Symmetry and Degeneracy in Density Functional Theory

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ABSTRACT: The superhamiltonian formalism is used to construct a totally symmetric superdensity for a system whose ground state corresponds to a multidimensional irreducible representation of the symmetry group of the Hamiltonian. A Hohenberg–Kohn theorem is proven and the Levy constrained-search procedure is adapted. An appropriate generalization allows the application of this procedure to degenerate excited states. © 2001 John Wiley & Sons, Inc. Int J Quantum Chem 85: 432–435, 2001

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Introduction

While density functional theory was originally formulated for a nondegenerate ground state [1], considerable attention has been paid to extensions that allow the treatment of degenerate as well as excited states. The principal approaches to the treatment of excited states within density functional theory are based on the ensemble density formalism that was originally introduced by Theophilou [2]. The latter is based on a variational inequality satisfied by the sum of any number of consecutive eigenvalues of the Hamiltonian operator, starting from the ground state, that had originally been derived by Fan [3]. Theophilou's approach was reformulated in terms of a ground state

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Hohenberg–Kohn theorem involving a superhamiltonian and a corresponding superdensity [4]. The ensemble point of view was further developed by Kohn et al. [5–8].

States that correspond to multidimensional irreducible representations of the symmetry group of the Hamiltonian are commonly treated by means of a symmetrized density-functional formalism that was introduced by Görling [9, 10]. Both the justification of this formalism from the point of view of the Hohenberg–Kohn theorem [9] and the implementation of a Kohn–Sham procedure for the symmetrized density [10] were considered. This approach has been used by several authors, a recent example being the series of articles by Filatov and Shaik [11].

The main purpose of this article is to provide a foundation for the symmetrized density formalism for a ground state that belongs to a multidimensional (i.e., degenerate) irreducible representation of the symmetry group of the system Hamiltonian

within the superhamiltonian formalism. A straight-forward extension allows the application of this formalism to degenerate excited states as well.

The Superhamiltonian

The system of interest is specified by the N-particle Hamiltonian of the conventional form

$$\mathcal{H}(I) = \sum_{i \in I} h_i + \sum_{(i,j) \in I_2} v_{ij}, \tag{1}$$

where h_i and v_{ij} are one- and two-body operators, respectively, and $I \equiv \{1, 2, \ldots, N\}$ is the set of particle indices. The set of distinct pair indices is given by $I_2 \equiv \{(i,j); i,j \in I, i < j\}$. Assuming that the N particles are identical, the Hamiltonian $\mathcal{H}(I)$ commutes with the permutations of the particle-indices, which form the symmetric group S_N. Assuming further that these N particles are fermions, we restrict our attention to the sector of the N-particle Hilbert space that is antisymmetric in these permutations.

We consider M replicas of this Hamiltonian with sets of particle indices $I^{(k)} \equiv \{1^{(k)}, 2^{(k)}, \ldots, N^{(k)}\}$, where $k = 1, 2, \ldots, M$. In terms of these replicas of the original Hamiltonian, we construct the super-hamiltonian

$$\mathcal{H}_S = \frac{1}{M} \sum_{k=1}^{M} \mathcal{H}(I^{(k)}) \tag{2}$$

which is the (normalized) sum of M noninteracting subsystems. Clearly, $\mathcal{H}_S$ is symmetric with respect to permutations of sets of particles $I^{(k)}$ distinguished by different superscripts $k = 1, 2, \ldots, M$.

The particle permutations and the set permutations together give rise to a wreath product of the symmetric groups S_N and S_M [12]. A typical element of the wreath product permutes superparticle indices and at the same type it permutes particle indices within individual replicas.

