The energy density functional formalism for excited states

Andreas K Theophilou

Nuclear Research Center 'Demokritos', Aghia Paraskevi Attikis, Greece

Abstract. In this paper it is shown that the density can be used as the basic variable for calculating the properties of excited states. The correspondence is not between an eigenstate and its density, as is the case with the ground state, but between the subspace spanned by the number of lowest-energy eigenstates and the sum of their densities. An extension of the Hohenberg–Kohn–Sham theory for excited states has also been developed. The equations derived are similar in form to those for the ground-state density but the interpretation is different. The lowest-order approximation of the present theory coincides with Slater's 'transition-state' theory.

1. Introduction

One of the early attempts to simplify the many-electron problem used the density as a basic variable: such attempts started with the Thomas–Fermi approximation. Later more sophisticated approximations were developed e.g. by March and Murray (1960, 1961) and Stoddard and March (1967).

In 1964 Hohenberg and Kohn (1964) proved that the ground state of a many-electron system is uniquely determined by the ground-state density. Further, they developed a variational principle which states that the energy expressed as a functional of the density assumes its minimum value for the correct ground-state density. Thus, they proved that in principle it is possible to determine the exact ground-state density and energy of a many-electron system by using the density as a basic variable if the exact kinetic energy and exchange and correlation energy density functionals, $T(\rho)$ and $E_{xc}(\rho)$ respectively, are known.

A further development based on the HK theory was given by Kohn and Sham (1965) who showed that in principle it is possible to determine the exact one-particle properties of a many-electron system by using a set of Schrödinger-type equations. This scheme can be viewed as a sophisticated version of the simplified Hartree–Fock approximation in which the exchange operator is approximated by a local potential.

This scheme, known as the KS or HKS scheme, cannot give exact results in applications to physical problems because at present the exact form of $E_{xc}(\rho)$ and $T(\rho)$, as in the case of HK theory, is not known. However, part of the kinetic energy of the interacting system is determined by that of the 'non-interacting' one. Thus, the HKS scheme gives better results than the HK one. The HKS scheme has been widely applied in solid state physics and particularly to surface problems (e.g. Lang and Kohn 1970, 1971; Smith

1969, 1970; Theophilou and Modinos 1972). A disadvantage of the HKS scheme compared with the Hartree–Fock approximation is that the many-particle wavefunction of this theory cannot be used to derive many-particle properties of the system, whereas the HF wavefunction can.

As the schemes developed by Hohenberg, Kohn and Sham are restricted to the ground state it is of interest to develop a similar scheme for excited states. Since a wide class of experiments in atoms, molecules and solids are spectroscopy experiments, the development of such a scheme is useful not only for calculating excited-state densities but also for excitation spectra. It is well known to solid state physicists that the energy band theory is widely used in interpreting spectroscopic data. However, most energy band calculations adopt an effective potential and quite often are successful in interpreting the experimental data. The justification for this will be given in this paper as an application of the theory developed here.

Before finishing this section we would like to point out that the generalisation of the HKS theory for excited states is not straightforward. The main difference is that subspaces have to be considered instead of eigenstates.

Earlier attempts to generalise the HKS scheme have also been made. Gunnarsson and Lundqvist (1976) noted that this scheme can be generalised for excited states which are the lowest-energy states of each symmetry. Further developments which include magnetic interactions have been given (Stoddart and March 1971, Barth and Hedin 1972, Rajagopal and Callaway 1973). Another generalisation of the HKS theory which dealt with thermodynamic properties was developed by Mermin (1965). Numerous papers concerning the kinetic and exchange and correlation energy density functionals have been presented in recent years; see e.g. Vinter (1978), Hedin and Lundqvist (1971), Rasolt and Vosko (1974). General properties of these functionals have been derived by Theophilou (1972) and Osaka (1974a, b).

In §2 some preliminary relations necessary for developing the HK and HKS theory for excited states are given. In §3 the scheme for excited states where the density is used as basic variable is presented. In §4 we develop the HKS theory for excited states and in §5 the difficulties associated with applications of the present scheme are discussed.

