and  $\overline{\sigma}$  a state of spin opposite to  $\sigma$ . The interaction *U* denotes the Coulomb repulsion of two electrons of opposite spin on the same site, and is taken to be site diagonal. More general spatial dependencies of the Coulomb interaction can be taken into account without undue effort. The correlated space corresponding to the Hamiltonian of the last expression is associated with a Hamiltonian of the form,

$$H_{ij;kl} = [H_{ii} + H_{jj}] \delta_{ik} \delta_{jl} + [H_{ik}(1 - \delta_{ik}) \delta_{jl} + H_{jl}(1 - \delta_{jl}) \delta_{ik}] + U \delta_{iikl}.$$
(51)

In this two-particle Hamiltonian the Coulomb repulsion appears along the main diagonal of the space, i=j=k=l. This Hamiltonian is used with a periodic linear ring of four sites a distance *a* apart, characterized by the values  $\epsilon_i=0$ , and hopping,  $H_{ij}\equiv t=1.0$ , for *i* and *j* nearest neighbors and zero otherwise. The correlated space of this four-site ring is a 16-site toroidal surface, with nearest-neighbor hopping.

It is useful to illustrate the geometry of two-particle space for the case of the infinite periodic line, as shown in Fig. 1. Each point (lattice site) on the infinite square lattice corresponds to a particular configuration of two particles on the line, with the matrix elements of the Hamiltonian being given by the last expression, Eq. (51). Thus, a point on the main diagonal, such as that indexed by (ii), where *i* is a site on the line, corresponds to two particles of opposite spin found on that site. For such site on the square the matrix elements of the Hamiltonian are given by

$$H_{ii,ii} = 2\epsilon_i + U. \tag{52}$$



FIG. 2. Single-particle DOS's for a periodic ring of four sites with U=0.0 (solid line), compared with corresponding results obtained from down folding the two-particle Green function (dashed line) and the four-particle Green function (dotted line).

Sites with indices ij,  $i \neq j$ , correspond to two particles found on two different sites on the line with a corresponding matrix element of

$$H_{ij,ij} = 2[\epsilon_i + \epsilon_j]. \tag{53}$$

The remaining, off-diagonal Hamiltonian matrix elements on the square are equal to t for near-neighbor sites and zero otherwise.

The following figures show one- two- and four-particle spectra for a uniform finite ring of four sites described by a Hubbard Hamiltonian, and illustrate a number of points of the formalism presented in the text. The spectra are shown at complex energies with an imaginary part ImE = t/4, which allows the  $\delta$ -function like spectra to be displayed for graphical purposes.

The single-particle density of states (DOS) for the periodic four-site ring, defined by the expression,

$$n(E) = -\frac{1}{\pi} \text{Im}G_{ii}(E), \qquad (54)$$

and for U=0 is shown by the solid line in Fig. 2. The figure also shows the corresponding DOS obtained from the singleparticle Green function obtained the two-particle Green function, (dashed line), and to the four-particle Green function (dotted line). In each case, single-particle quantities are obtained by integrating out the coordinates of all other particles. We will refer to this process as *down folding*. For example, given a two-particle Green function, we have

$$G_{ij} = \frac{1}{N} \sum_{kl} G_{ik;jl}.$$
(55)

An illustration of this reduction procedure in a special case can be obtained by reconsidering the case of the Be atom discussed above. It is easy to see that in order to obtain the contribution to the single-particle density of a given state  $\alpha$ , from a two-particle density, one sums over all two-particle states corresponding, in the noninteracting limit to one particle being in state  $\alpha$ .

The four-particle calculation is carried out on a fourdimensional space formed by the combination of two twodimensional spaces. This results in a four-dimensional cubic structure with 256 sites, reflecting the number of configura-



FIG. 3. Two- (solid line) and four-particle (dashed line) DOS's for a periodic ring of four sites with U=0.0.

tions of four particles with total spin zero arranged on four sites, and with each site having eight nearest neighbors (connectivity of 8). Neglecting the Pauli principle and seting U=0, the sites, ijkl, of the four dimensional torus are assigned an energy of  $\epsilon_i + \epsilon_j + \epsilon_k + \epsilon_l$ . All curves in this figure display the same structure inside the band, but the downfolded curves are displaced with respect to the results obtained directly from the single-particle Green function by the average energy of the additional particles. As discussed in the text, this energy equals 2t=2.0 and 6t=6.0 for the two-particle and four-particle results, respectively.