Let $\psi_1, \psi_2, \ldots, \psi_M$ be eigenfunctions of the Hamiltonian $\mathcal{H}$, with eigenvalues $E_1, E_2, \ldots, E_M$, respectively. The determinantal wavefunction

$$\Psi_S = \frac{1}{\sqrt{M!}} \begin{vmatrix} \psi_1(I^{(1)}) & \psi_2(I^{(1)}) & \cdots & \psi_M(I^{(1)}) \\ \psi_1(I^{(2)}) & \psi_2(I^{(2)}) & \cdots & \psi_M(I^{(2)}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(I^{(M)}) & \psi_2(I^{(M)}) & \cdots & \psi_M(I^{(M)}) \end{vmatrix} \tag{3}$$

is an eigenfunction of the superhamiltonian, with the eigenvalue $E_S = (1/M)(E_1 + E_2 + \cdots + E_M)$. This wavefuction is antisymmetric with respect to

permutations of the set indices. To distinguish between this antisymmetry property and the physical antisymmetry due to the fermionic nature of the N constituent particles, we call the former set-antisymmetry. The set-antisymmetric ground state of the superhamiltonian is constructed in terms of the set of the M lowest lying eigenstates of the original Hamiltonian.

A corresponding superdensity

$$\rho_S(\vec{r}) = \left\langle \Psi_S \left| \frac{1}{M} \sum_{i=1}^{M} \sum_{j \in I^{(i)}} \delta(\vec{r} - \vec{r}_j) \right| \Psi_S \right\rangle$$

$$= \frac{1}{M} \sum_{i=1}^{M} \left\langle \psi_i \left| \sum_{j \in I^{(i)}} \delta(\vec{r} - \vec{r}_j) \right| \psi_i \right\rangle$$

$$= \frac{1}{M} \sum_{i=1}^{M} \rho_i(\vec{r}) \tag{4}$$

can be introduced. Here, ρ_i is the ordinary density that derives from the state ψ_i. Since ψ_i is an N-electron wavefunction, $\int \rho_i \, d^3\vec{r} = N$. The super-density is normalized by means of the factor $1/M$ so that ρ_S is still an N-electron density, i.e., $\int \rho_S \, d^3\vec{r} = N$.

The Hohenberg–Kohn Theorem for the Superhamiltonian

A Hohenberg–Kohn-like theorem can easily be formulated with respect to the superdensity.

Let $h_i = t_i + v_i$, where t_i is a universal one-body operator (usually, the kinetic energy operator), and v_i is a local one-body potential. The Hohenberg–Kohn theorem deals with a family of Hamiltonians with common t_i and v_{ij}, and arbitrary v_i.

Note that

$$\langle \Psi_S | \mathcal{H}_S | \Psi_S \rangle = \frac{1}{M} \sum_{i=1}^{M} \langle \psi_i | \mathcal{H} | \psi_i \rangle$$

$$= \frac{1}{M} \sum_{i=1}^{M} \langle \psi_i | \mathcal{F} | \psi_i \rangle + \int v \rho_S \, d^3\vec{r},$$

where $\mathcal{F} = \sum_{i \in I} t_i + \sum_{(i,j) \in I_2} v_{ij}$. It will be convenient to define

$$\mathcal{F}_S = \frac{1}{M} \sum_{i=1}^{M} \mathcal{F}(I^{(i)}).$$

A Hohenberg–Kohn theorem stating that v_i is uniquely determined by the ground state superdensity ρ_S can be established. The proof follows that of

the original Hohenberg–Kohn theorem [1]. Assuming that two different local potentials v_i and v_i' give rise to ground state superwavefunctions Ψ_S and Ψ_S' with a common superdensity ρ_S, we obtain by use of the variational principle

$$E_S = \langle \Psi_S | \mathcal{F}_S | \Psi_S \rangle + \int v \rho_S \, d^3\vec{r}$$

$$\leq \langle \Psi_S' | \mathcal{F}_S | \Psi_S' \rangle + \int v \rho_S \, d^3\vec{r} \qquad (5)$$

$$E_S' = \langle \Psi_S' | \mathcal{F}_S | \Psi_S' \rangle + \int v' \rho_S \, d^3\vec{r}$$

$$\leq \langle \Psi_S | \mathcal{F}_S | \Psi_S \rangle + \int v' \rho_S \, d^3\vec{r}. \qquad (6)$$

Hence, $\langle \Psi_S | \mathcal{F}_S | \Psi_S \rangle + \langle \Psi_S' | \mathcal{F}_S | \Psi_S' \rangle \leq \langle \Psi_S' | \mathcal{F}_S | \Psi_S' \rangle + \langle \Psi_S | \mathcal{F}_S | \Psi_S \rangle$ which is only possible if both Eq. (5) and Eq. (6) are equalities. Since Ψ_S is, by construction, nondegenerate, it follows that, up to an overall phase factor, $\Psi_S' = \Psi_S$.