2. Preliminary relations

We consider the many-electron Hamiltonian

$$H = H_0 + \int \hat{\rho}(r)\, V(r)\, \mathrm{d}^3 r \tag{2.1a}$$

where

$$H_0 = \tfrac{1}{2} \int \nabla \psi^+(r) \cdot \nabla \psi(r)\, \mathrm{d}^3 r + \tfrac{1}{2} \int \int \frac{\psi^+(r)\, \hat{\rho}(r')\, \psi(r)}{|r' - r|}\, \mathrm{d}^3 r\, \mathrm{d}^3 r' \tag{2.1b}$$

$$\hat{\rho}(r) = \psi^+(r)\, \psi(r). \tag{2.1c}$$

V (r) is the external potential and $\psi^+(r)$, $\psi(r)$ are the fermion field operators.

In order to develop the energy density functional formalism for excited states it is necessary to prove some auxiliary theorems.

Theorem 1. If A is a linear operator and S an N-dimensional subspace of the Hilbert

space $\mathscr{H}$ spanned by the linear combinations of the orthonormal states $|\psi_i\rangle$ then the quantity

$$G_A = \frac{1}{N} \sum_{i=1}^{N} \langle \psi_i | A | \psi_i \rangle, \qquad |\psi_i\rangle \in S$$

is a functional of the subspace S, i.e. its value is determined only by the subspace S and not by the particular choice of the basis. The proof of this theorem is given in Appendix 1.

As G_A is a functional of S, in the rest of this paper the following notation will be used

$$G_A(S) = \frac{1}{N} \sum_{i=1}^{N} \langle \psi_i | A | \psi_i \rangle, \qquad \langle \psi_i | \psi_j \rangle = \delta_{ij}.$$

Theorem 2. The functional

$$G_H(S) = \tfrac{1}{2}(\langle \psi_0 | H | \psi_0 \rangle + \langle \psi_1 | H | \psi_1 \rangle) \tag{2.2a}$$

under the conditions

$$\langle \psi_0 | \psi_1 \rangle = 0 \tag{2.2b}$$

$$\langle \psi_0 | \psi_0 \rangle = 1, \qquad \langle \psi_1 | \psi_1 \rangle = 1 \tag{2.2c}$$

assumes its minimum value when $|\psi_0\rangle$ and $|\psi_1\rangle$ are any two orthonormal states in the subspace S spanned by the linear combinations of the ground state $|\phi_0\rangle$ and the first excited state $|\phi_1\rangle$ of the Hamiltonian H. An equivalent formulation of theorem 2 is: $G_H(S) < G_H(S')$ for $S' \neq S$.

Theorem 2 can easily be proved by expanding in terms of the complete set of eigenstates of H, although not all Hamiltonians possess a complete set of eigenstates in the Hilbert space $\mathscr{H}$. For most physicists however, this is not a serious problem since the physical situation does not change if we add to the external potential $V(r)$ a potential which is zero inside a cube and $+\infty$ outside and take the volume of the cube to be very large but not infinite. In this way we can get a complete set of eigenstates with discrete eigenvalues and hence deal with the problem.

For the mathematical proof of theorem 2 it is necessary to consider Hamiltonians which have their continuous spectrum above the first excited state. We also consider Hamiltonians for which the two lowest-energy eigenvalues are non-degenerate.

Proof of theorem 2. From theorem 1 we notice that for any orthonormal basis of the subspace S spanned by the linear combinations of the two lowest-energy eigenstates of H, $|\phi_0\rangle$ and $|\phi_1\rangle$, the following relation holds:

$$\langle \psi_0 | H | \psi_0 \rangle + \langle \psi_1 | H | \psi_1 \rangle = E_0 + E_1 \tag{2.3a}$$

where the states $|\psi_i\rangle$ form an orthonormal basis in S, i.e.

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{2.3b}$$

and

$$H |\phi_i\rangle = E_i |\phi_i\rangle. \tag{2.3c}$$

Any subspace S' different from S is spanned by the orthonormal states $|\phi'_0\rangle$ and $|\phi'_1\rangle$,

$$|\phi'_0\rangle = a_{00} |\phi_0\rangle + a_{01} |\phi_1\rangle + b_0 |\chi_0\rangle \tag{2.4a}$$

$$|\phi'_1\rangle = a_{11} |\phi_1\rangle + b_1 |\chi_1\rangle \tag{2.4b}$$

where the states $|\chi_i\rangle$ are normal to the subspace S, i.e.

$$\langle \chi_i | \phi_j \rangle = 0, \qquad i, j = 0, 1. \tag{2.4c}$$

When both coefficients b_i are equal to zero the subspace S' coincides with the subspace S. The states $|\chi_i\rangle$ are not necessarily orthogonal to each other. Because of the orthogonality of the states $|\phi_i'\rangle$, the following relation holds

$$a_{01}^* a_{11} + b_0^* b_1 \langle \chi_0 | \chi_1 \rangle = 0$$

The existence of a basis of the above form can be shown by taking a basis in S' and performing a unitary transformation so that one of the states of the new basis has a projection in the subspace S normal to $|\phi_0\rangle$.