Figure 3 shows two- (solid line) and four-particle (dashed line) DOS corresponding to two and four particles occupying the same site on the ring (we continue to ignore the Pauli principle). The important feature to notice here is the progressive increase in bandwidth with an increasing number of particles (dimensionality of space). This is the result of the greater connnectivity, increasing the number of nearest neighbors, in the higher-dimensional space.

We now present results in which the Pauli principle is taken fully into account, and the interparticle interaction is gradually increased in value. To take account of the Pauli principle within the present model, we assign a very large (in principle infinite) energy to any configuration of the system corresponding to two particles of the same spin occupying the same site on the ring. Two-particle DOS corresponding to two particles of opposite spin on the same site of the ring and on near-neighbor sites are shown, respectively, by the solid and the dashed lines in the three panels of Fig. 4, the panels containing the results for U=0.1 upper panel, U=1.0, middle panel, and for U=10.0, lower panel. We note that these spectra contain an impuritylike resonant state at energies E = U, in agreement with the interpretation of interparticle interactions appearing as external potentials in appropriately defined higher-dimensional spaces. This state is clearly illustrated in the case of U=10.0, where it falls outside the band. Note also, that the four-particle spectrum contains a resonance at E = 2U corresponding to two-particle pairs on two different sites. The complete four-particle spectrum is shown in Fig. 5 for the case U = 10.0, corresponding to two pairs of particles of zero spin. Note that in all cases, particularly in that of low U, the band narrows in hyperspace which is caused by the Pauli principle. In the present case, the Pauli principle is taken fully into account by assigning an



FIG. 4. Two-particle DOS for on-site occupancy (dashed line) and near-neighbor occupancy (solid line) for a ring of four sites with U=0.1, upper panel, U=1.0, middle panel, and U=10.0, lower panel. Even for the strong-interaction case, U=10.0, the near-neighbor spectra resemble closely those of the noninteraction case (solid line in previous figure).



FIG. 5. Four-particle spectrum for two pairs of total zero spin occupying adjacent sites in a ring of four site with U=10.0.



FIG. 6. Single-particle spectra for a ring with four sites. The solid line is the spectrum for noninteracting particles, while the dashed line is the single-particle spectrum obtained from down folding the two-particle Green function, and the dotted line the four-particle Green function for U=0.1.

"infinite" energy of  $10^3$  to every site in hyperspace which corresponds to a forbidden configuration, thus removing such sites from the system. It is this effect which reduces connectivity and the associated bandwidth.

The following three figures show single-particle spectra for the three values of the on-site interaction stated above, and with the Pauli principle taken fully into account. Figure 6 shows a comparison of the noninteracting single-particle spectrum (solid line) for a particle on the ring and the corresponding results for U=0.1 obtained from down-folding the two-particle Green function (dashed line) and the fourparticle Green function (dotted line). In the procedure used here, the single-particle spectrum is shifted by the average energy of the particles whose coordinates are integrated (summed) in the down-folding process. The various curves in the figures have been shifted by the average energies of particles in order for the centers of the bands to coincide. For this small value of U, the main difference between the spectra is a narrowing of the band in the spectrum obtained from the four-particle Green function produced by the removal of forbidded configurations in four-particle space. Note that no narrowing is indicated in the spectrum obtained from the two-particles Green function because that Green function describes two particles of opposite spin and hence is not affected by the Pauli principle.

Results analogous to those in Fig. 6 but for the cases U=1.0 and U=10.0 are shown, respectively, in Figs. 7 and



FIG. 7. Results analogous to those of the previous figure but for U = 1.0.



FIG. 8. Results analogous to those of the previous figure but for U = 10.0.

8. We note in all cases the resonancelike state at values of the energy aproximately equal to U. This is a remnant of the states in higher-dimensional spaces whose position is slightly altered in the down-folding process.

The next figure illustrates the role played by the density of particles in determining the single-particle spectrum of a system of particles. Figure 9 shows the single-particle spectrum obtained from down-folding the two-particle Green function for U=10.0 and for periodic rings of 4, 10, and 20 sites, as indicated by the solid-line, dashed-line, and dotted-line curves, respectively. We note that the strentgh of the peak at E=U decreases with increasing numbers of sites since the likelihood of finding two particles on the same site decreases with increasing volume (decreasing density). Therefore, an application of the formalism to the study of interacting systems along the lines of *n*DFT and *n*LDA hinges crucially on the presence of a finite-particle density and its treatment.