The theorem just derived implies the existence of a universal functional

$$F_{S,M}[\rho_S] = \langle \Psi_S^{(0)}[v[\rho_S]] | \mathcal{F}_S | \Psi_S^{(0)}[v[\rho_S]] \rangle.$$

Here, $v[\rho_S]$ is the unique (up to an additive constant) local potential giving rise to the superdensity ρ_S. $\Psi_S^{(0)}$ is the (nondegenerate) ground state of the superhamiltonian with this external potential.

The second Hohenberg–Kohn theorem [1], stating that $F_{S,M}[\rho_S] + \int v \rho_s \, d^3\vec{r}$ obtains its minimal value at $\rho_S^{(0)}$, the ground state superdensity, is a direct consequence of the quantum mechanical variational principle. The nature of the dependence of $F_{S,M}$ on M is at present an entirely open problem.

Levy's constrained search procedure [13] can very easily be adapted to the present situation, following Pathak [14]. The energy density functional corresponding to the superhamiltonian ground state is given by means of

$$E = \min_{\rho_S} \left\{ \min_{\Psi_S \to \rho_S} \langle \Psi_S | \mathcal{F}_S | \Psi_S \rangle + \int v \rho_S \, d^3\vec{r} \right\}.$$

This procedure avoids the v-representability problem that the original Hohenberg–Kohn procedure poses. It does imply an N-representability problem for the superdensity, but the latter can be dealt with by means of an adaptation of the procedures introduced by Gilbert [15], Harriman [16], and Zumbach and Mashke [17].

SUPERSYMMETRY OPERATORS

Let the Hamiltonian $\mathcal{H}$ have a symmetry group $\mathcal{G} = \{e, g_2, \ldots, g_m\}$ and let the ground state belong

to an irreducible representation Γ of dimension M. This means that $[\mathcal{H}, g_i] = 0$ for $i = 1, 2, \ldots, m$. Since g_i are symmetry operators, we can assume that they act unitarily on functions in the Hilbert state of the Hamiltonian $\mathcal{H}$. Thus, $g_\ell = \exp(i\gamma_\ell)$, where γ_ℓ is hermitian.

The operators $g_i^S = \prod_{k=1}^{M} g_i(I^{(k)})$ can easily be shown to form a group that we can denote $\mathcal{G}_S$ that is isomorphic with $\mathcal{G}$. The elements of $\mathcal{G}_S$ commute with $\mathcal{H}_S$.

Since $\psi_1, \psi_2, \ldots, \psi_M$ form a basis for the (irreducible) invariant subspace Γ with respect to the symmetry group $\mathcal{G}$, we can write

$$g_i \psi_\ell = \sum_{k=1}^{M} \psi_k D_{k,\ell}, \qquad i = 1, 2, \ldots, m;$$

$$\ell = 1, 2, \ldots, m, \quad (7)$$

where $D_{k,\ell}$ is shorthand for $D_{k,\ell}^{(\Gamma)}(g_i)$. It follows that

$$g_i^S \Psi_S = \frac{1}{\sqrt{M!}}$$

$$\times \begin{vmatrix} g_i(I^{(1)})\psi_1(I^{(1)}) & g_i(I^{(1)})\psi_2(I^{(1)}) & \cdots & g_i(I^{(1)})\psi_M(I^{(1)}) \\ g_i(I^{(2)})\psi_1(I^{(2)}) & g_i(I^{(2)})\psi_2(I^{(2)}) & \cdots & g_i(I^{(2)})\psi_M(I^{(2)}) \\ \vdots & \vdots & \ddots & \vdots \\ g_i(I^{(M)})\psi_1(I^{(M)}) & g_i(I^{(M)})\psi_2(I^{(M)}) & \cdots & g_i(I^{(M)})\psi_M(I^{(M)}) \end{vmatrix}$$