Because of the minimum property of the ground state the following relation holds

$$\langle \phi_0 | H | \phi_0 \rangle \leqslant \langle \phi_0' | H | \phi_0' \rangle. \tag{2.5a}$$

Since the first excited state of the Hamiltonian H can be defined as the normalised state for which the functional $\langle \psi | H | \psi \rangle$ assumes its minimum value in the subspace of the Hilbert space $\mathscr{H}$ normal to $|\phi_0\rangle$, i.e. in the subspace $[I - |\phi_0\rangle \langle \phi_0|]\mathscr{H}$, we have

$$\langle \phi_1 | H | \phi_1 \rangle \leqslant \langle \phi_1' | H | \phi_1' \rangle \tag{2.5b}$$

because the state $|\phi_1'\rangle$ is normal to $|\phi_0\rangle$. By adding by parts inequalities (2.5a) and (2.5b) the following inequality results

$$\langle \phi_0 | H | \phi_0 \rangle + \langle \phi_1 | H | \phi_1 \rangle \leqslant \langle \phi_0' | H | \phi_0' \rangle + \langle \phi_1' | H | \phi_1' \rangle. \tag{2.6}$$

However, the equality sign holds only when $S' = S$. Finally, by expressing the quantities in (2.6) as functionals of the subspaces (see theorem 1) we get

$$G_H(S) < G_H(S'), \qquad S' \neq S. \tag{2.7}$$

An equivalent proof of theorem 1 is obtained by using variational principles to determine the minimum of $G_H(S)$ in a two-dimensional subspace under conditions (2.2b) and (2.2c). By using Lagrange multipliers for the conditions and varying S, the following equations result

$$H|\psi_0\rangle - \mu|\psi_1\rangle = \epsilon_0'|\psi_0\rangle \tag{2.8a}$$

$$H|\psi_1\rangle - \mu|\psi_1\rangle = \epsilon_1'|\psi_1\rangle \tag{2.8b}$$

it can easily be verified that any pair of orthonormal eigenstates of H satisfies these equations with $\mu = 0$ and that when $\mu \neq 0$, the solutions are linear combinations of these eigenstates. The lowest value of $G_H(S)$ is assumed when S is the subspace spanned by $|\phi_0\rangle$ and $|\phi_1\rangle$.

Theorem 3. For Hamiltonians of the form

$$H_V = H_0 + \int \hat{\rho}(r) \, V(r) \, \mathrm{d}^3 r \tag{2.9}$$

there is a one-to-one correspondence between the subspace S, spanned by the lowest-energy eigenstates of H_V, and the external potential $V(r)$.

It must be noted that equivalent potentials, i.e. potentials differing by a constant, are

considered as identical since their corresponding Hamiltonians possess the same set of eigenstates. The eigenstates of H_V will be denoted by $|\phi_i^V\rangle$.

Proof of theorem 3. The two lowest-energy eigenstates of the Hamiltonian H_V are uniquely defined since they are non-degenerate. Hence, the subspace spanned by the lowest-energy eigenstates of H_V is uniquely defined by $V(r)$. Therefore, only one S to one $V(r)$ corresponds. This subspace will be denoted by S_V.

We next have to prove that $S_V \neq S_{V'}$ when V and V' are not equivalent potentials. The proof which follows is by *reductio ad absurdum*. Assume the opposite is true, i.e. $S_V = S_{V'}$. Then, since the two subspaces are identical we can go from the orthonormal basis $|\phi_0^V\rangle, |\phi_1^V\rangle$ to the orthonormal basis $|\phi_0^{V'}\rangle, |\phi_1^{V'}\rangle$ by a unitary transformation. Thus

$$|\phi_0^{V'}\rangle = C_0|\phi_0^V\rangle + C_1|\phi_1^V\rangle \tag{2.10a}$$

$$|\phi_1^{V'}\rangle = C_1^*|\phi_0^V\rangle - C_0^*|\phi_1^V\rangle, \tag{2.10b}$$

but since

$$H_0^{V'}|\phi_0^{V'}\rangle = E_0'|\phi_0^{V'}\rangle, \tag{2.11}$$

then by substituting equation (2.10) into equation (2.11) we have

$$H_0^{V'}(C_0|\phi_0^V\rangle + C_1|\phi_1^V\rangle) = E_0'(C_0|\phi_0^V\rangle + C_1|\phi_1^V\rangle).$$