Clearly, a full implementation of the LDA on the basis of two-particle states is not feasible at present. However, as a precursor to such an application, we consider the results of applying a strictly two-particle formalism in the presence of nonvanishing density. Thus, we average the Green functions corresponding to two-particle states in the presence of another pair, but we neglect the interactions among the various four-particle configurations. This leads to an approximate two-particle Green function and a corresponding singleparticle Green function which can be compared to exact values and to the results of other approximation schemes.

In order to illustrate further the role played by the twoparticle density in the determination of the electronic struc-



FIG. 9. Single-particle spectrum obtained from the two-particle Green function with U = 10.0, for a ring of four sites (solid line), 10 sites (dashed line), and 20 sites (dotted line).

ture, and to contrast the present method with existing approaches, we show now the comparison between exact (solid lines) single-particle Green functions and spectra obtained by down-folding the four-particle Green function for the foursite ring with those obtained by down-folding a two-particle Green function (dashed line) which is the average over the Green functions describing two-particle states in the presence of an additional pair of particles on the ring, and the results obtained within a version of the *GW* approximation (dotted line). Here, the single-particle self-energy,

$$\Sigma_{ij}(E) = \lim_{\eta \to 0} \frac{1}{2\pi} \int e^{-i\omega\eta} W_{ij}(\omega) G_{ij}(E-\omega) d\omega, \quad (56)$$

is given in terms of the exact single-particle Green function and the exact screened interaction which is determined in terms of the noninteracting, zero superscript, and exact twoparticle Green functions,  $W_{ij;kl}(E) = \{G_{ij;kl}^{(0)}^{-1} - G_{ij;kl}^{-1}\}$ . The results corresponding to U=0.1, U=1.0, and U=10.0are exhibited in the upper, middle, and lower panels, respectively, of Fig. 10.

As is seen in these figures, the 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 than that approximation. We note the resonance at U=1.0 which is missed in the GW results, and that both approximate results are displaced somewhat with respect to the exact ones. Much of this effect, along with the wider gap in the strong U limit can be traced back to the incomplete treatment of the Pauli principle, i.e., the neglect of configuration interactions between the configurations being averaged and in the GW approximation. Both of these approximations can be expected to improve with increased dimensionality and lattice connectivity. More detailed discussions of these and other numerical results will be given in a future publication.

### V. DISCUSSION AND CONCLUSIONS

The formal framework presented in this paper introduces a different approach in the study of interacting quantum systems. In this viewpoint, quantum systems are considered from a higher-dimensional perspective corresponding to the unified treatment of sets of two or more particles as a single particle. The formal aspects of the ensuing treatment are often indistinguishable, apart from technical considerations, from those used within a single-particle picture. The final formal and computational results, however, can be of considerable interest providing direct insights into issues, such as the effects of correlations, not easily resolved within a single-particle framework.

We can also give a more physical perspective of the method. A central aim of canonical many-body theory is the calculation of the single-particle self-energy, describing the



FIG. 10. Exact single-particle spectra obtained for a ring of four sites (solid line) compared to those corresponding to an average of two-particle Green functions (dashed line), and the *GW* approximation (dotted line). Here, U=0.1, upper panel, U=1.0, middle panel, and U=10.0, lower panel.

single-particle (or single quasiparticle) excitation spectrum of the system. This method works very well in the case of weakly correlated systems, but its application to systems characterized by increasingly correlated electron motion becomes less accurate. Similarly, in the treatment of semiconductors and insulators, systems generally known to be characterized by interparticle interactions of increased strength compared to metals—where the LDA can be said to be fairly accurate—the application of the LDA can lead to quite inaccurate results in many cases. It is conceivable, that for systems where the quasiparticle picture becomes less accurate, a treatment in terms of quasipairs may provide an improved description of the electronic states and properties of the system. It is with this in mind that the present methodology is developed.

It is also relevant to compare this new methodology with other approaches used in the study of interacting quantum systems, both conceptually as well as in terms of its implementation. First, at least formally, the method provides an improved treatment of correlations in a many-particle system in a unified manner. Thus it fills the long existing gap between many-body theory and the so-called band theory based on an independent-particle picture. Like ordinary band theory, the method can be applied to specific systems under variable external conditions so that it can be used in the study of materials behavior and materials properties. Thus, properties such as structural stability, alloy phase stability, and transport are well within its purview. In addition, the method is based on a minimum (extremal) principle which can be used to guide an iterative procedure to convergence. This last feature is possibly the most distinct advantage of this method when compared to traditional many-body techniques as applied to solids, such as the Hartree-Fock, the random phase approximation, diagramatic summations, and others. For example, none of these methods has been as yet associated with the study of phase stability in alloys. Such a study is feasible within the present formalism.