$$= \frac{1}{\sqrt{M!}} \sum_{k_1=1}^{M} \sum_{k_2=1}^{M} \cdots \sum_{k_M=1}^{M}$$

$$\begin{vmatrix} \psi_{k_1}(I^{(1)}) & \psi_{k_2}(I^{(1)}) & \cdots & \psi_{k_M}(I^{(1)}) \\ \psi_{k_1}(I^{(2)}) & \psi_{k_2}(I^{(2)}) & \cdots & \psi_{k_M}(I^{(2)}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{k_1}(I^{(M)}) & \psi_{k_2}(I^{(M)}) & \cdots & \psi_{k_M}(I^{(M)}) \end{vmatrix}$$

$$\times D_{k_1,1} D_{k_2,2} \cdots D_{k_M,M}.$$

The only contributions to the last sum are due to terms in which all M indices $k_1, k_2, \ldots, k_M$ are distinct. Since these coefficients can assume precisely M values, it follows that there are precisely $M!$ nonvanishing terms, in which $k_1, k_2, \ldots, k_M$ are the $M!$ permutations of $1, 2, \ldots, M$. The determinant in each of these terms can be brought into the form Ψ_S by an appropriate permutation of columns that gives rise to a parity factor. Pulling out the common factor Ψ_S, the remaining sum of products of the coefficients, along with the parity factors left behind, can be written as an $M \times M$ determinant. Thus,

$$g_i^S \Psi_S = \Psi_S \begin{vmatrix} D_{1,1} & D_{1,2} & \ldots & D_{1,M} \\ D_{2,1} & D_{2,2} & \ldots & D_{2,M} \\ \vdots & \vdots & \ddots & \vdots \\ D_{M,1} & D_{M,2} & \ldots & D_{M,M} \end{vmatrix}.$$

Since Γ can be assumed to be a unitary representation, it follows that the determinant of the matrix representing the group element g_i has modulo 1. Thus, the wavefunction Ψ_S is an eigenfunction of every group element $g_i^S \in \mathcal{G}_S$ with an eigenvalue whose absolute value is equal to 1. It follows that the corresponding superdensity is totally symmetric with respect to $\mathcal{G}_S$.

Spin degeneracy can easily be taken care of within the formalism developed above. A system possessing a total spin quantum number σ is $(2\sigma + 1)$-fold degenerate. Constructing an appropriate superground state in terms of a $(2\sigma + 1) \times (2\sigma + 1)$ determinant, we note that the latter is a supersinglet state relative to the superspin operator $\vec{S}_S = \sum_{i=1}^{2\sigma+1} \vec{S}_i$.

Examples

THE BORON ATOM GROUND STATE

The ground state of the boron atom is specified by the configuration $1s^2 2s^2 2p$. This state is obviously a ^2P. Each of its two spin components belongs to a three-dimensional irreducible representation of the spacial symmetry group of the atomic Hamiltonian, i.e., the three-dimensional rotation group. A spherically symmetric density is introduced by noting that $2p_x^2 + 2p_y^2 + 2p_z^2$ is spherically symmetric.

THREE ELECTRONS IN A QUANTUM DOT

Since the atomic orbital ordering $1s < 2s < 2p < \cdots$ is so deeply ingrained in the chemist's mind, the ground state of an (interacting) three electron system is expected to be represented by the spherically symmetric, spatially nondegenerate state specified by the configuration $1s^2 2s$. This is certainly true for the lithium atom, but the situation can be different for three electrons in a quantum dot.

The orbital ordering for the three-dimensional isotropic (i.e., spherically symmetric) harmonic oscillator, as well as for the spherical box, provided that it is deep enough to support a sufficient number of bound states, is $1s < 2p < 2s < \cdots$. Assuming that the interaction does not upset this orbital ordering, it follows that the ground state for three electrons in a quantum dot which can be modelled by a single-particle potential of the box or oscillator type could be the triply degenerate state corresponding to the configuration $1s^2 2p$.

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