By taking into account that

$$H_0^{V'} = H_0^V + \int \hat{\rho}(r)(V'(r) - V(r))\,\mathrm{d}^3r \tag{2.12}$$

and using the fact that the states $|\phi_i^V\rangle$ are eigenstates of H_V we get

$$\left(\int \hat{\rho}(r)(V'(r) - V(r))\,\mathrm{d}^3r\right)(C_0|\phi_0^V\rangle + C_1|\phi_1^V\rangle)$$

$$= E_0'(C_0|\phi_0^V\rangle + C_1|\phi_1^V\rangle) - E_0 C_0|\phi_0^V\rangle - E_1 C_1|\phi_1^V\rangle. \tag{2.13}$$

A similar relation holds for $|\phi_1^{V'}\rangle$ i.e.

$$\left(\int \hat{\rho}(r)(V'(r) - V(r))\,\mathrm{d}^3r\right)(C_1^*|\phi_0^V\rangle - C_0^*|\phi_1^V\rangle)$$

$$= E_1'(C_1^*|\phi_0^V\rangle - C_0^*|\phi_1^V\rangle) - E_0 C_1^*|\phi_0^V\rangle - E_1 C_0^*|\phi_1^V\rangle. \tag{2.14}$$

Then since the operator

$$H_{V'} - H_V = \int \hat{\rho}(r)(V'(r) - V(r))\,\mathrm{d}^3r$$

maps both states of the orthonormal basis of S_V into states in S_V it follows that S_V is an invariant subspace of this operator, i.e. every state in S_V is mapped into a state in S_V. It follows then that $H_{V'} - H_V$ has eigenstates in S_V because of a theorem of linear algebra: if a Hermitian operator leaves a finite dimensional subspace invariant then this operator has eigenstates in this subspace. But the operator $H_{V'} - H_V$ has no eigenstates in the Hilbert space $\mathcal{H}$ unless $V(r)$ is a constant. Therefore, it follows that the assumption $S_V = S_{V'}$ is not true.

Hence, there is a one-to-one correspondence between S_V and V, i.e. two different

subspaces correspond to two non-equivalent potentials. The fact that

$$H_{V'} - H_V = \int \hat{\rho}(r)[V'(r) - V(r)] \, \mathrm{d}^3 r$$

has no eigenstates in a Hilbert space follows easily if the usual wavefunction representation is used.

$$H_{V'} - H_V = \sum_i [V'(r_i) - V(r_i)]$$

Then if $\psi(r_1, r_2, \ldots, r_N)$ is an eigenfunction of this operator we have

$$\sum_i (V'(r_i) - V(r_i)) \, \psi(r_1, r_2, \ldots, r_N) = \lambda \psi(r_1, r_2, \ldots, r_N) \tag{2.15a}$$

$$\left(\lambda - \sum_i (V'(r_i) - V(r_i)) \right) \psi(r_1, r_2, \ldots, r_N) = 0. \tag{2.15b}$$

In order to satisfy this equation with $\psi(r_1, r_2, \ldots, r_N)$ not identically zero we must have

$$\sum_i (V'(r_i) - V(r_i)) = \lambda$$

i.e. the two external potentials must be equivalent, a fact which is contrary to our initial assumption.

It must be noted that the δ-function is not a square integrable function and therefore does not belong to the Hilbert space $\mathscr{H}$. Thus a δ-function solution to equation (2.15b) is not acceptable.

Theorem 4. For Hamiltonians of the form

$$H = H_0 + \int \hat{\rho}(r) \, V(r) \, \mathrm{d}^3 r \tag{2.16}$$

the following inequality holds

$$- \int (\rho_{V'}(r) - \rho_V(r)) (V'(r) - V(r)) \, \mathrm{d}^3 r > 0 \tag{2.17}$$

for non-equivalent potentials, i.e. for potentials not differing by a constant.