At the same time, as already mentioned, its numerical implementation becomes considerably more difficult with increasing size of the numbers of particles treated as a single unit. It is evident that an application of the two-particle picture, and by extension an *m*-particle picture within DFT, requires a significant computational effort as well as the establishment of new quantities, e.g., the exchange and correlation functional in two-particle space, compared with threedimensional (single-particle) applications of the theory. At the same time, the method allows the analysis of experimental results just as current approaches. Specific details along these lines are currently being developed such as, for example, the determination of the two-particle spectrum of a random substitutional alloy. It can only be hoped that continuing advances in computational power will make the use of this method feasible in the not too distant future.

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# APPENDIX A: HYPERSPHERICAL HARMONICS

This appendix contains a number of basic notions about n-dimensional Euclidean space, leading to expressions which are useful in the solution of the wave equation.

#### 1. Introductory notions

A vector  $\mathbf{r}$  in *n*-dimensional space (*n* space) is defined by a set of numbers,

$$\mathbf{r} = (x_1, x_2, \cdots, x_n), \tag{A1}$$

where  $x_i$  is called the component of **r** along the *i*th direction. The length of a vector and the inner (dot) product of two vectors in n space are defined as a natural generalization of the corresponding concepts in three space. Thus, we have

$$r^2 = \sum_i x_i^2 \tag{A2}$$

for the length, and

$$\mathbf{r}_1 \cdot \mathbf{r}_2 = \sum_i x_i y_i = r_1 r_2 \cos \omega_{(n)}, \qquad (A3)$$

for the dot product of two vectors,  $\mathbf{r}_1 = (x_1, x_2, \dots, x_n)$  and  $\mathbf{r}_2 = (y_1, y_2, \dots, y_n)$ . The last expression also defines the angle between two vectors. In particular, for two unit vectors,  $\hat{\mathbf{r}}_1$  and  $\hat{\mathbf{r}}_2$ , we have

$$\cos\omega_{(n)} = \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2. \tag{A4}$$

A vector of length r in n-dimensional space is characterized by a set of angles,  $\theta_{n-2}$ ,  $\theta_{n-3}$ ,  $\dots$ ,  $\theta_1$ ,  $\phi$ , which are defined by the relationships,

$$x_1 = r\sin\theta_1 \sin\theta_2 \cdots \sin\theta_{n-2} \cos\phi,$$
  

$$x_2 = r\sin\theta_1 \sin\theta_2 \cdots \sin\theta_{n-2} \sin\phi,$$
  

$$x_3 = r\sin\theta_1 \sin\theta_2 \cdots \cos\theta_3,$$

$$x_{n-1} = r\sin\theta_1 \cos\theta_2,$$
  
$$x_n = r\cos\theta_1.$$
 (A5)

We note that the angle  $\omega_{(n)}$  formed by two vectors in *n* space can be expressed in terms of the angles each vector makes with the *n*th axis,  $\theta_1$ , and the angle  $\omega_{(n-1)}$  made by the projections of the vectors onto (n-1) space,

$$\cos\omega_n = \cos\theta_1^1 \cos\theta_1^2 + \sin\theta_1^1 \sin\theta_1^2 \cos\omega_{(n-1)}.$$
 (A6)

Often, the subscript (n) indicating *n*-dimensional quantities will be omitted, and used only to render emphasis to specific results.

The generalized Laplacian operator  $\nabla^2_{(n)} \equiv \Delta_{(n)}$  is defined also in analogy with three-dimensional space,

$$\Delta_{(n)} = \sum_{i=1}^{n} \frac{\partial^2}{\partial x_i^2}.$$
 (A7)

The Laplacian operator can be written in the form,

$$\Delta_{(n)} = \sum_{i=1}^{n} \frac{\partial^2}{\partial x_i^2} = \frac{1}{r^{n-1}} \frac{\partial}{\partial r} r^{n-1} \frac{\partial}{\partial r} - \frac{\Lambda^2}{r^2}, \qquad (A8)$$

where  $\Lambda^2$  is the square of the generalized angular momentum operator defined by the expression,

 $\Lambda^2 = -\sum_{i>j}^n \Lambda_{ij}^2, \tag{A9}$ 

where

$$\Lambda_{ij} \equiv x_i \frac{\partial}{\partial x_i} - x_j \frac{\partial}{\partial x_i}.$$
 (A10)