By $\rho_V(r)$ we denote the sum of the ground-state density and first-excited-state density divided by two,

$$\rho_V(r) = \tfrac{1}{2}(\langle \phi_0^V | \hat{\rho}(r) | \phi_0^V \rangle + \langle \phi_1^V | \rho(r) | \phi_1^V \rangle). \tag{2.18}$$

Proof. Since by theorem 3 the subspace spanned by $|\phi_0^V\rangle$ and $|\phi_1^V\rangle$ does not coincide with $S_{V'}$, the subspace spanned by $|\phi_0^{V'}\rangle, |\phi_1^{V'}\rangle$, we have

$$G_{H_V}(S_V) < G_{H_V}(S_{V'}) \tag{2.19a}$$

$$G_{H_{V'}}(S_{V'}) < G_{H_{V'}}(S_V) \tag{2.19b}$$

By adding (2.19a) and (2.19b) by parts and noting that $G_{H_0}(S_V) + G_{H_0}(S_{V'})$ appears on both sides, inequality (2.17) follows.

Theorem 5. Different densities $\rho_V(r)$ and $\rho_{V'}(r)$ correspond to two different external potentials V and V'.

The densities $\rho_V(r)$ and defined by equation (2.18). The proof of this theorem derives from the fact that $\rho_V(r) = \rho_{V'}(r)$ contradicts inequality (2.17).

The general conclusion of this section is that there is a one-to-one correspondence between the sum of the densities of the two lowest-energy eigenstates and the external potential $V(r)$. The correspondence relations proved in this section can be described schematically as follows:

$$V \; \rightleftarrows \; S_V$$
$$\nwarrow \qquad \swarrow$$
$$\boxed{\rho_V(r)}$$

3. The generalisation of the Hohenberg and Kohn theory for excited states

In the previous section it was shown that there is a one-to-one correspondence between the subspace S and the density

$$\rho_V(r) = \tfrac{1}{2}(\langle \phi_0^V|\hat{\rho}(r)|\phi_0^V\rangle + \langle \phi_1^V|\hat{\rho}(r)|\phi_1^V\rangle). \tag{3.1}$$

From theorem 1 it follows that any quantity

$$G_A = \tfrac{1}{2}(\langle \phi_0^V|A|\phi_0^V\rangle + \langle \phi_1^V|A|\phi_1^V\rangle) \tag{3.2}$$

is uniquely determined by the subspace S_V, i.e. $G_A = G_A(S)$. But since S_V is uniquely determined by $\rho_V(r)$ so is $G_A(S_V)$ i.e.

$$G_A(S_V) = A(\rho_V).$$

Let us consider the Hamiltonian 2.1. By theorem 2 for first-order variations of the subspace S_V

$$\delta G_{H_V}(S_V) = 0. \tag{3.3}$$

However, since variations of S_V correspond to variations of $\rho_V(r)$, we can vary $\rho_V(r)$ instead of S_V, as in the case of Hohenberg and Kohn (1964). By taking into account the equation $\int \rho(r)\,d^3r = N$, the equation resulting from the stability of $H_V(\rho_V)$ is

$$[\delta H_V(\rho)/\delta \rho(r)] - \mu = 0. \tag{3.4}$$

From the previous discussion it follows that $H_V(\rho)$ has the following form

$$H_V(\rho) = T(\rho) + \int \rho(r)\,V(r)\,d^3r + \tfrac{1}{2}\iint \frac{\rho(r)\,\rho(r')}{|r' - r|}\,d^3r\,d^3r' + E_{xc}(\rho) \tag{3.5}$$

where $E_{xc}(\rho)$ is the term resulting from the electron–electron interaction energy (see equation 2.1) after subtracting the corresponding Coulomb energy. The interaction term as a functional of S can also be expressed as a functional of the density.

The functional form of $T(\rho)$ and $E_{xc}(\rho)$, i.e. of the kinetic energy and exchange and correlation energy is a separate problem by itself and will be treated in another paper. In this paper only rigorous results are given. By applying the variational principle (3.4) to equation (3.5) we get

$$\frac{\delta T(\rho)}{\delta \rho(r)} + V(r) + \int \frac{\rho(r')}{|r' - r|}\,d^3r' + \frac{\delta E_{xc}(\rho)}{\delta \rho(r)} = \mu \tag{3.6}$$

i.e. the resulting equations are similar in form to those of Hohenberg and Kohn. Thus, from equation (3.6) the 'density' $\rho(r) = \frac{1}{2}(\rho_0(r) + \rho_1(r))$ and energy $E_0 + E_1$ can be determined. Since $\rho_0(r)$ and E_0 can be determined from the HK theory, the density and energy of the first excited state can be determined.

Before finishing this section we would like to point out that the variational principle holds under the hypothesis that every positive function $\rho(r)$, $\int \rho(r)\,\mathrm{d}^3r = N$ in an open neighbourhood of $\rho_V(r)$ can be written in the form $\rho(r) = \frac{1}{2}\langle \phi_0^{V'}|\hat{\rho}(r)|\phi_0^{V'}\rangle + \langle \phi_1^{V'}|\hat{\rho}(r)|\phi_1^{V'}\rangle$. The topology here can be defined by using the following definition for the distance:

$$d(\rho, \rho') = [(\rho(r) - \rho'(r))^2\,\mathrm{d}^3r]^{1/2}.$$

See also a footnote in the paper by Hohenberg and Kohn (1964) and Gilbert (1975).

4. The generalisation of the HKS theory for excited states

A careful analysis of the Kohn and Sham theory shows that it can be formulated by assuming that the ground state of the interacting system corresponds to the ground-state of a non-interacting system i.e. to a state which is an eigenstate of the Hamiltonian H_U',

$$H_U' = \frac{1}{2}\int \nabla\psi^+(r)\,.\,\nabla\psi(r)\,\mathrm{d}^3r + \int \hat{\rho}(r)\,U(r)\,\mathrm{d}^3r. \tag{4.1a}$$

The correspondence is through the relation

$$\langle \phi_0|\hat{\rho}(r)|\phi_0\rangle = \langle \psi_0|\hat{\rho}(r)|\psi_0\rangle. \tag{4.1b}$$

In developing the HKS theory for excited states the subspace S of the interacting system is assumed to correspond to the subspace S' of the non-interacting system in such a way that the densities corresponding to the two subspaces are equal, i.e.

$$\frac{1}{2}(\langle \phi_0|\hat{\rho}(r)|\phi_0\rangle + \langle \phi_1|\hat{\rho}(r)|\phi_1\rangle) = \frac{1}{2}(\langle \psi_0|\hat{\rho}(r)|\psi_0\rangle + \langle \psi_1|\hat{\rho}(r)|\psi_1\rangle). \tag{4.2}$$

The kinetic energy of the interacting system $G_T(S_V)$ is

$$\langle \psi_0|T|\psi_0\rangle + \langle \psi_1|T|\psi_1\rangle = \langle \phi_0|T|\phi_0\rangle + \langle \phi_1|T|\phi_1\rangle + \Delta T(\rho) \tag{4.3a}$$

$$T = \frac{1}{2}\int \nabla\psi^+(r)\,.\,\nabla\psi(r)\,\mathrm{d}^3r. \tag{4.3b}$$

The functional $\Delta T(\rho)$ is positive. This follows from the fact that for Hamiltonians of the form (4.1a) the following relation holds because of theorem 2:

$$G_{H_U'}(S_U') < G_{H_U'}(S) \qquad S \neq S_U'. \tag{4.4}$$

By taking S as the subspace of the two lowest-energy eigenstates of a Hamiltonian of the form (2.1) for which the corresponding subspace densities are equal, equation (4.4) becomes

$$\langle \phi_0^U|T|\phi_0^U\rangle + \langle \phi_1^U|T|\phi_1^U\rangle + 2\int \rho(r)U(r)\,\mathrm{d}^3r$$

$$< \langle \psi_0^V|T|\psi_0^V\rangle + \langle \psi_1^V|T|\psi_1^V\rangle + 2\int \rho(r)U(r)\,\mathrm{d}^3r. \tag{4.5}$$

Then $G_T(S'_U) < G_T(S_V)$. Obviously the same relation is also true for the ground-state kinetic energy.

It must be noted that assuming the correspondence of the subspace of the interacting system to that of the 'non-interacting' system implies the hypothesis that the sets of the corresponding subspace densities coincide. This hypothesis is also made in the HKS formalism (see footnote to Hohenberg and Kohn 1964). The essential difference between the eigenstates of the non-interacting system and those of the interacting one is that the eigenstates of the former can be expressed by single Slater determinants, whereas those of the second cannot. One way in which this can be shown, although an indirect method, is by noting that if the eigenstates of the interacting system could be expressed by single Slater determinants, the Hartree–Fock approximation would give the exact ground state. As is well known, this is not true.