The hyperspherical harmonics are defined<sup>25</sup> as the eigenfunctions of  $\Lambda^2$ ,

$$\Lambda^2 Y_{\Lambda}(\Omega) = \lambda(\lambda + n - 2) Y_{\Lambda}(\Omega), \qquad (A11)$$

which is analogous to the relation,

$$L^{2}Y_{\ell m}(\Omega) = \ell(\ell+1)Y_{\ell m}(\Omega), \qquad (A12)$$

satisfied by the ordinary, three-dimensional, spherical harmonics. The subscript  $\Lambda$  is a combined index, analogous to the index  $L = (\ell, m)$  in three dimensions. It denotes a set of indices,  $\Lambda = (\lambda, \mu_1, \mu_2, \cdots)$ , also usually written in the condensed notation,  $\Lambda = (\lambda, \mu)$ . The spherical harmonics form an orthonormal set on the unit sphere in *n*-dimensional space,

$$\int d\Omega \ Y^*_{\Lambda'}(\Omega) Y_{\Lambda}(\Omega) = \int d\Omega \ Y^*_{\lambda'\mu'}(\Omega) Y_{\lambda\mu}(\Omega)$$
$$= \delta_{\lambda\lambda'} \delta_{\mu\mu'}, \qquad (A13)$$

where  $\delta_{\mu\mu'}$  implies  $\mu_1 = \mu'_1$ ,  $\mu_2 = \mu'_2$ , etc. The solid angle element  $d\Omega$  integrates to the *n*-dimensional solid angle,

$$I(0) = \int d\Omega = \int \sin\theta_1^{n-2} \sin\theta_2^{n-3} \cdots$$
$$\times \sin\theta_1 d\theta_{n-2} d\theta_{n-3} \cdots d\theta_1 d\phi$$
$$= \frac{2\pi^{n/2}}{\Gamma(n/2)}, \tag{A14}$$

where  $\Gamma(x)$  is the  $\Gamma$  function. For x integral,  $\Gamma(x)=x!$ . In four-space,  $\Lambda = (\lambda, \mu_1, \mu_2)$ , where  $0 \le \mu_1 \le \lambda$ , and  $-\mu_1 \le \mu_2 \le \mu_1$ , so that the degeneracy associated with a given  $\lambda$  equals  $(\lambda + 1)^2$ . An extensive discussion of the hyperspherical harmonics with many applications to quantum physics is given by Avery.<sup>25</sup>

#### 2. Gegenbauer polynomials and the addition theorem

In *n*-dimensional space, the Gegenbauer polynomials,  $C_{\lambda}(\hat{r}_1 \cdot \hat{r}_2)$ , are defined so that for any vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ ,

$$\frac{1}{|\mathbf{r}_{1} - \mathbf{r}_{2}|^{n-2}} = \frac{1}{(r_{1} + r_{2} - 2r_{1}r_{2}\cos\omega_{(n)})^{(n-2)/2}}$$
$$= \frac{1}{r_{>}^{n-2}} \sum_{\lambda=0}^{\infty} \left(\frac{r_{<}}{r_{>}}\right)^{\lambda} C_{\lambda}^{\alpha}(\hat{\mathbf{r}}_{1} \cdot \hat{\mathbf{r}}_{2}), \qquad (A15)$$

where  $r_{>}$  ( $r_{<}$ ) is the larger (smaller) of the lengths of the vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . In three dimensions, this reduces to the familiar expansion in terms of Legendre polynomials,

In general, the Gegenbauer polynomials are given by the expression,<sup>25</sup>

$$C_{\lambda}^{\alpha}(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}') = \sum_{t=0}^{[1/2\lambda]} \frac{(-1)^{t} [\alpha_{\lambda-t}(2\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}')]^{\lambda-2t}}{t!(\lambda-2t)!}, \quad (A17)$$

where

$$\alpha \equiv \frac{1}{2}n - 1 \tag{A18}$$

and

$$(\alpha)_{j} \equiv \alpha(\alpha+1)(\alpha+2)\cdots(\alpha+j-1).$$
(A19)

In Eq. (A17), the symbol  $\left[\frac{1}{2}\lambda\right]$  stands for the largest integer smaller than  $\lambda/2$ .