The subspace density $G_{\rho(r)}(S)$ will be denoted by $\rho(r; S)$ for convenience. Because of the one-to-one correspondence between the subspace S of the interacting system and the subspace S' of the non-interacting system every quantity $G_A(S)$ can be expressed as a functional of S', i.e. since $G_A(S) = A(\rho(S'))$, we must have

$$G_A(S) = F_A(S').$$

The functionals $G_A(S)$, expressed in terms of S', do not assume the simple form given by theorem 1 unless A is an operator which involves only the density $\hat{\rho}(r)$. When the kinetic energy functional in equation (3.5) is replaced by the right-hand side of equation (4.3a) the resulting new functional is

$$F_H(S') = \tfrac{1}{2}(\langle \phi_0|T|\phi_0\rangle + \langle \phi_1|T|\phi_1\rangle) + \Delta T(\rho)$$

$$+ \int \rho(r, S') V(r) \, \mathrm{d}^3r + \tfrac{1}{2}\iint \frac{\rho(r, S')\rho(r', S')}{|r' - r|} \mathrm{d}^3r \, \mathrm{d}^3r' + E_{xc}(\rho). \qquad (4.6)$$

Since variations of S' produce variations of the density, $|\phi_0\rangle$ and $|\phi_1\rangle$ can be varied instead of $\rho(r)$. The resulting equations for the minima of equation (4.6) are

$$T|\phi_i\rangle + \int \hat{\rho}(r) V(r) \, \mathrm{d}^3r + \int \frac{\rho(r')}{|r' - r|} \hat{\rho}(r) \, \mathrm{d}^3r \, \mathrm{d}^3r' + \int V_{xc}(\rho, r) \hat{\rho}(r) \, \mathrm{d}^3r = E_i|\phi_i\rangle,$$

$$\rho(r) = \tfrac{1}{2}(\langle \phi_0|\hat{\rho}(r)|\phi_0\rangle + \langle \phi_1|\hat{\rho}(r)|\phi_1\rangle), \qquad i = 1, 2 \qquad (4.7a)$$

where
$$V_{xc}(\rho, r) = (\delta/\delta\rho(r))(E_{xc}(\rho) + \Delta T(\rho)). \qquad (4.7b)$$

Since $|\phi_0\rangle$ and $|\phi_1\rangle$ can be written in the form of single Slater determinants, i.e.

$$|\phi_0\rangle = a_1^+ a_2^+ \dots a_N^+ |0\rangle$$
$$|\phi_1\rangle = a_1^+ a_2^+ \dots a_{N-1}^+ a_{N+1}^+ |0\rangle, \qquad (4.8)$$

the above equations are equivalent to the following system of one-particle equations

$$-\tfrac{1}{2}\nabla^2 u_k(r) + \left(V(r) + V_{xc}(r) + \int \frac{\rho(r')}{|r' - r|} \mathrm{d}^3r'\right) u_k(r) = \epsilon_k u_k(r), \qquad k = 1, 2, N + 1$$

$$(4.9a)$$

$$\rho(r) = \tfrac{1}{2}\left[2 \sum_{k=1}^{N-1} |u_k(r)|^2 + |\varphi_N(r)|^2 + |u_{N+1}(r)|^2\right]. \qquad (4.9b)$$

Thus, the equations obtained are similar in form to those of Kohn and Sham (1965).

5. Discussion

The scheme developed here for calculating the first excited-state densities can be generalised for the highest states. In such a case it can be proved that the subspace spanned by the M lowest-energy eigenstates is uniquely defined by the sum of the M lowest-energy eigenstate densities.

The problem with this scheme is to determine $\Delta T(\rho)$ and $E_{xc}(\rho)$. By using scaling arguments it can be shown that the lowest-order correction for the kinetic energy is

$$\Delta T(\rho) = C_T \int \rho^{5/3}(r)\, d^3 r$$

and the local term of the exchange and correlation energy is

$$E_{xc}(\rho) = C_{xc} \int \rho^{4/3}(r)\, d^3 r$$

i.e. the functional form is the same as that of the ground state. See also Slater 1974.

As a simple application of the scheme developed here we consider a crystal for which the ground-state density has been determined by using the HKS scheme. In applying the present scheme to determine the first excited state we have to consider equations (4.9).

Since $\rho_0(r)$ is known we can try for an approximate solution of equation (4.9) by setting $\rho(r) \simeq \rho_0(r)$. Then the resulting density will be as that of the ground state. By solving these equations we get for the output density $\rho_{out}(r) = \rho_0(r) + (|u_{N+1}(r)|^2 - |u_N(r)|^2)/2$. Since $(|u_{N+1}(r)|^2 - |u_N(r)|^2)/2$ is small compared with $\rho_0(r)$ the output density is very close to the self-consistent density. The first excited-state energy found in this way is $(E_0 + E_1) - E_0 \simeq \epsilon_{N+1} - \epsilon_N + E_0$.

This result justifies the use of the energy band theory in deriving the low-lying excited states of metals. Obviously, the approximation used here will not be as good when applied to deriving excited-state energies far from the ground state. In this case, equation (4.9) has to be solved self-consistently.

Note that the expression for the density given by equation (4.9b) involves half-filled orbitals. Similarly, the kinetic energy expression in equation (4.6) involves half-filled orbitals since

$$\tfrac{1}{2}(\langle \phi_0 | T | \phi_0 \rangle + \langle \phi_1 | T | \phi_1 \rangle) = \tfrac{1}{2}\left(\sum_{k=1}^{N-1} \int \nabla u_k^* \cdot \nabla u_k\, d^3 r \right.$$

$$\left. + \tfrac{1}{2} \int \nabla \varphi_N^* \cdot \nabla \varphi_N\, d^3 r + \tfrac{1}{2} \int \nabla u_{N+1}^* \cdot \nabla u_{N+1}\, d^3 r \right).$$

The same expressions appear in the Slater 'transition-state' theory for treating optical excitations. This theory according to Slater (1974) gives very good approximations to the experimental excitation energy. In fact if $\Delta T(\rho)$ is absolutely neglected in the present approximation and the X_α method is used for determining C_{xc}, the resulting equations which have to be solved self-consistently, are the same as those of Slater's transition state theory. Thus, the lower-order approximation of the present method derives Slater's transition state theory from basic principles (variational principles for subspaces) and explains the origin of half-filled orbitals.

From theorems 1 and 2 of the present paper we can derive the Hartree–Fock method for excited states by minimising the quantity $\langle \phi_0 | H | \phi_0 \rangle + \langle \phi_1 | H | \phi_1 \rangle$ when $|\phi_0\rangle$ and

$|\phi_1\rangle$ are restricted to the space of Slater determinants, i.e. $|\phi_0\rangle$ and $|\phi_1\rangle$ have the form given by equation (4.8).

For higher-order corrections for the excitation energies it is necessary to derive better approximations for $E_{xc}(\rho)$ and $\Delta T(\rho)$. This problem has now become a separate topic and will not be dealt with in this paper.

Acknowledgments

Appendix 1

Theorem 1. If A is a linear operator and S an N-dimensional subspace of $\mathcal{H}$ spanned by N orthonormal states $|\psi_i\rangle$, $i = 1, \ldots, N$ then the quantity

$$G_A = \frac{1}{N} \sum_{i=1}^{N} \langle \psi_i | A | \psi_i \rangle$$

is a functional of the subspace, i.e. its value is determined only by the subspace S and not by the particular choice of the orthonormal basis.

Proof. Let $|\psi_i'\rangle$ $(i = 1, 2, \ldots, N)$ be another orthonormal basis in S. As two orthonormal bases in a subspace are connected by a unitary transformation, U, then

$$|\psi_i'\rangle = \sum_{j=1}^{N} U_{ij} |\psi_j\rangle$$

and

$$\sum_{i=1}^{N} \langle \psi_i' | A | \psi_i' \rangle = \sum_{i,j,k=1}^{N} U_{ij}^* \langle \psi_j | A | \psi_k \rangle U_{ik}.$$

By performing the summation first on i and taking into account that for unitary transformations

$$\sum_{i=1}^{N} U_{ij}^* U_{ik} = \delta_{jk}$$

we get

$$\sum_{i=1}^{N} \langle \psi_i' | A | \psi_i' \rangle = \sum_{i=1}^{N} \langle \psi_i | A | \psi_i \rangle$$

i.e. G_A does not depend on the particular choice of the basis.

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