The n-dimensional Gegenbauer polynomials satisfy an addition theorem which is exactly analogous to the corresponding result in three space,

$$C^{\alpha}_{\lambda}(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}') = \sum_{\mu} K_{\lambda}Y^{*}_{\lambda\mu}(\Omega)Y_{\lambda\mu}(\Omega'), \qquad (A20)$$

where  $\Omega$  (  $\Omega^{\,\prime})$  are the directional angles defined by the vectors r and  $r^{\prime},$  and

$$K_{\lambda} = \frac{(n-2)I(0)}{n+2\lambda-2}.$$
 (A21)

For n=3, this expression reduces to the familiar result,

$$P_{\mathscr{I}}(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}') = \frac{4\pi}{2\mathscr{I}+1} \sum_{m} Y^*_{\mathscr{I}m}(\Omega) Y_{\mathscr{I}m}(\Omega'). \quad (A22)$$

#### 3. Green functions

It can be shown<sup>25</sup> that  $[1/(|\mathbf{r}-\mathbf{r}'|^{n-2})]$  is the Green function for the *n*-dimensional Laplacian so that

$$\Delta_{(n)} \frac{1}{|\mathbf{r} - \mathbf{r}'|^{n-2}} = -(n-2)I(0)\,\delta(\mathbf{r} - \mathbf{r}'), \quad (A23)$$

where  $\delta(\mathbf{r} - \mathbf{r}')$  is the *n* dimensional Dirac  $\delta$  function.

In general, given a differential operator  $D_{(n)}$  in *n* space, the corresponding Green function is defined formally by means of the identity,

$$D_{(n)}G_{(n)} = -(n-2)I(0)\mathbf{I}.$$
 (A24)

The symbol **I** represents the identity in the sense of distributions. Thus, in the coordinate representation, we have

$$D_{(n)}(\mathbf{r})G_{(n)}(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'), \qquad (A25)$$

where it is convenient to absorb the inverse of the prefactor -(n-2)I(0) into the definition of the Green function.

### 4. Expansions in spherical functions

As in three space, a plane wave in n dimensions can be expanded<sup>25</sup> in terms of Gegenbauer polynomials and hyperspherical harmonics,

$$e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{\lambda=0}^{\infty} i^{\lambda}(n+2\lambda-2)(n-4)!!j^{n}_{\lambda}(kr)C^{\alpha}_{\lambda}(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}})$$
$$= (n-2)!!I(0)\sum_{\lambda}^{\infty} i^{\lambda}j^{n}_{\lambda}(kr)\sum_{\mu} Y^{*}_{\lambda\mu}(\hat{\mathbf{k}})Y_{\lambda\mu}(\hat{\mathbf{r}}).$$
(A26)

Here, the *n*-dimensional spherical Bessel function is defined in terms of ordinary Bessel functions,

$$j_{\lambda}^{n}(x) = \frac{\Gamma(\alpha)2^{\alpha-1}J_{\alpha+\lambda}(x)}{(n-2)!!x^{\alpha}} = \sum_{t=0}^{\infty} \frac{(-1)^{t}x^{2t+\lambda}}{(2t)!!(n+2t+2\lambda-2)!!}.$$
(A27)

It is easily checked that in three dimensions Eq. (A26) reduces to Bauer's identity,

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} i^{\ell} j_{\ell}(kr) \sum_{m} Y_{\ell m}^{*}(\hat{\mathbf{k}}) Y_{\ell m}(\hat{\mathbf{r}}). \quad (A28)$$

The n-dimensional plane waves are solutions of the n-dimensional Helmholtz equation

$$[\Delta_{(n)} + E]\Psi = 0, \qquad (A29)$$

where  $E = k^2$ , and satisfy the usual conditions of orthonormality and completeness,

$$\frac{1}{(2\pi)^n} \int d^n r e^{i\mathbf{r} \cdot (\mathbf{k} - \mathbf{k}')} = \delta(\mathbf{k} - \mathbf{k}'), \qquad (A30)$$

and

$$\frac{1}{(2\pi)^n} \int d^n k e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} = \delta(\mathbf{r} - \mathbf{r}').$$
(A31)

It follows that any function of the coordinates in n-dimensional space can be expanded in plane waves. For example, the Green function of the generalized Laplacian operator can be written in the form

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|^{n-2}} = \frac{(n-2)I(0)}{(2\pi)^n} \int d^n k \frac{1}{k^2} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')}.$$
 (A32)

It can be checked<sup>25</sup> that this function satisfies the defining equations for the Green function, Eq. (A24). For n=3, the last expression reduces to

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{2\pi^2} \int d^3k \frac{1}{k^2} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')},$$
 (A33)

while for n = 4 we have

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|^2} = \frac{1}{4\pi^2} \int d^4k \frac{1}{k^2} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')}.$$
 (A34)

In addition to the Green functions of the Laplacian, we also need the Green functions of the generalized Helmholtz operator which are defined by means of the relation,

$$(\Delta_{(n)} + E)G(E; \mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \qquad (A35)$$

where a factor of  $-\{1/[(n-2)I(0)]\}\$  has been absorbed into *G*. In what follows, the dependence of the Green function on the energy will not be shown explicitly unless it is necessary to clarify the content of the discussion. We note that in the limit  $E \rightarrow 0$  the Helmholtz operator becomes the Laplace operator and correspondingly the Green function of the former becomes that of the latter.

The Green function introduced in the last equation can be expanded<sup>25</sup> in hyperspherical harmonics in the form

$$G(E;\mathbf{r}-\mathbf{r}') = \sum_{\Lambda} \frac{2}{(rr')^{\alpha}} I_{\lambda+\alpha}(kr_{<})$$
$$\times K_{\lambda+\alpha}(kr_{>}) \sum_{\mu} \frac{1}{K_{\lambda}} Y_{\lambda\mu}^{*}(\hat{\mathbf{r}}) Y_{\lambda\mu}(\hat{\mathbf{r}}'),$$
(A36)

where  $I_{\lambda+\alpha}$  and  $K_{\lambda+\alpha}$  [ $\alpha = (n/2)-1$ ] are modified Bessel functions, being, respectively, the regular and irregular solution of the modified Bessel equation in *n* space. We emphasize the condition placed on the arguments of these functions in the last expansion. This expansion converges only when the smaller of the two vectors is associated with  $I_{\lambda+\alpha}$  and the larger with  $K_{\lambda+\alpha}$ .

Defining the functions

$$J_{\Lambda}(kr) = \sqrt{\frac{2}{K_{\lambda}}} \frac{1}{r^{\alpha}} I_{\lambda+\alpha}(kr) Y^{*}_{\lambda\mu}(\hat{\mathbf{r}}) \equiv j^{n}_{\lambda}(kr) Y^{*}_{\lambda\mu}(\hat{\mathbf{r}}),$$
(A37)

and

$$N_{\Lambda}(kr) = \sqrt{\frac{2}{K_{\lambda}}} \frac{1}{r^{\alpha}} K_{\lambda+\alpha}(kr) Y_{\lambda\mu}(\hat{\mathbf{r}}) \equiv n_{\lambda}^{n}(kr) Y_{\lambda\mu}(\hat{\mathbf{r}}),$$
(A38)

we can write

$$G(\mathbf{r}-\mathbf{r}') = \sum_{\Lambda} J_{\Lambda}(k\mathbf{r}_{<})N_{\Lambda}(k\mathbf{r}_{>}).$$
(A39)

The function  $n_{\lambda}^{n}$  defined above is the modified spherical Neumann function. We can also define the modified spherical Hankel functions of the first (+) and second (-) kinds

$$h_{\lambda}^{n(\pm)} = j_{\lambda}^{n} \pm i n_{\lambda}^{n}, \qquad (A40)$$

and the function

$$H_{\Lambda}^{\pm}(\mathbf{x}) = h_{\lambda}^{n(\pm)}(x) Y_{\lambda\mu}(\mathbf{\hat{x}}).$$
(A41)

Denoting  $h^+$  simply by h, we can also write the expansion of the Green function of the Helmholtz operator in the form

$$G(\mathbf{r}-\mathbf{r}') = \sum_{\Lambda} J_{\Lambda}(k\mathbf{r}_{<})H_{\Lambda}(k\mathbf{r}_{>}).$$
(A42)

All the relations exhibited above reduced to well-known<sup>31</sup> results in three space. Also, it is always possible to use hyperspherical harmonics which are real in which case the designation of complex conjugates is not necessary.

### 5. Expansions about shifted origins

We now derive a number of useful relations connecting the Bessel functions of argument  $\mathbf{r} + \mathbf{a}$  to their undisplaced values at  $\mathbf{r}$ . From Eq. (A26), we have

$$e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{a})} = (n-2)!!I(0)\sum_{\lambda}^{\infty} i^{\lambda}j_{\lambda}^{n}(k|\mathbf{r}+\mathbf{a}|)$$

$$\times \sum_{\mu} Y_{\lambda\mu}^{*}(\hat{\mathbf{k}})Y_{\lambda\mu}(\mathbf{r}+\hat{\mathbf{a}})$$

$$= [(n-2)!!I(0)]^{2}\sum_{\lambda_{1}}^{\infty} i^{\lambda_{1}}j_{\lambda_{1}}^{n}(kr)\sum_{\mu_{1}} Y_{\lambda_{1}\mu_{1}}^{*}(\hat{\mathbf{k}})$$

$$\times Y_{\lambda_{1}\mu_{1}}(\hat{\mathbf{r}})\sum_{\lambda_{2}}^{\infty} i^{\lambda_{2}}j_{\lambda_{2}}^{n}(kr)\sum_{\mu_{2}} Y_{\lambda_{2}\mu_{2}}^{*}(\hat{\mathbf{k}})Y_{\lambda_{2}\mu_{2}}(\hat{\mathbf{r}}).$$
(A43)

Multiplying the two expansions by  $Y_{\lambda_3\mu_3}(\hat{\mathbf{k}})$ , integrating over the angles of  $\hat{\mathbf{k}}$ , and using the orthonormality property of the hypespherical harmonics and the definition in Eq. (A37), we obtain the expansion for the shifted Bessel functions

$$J_{\Lambda}[k(\mathbf{r}+\mathbf{a})] = (n-2)!!I(0)\sum_{\Lambda'} g_{\Lambda\Lambda'}(\mathbf{a})J_{\Lambda'}(k\mathbf{r}),$$
(A44)

where the expansion coefficients  $g_{\Lambda\Lambda'}(\mathbf{a})$  are the matrix elements in an angular momentum basis of the translation operator<sup>31</sup> and are defined by the expression

$$g_{\Lambda\Lambda'}(k\mathbf{a}) = (n-2)!!I(0)$$

$$\times \sum_{\Lambda''} i^{\lambda'-\lambda+\lambda''} C(\Lambda,\Lambda',\Lambda'') J_{\Lambda''}(k\mathbf{a}),$$
(A45)

with  $C(\Lambda, \Lambda', \Lambda'')$  being a generalized Gaunt number, or an integral of three hyperspherical harmonics,

$$C(\Lambda,\Lambda',\Lambda'') = \int d\Omega \ Y^*_{\Lambda}(\Omega) Y^*_{\Lambda'}(\Omega) Y_{\Lambda''}(\Omega).$$
(A46)

Now, Eq. (A44) can be written in a vector/matrix notation,

$$|J[k(\mathbf{r}+\mathbf{a})]\rangle = g(k\mathbf{a})|J[k(\mathbf{r})]\rangle, \qquad (A47)$$

where the symbol  $|\rangle$  denotes a ket vector whose components are indexed by  $\Lambda$ , and the matrix elements of  $g(\mathbf{a})$  are given explicitly in Eq. (A45). We note that since the translation operator is unitary, we have

$$\underline{g}(k\mathbf{a})\underline{g}(-k\mathbf{a}) = \underline{g}(k\mathbf{a})\underline{g}^{\dagger}(k\mathbf{a}) = 1.$$
 (A48)

Expansions analogous to that for  $|J[k(\mathbf{r})]\rangle$  hold for the modified Neumann and Hankel functions. For example, noting that for any vectors such that  $|\mathbf{R}| > |\mathbf{r}|$ , there exist otherwise arbitrary vectors  $\boldsymbol{\rho}$  such that  $|\mathbf{r} - \boldsymbol{\rho}| < |\mathbf{R}|$  and  $|\mathbf{R} - \mathbf{r}| > |\boldsymbol{\rho}|$ , we have

$$G(\mathbf{r} - \boldsymbol{\rho} - \mathbf{R}) = \langle H(k\mathbf{R}) | J[k(\mathbf{r} - \boldsymbol{\rho})] \rangle.$$
(A49)

We can also write

$$G(\mathbf{r} - \boldsymbol{\rho} - \mathbf{R}) = \langle H[k(\mathbf{R} - \mathbf{r})] | J(k\boldsymbol{\rho}) \rangle.$$
 (A50)

This expression can be compared to the previous one and in view of Eq. (A47) yields the expansion

$$|H[k(\mathbf{R}-\mathbf{r})]\rangle = \underline{g}(k\mathbf{r})|H(k\mathbf{R})\rangle = \underline{G}(k\mathbf{R})|J(k\mathbf{r})\rangle.$$
(A51)

Here we have defined the real-space, *n*-dimensional structure constant in terms of its matrix elements

$$G_{\Lambda\Lambda'}(k\mathbf{a}) = (n-2)!!I(0)$$

$$\times \sum_{\Lambda''} i^{\lambda'-\lambda+\lambda''} C(\Lambda,\Lambda',\Lambda'') H_{\Lambda''}(k\mathbf{a}).$$
(A52)

These expansion relations are straightforward generalizations of the corresponding ones in three-dimensional space.<sup>29,31</sup>

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