

Self-consistent second-order perturbation treatment of multiplet structures using local-density theory

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Various ways of calculating the multiplet structure from a local-density theory are discussed. They are based on a second-order expansion of the total energy in the changes of the occupation numbers from a given reference state. The method is first applied to single determinantal states whose energies are considered as averages over the true multiplet states. In this case, the problem is reduced to the evaluation of a few fundamental parameters which, in general, must be calculated self-consistently. For states which are degenerate by symmetry it is shown that internal consistency imposes relationships between these parameters. These relationships have a unique solution for the $A_1^2 T_2^2$ configuration in T_d symmetry. This example includes the neutral vacancy in silicon and, as a limiting case, the $s^2 p^2$ configurations of column-IV atoms. An extension of the method is then proposed to treat directly linear combinations of Slater determinants. This leads to a formalism which closely parallels term-dependent Hartree-Fock theory. Finally, the method is extended to include configuration interaction. A unique solution is again possible for the free carbon atom yielding improved term values.

I. INTRODUCTION

In recent theoretical work, Ziegler, Rauk, and Baerends,¹ as well as von Barth,² pointed out that local-density theory should be applicable with some care to the calculation of the multiplet structure of free atoms. In principle, the original Hohenberg-Kohn-Sham theory^{3,4} can be applied to obtain the energy of the lowest state of any given symmetry. However, this remains a formal statement since the state-dependent form of the exchange correlation functional is not known. One is thus led to use approximate forms for this functional, the most popular being the local-density approximation derived from the free-electron gas. The problem is then to know to what extent local-density theory can be used for an accurate calculation of the multiplet structures. This problem is important since it occurs not only in free atoms but also for deep levels in insulators and semiconductors. Two important examples are the vacancy in diamond or silicon⁵⁻⁷ and transition-metal ions in silicon or gallium arsenide.^{8,9}

The multiplet-splitting problem arises when a localized and degenerate one-electron energy level is only partially filled with electrons. There exist different ways of distributing the electrons on the different spin orbitals of the degenerate level. In other words, one can build different Slater determinants between which there will be matrix elements of the many-electron Hamiltonian. These many-electron effects will lift the degeneracy of the ground state and lead to what is called the multiplet structure. For free atoms this has been usually treated using Hartree-Fock theory¹⁰ which in general leads to a good semiquantitative

understanding. However, this method is difficult to extend to larger systems in view of the complexity of the exchange terms. For this reason the much simpler local-density theory is of interest.

In this work we want to make a systematic analysis of the applicability of a local-density theory to the multiplet-splitting problem. We base our work on the statement made by Ziegler, Rauk, and Baerends¹ and by von Barth² that local density, in its simple usual form, can only be used to calculate the average energy of states corresponding to *single* Slater determinants. This is because the conventional free-electron form of the exchange-correlation potential does not contain the state dependence necessary to simulate the interaction between different Slater determinants. As shown in Refs. 1 and 2 this can lead to inconsistencies when calculating the energy of degenerate levels from their different basis states. Here we intend to analytically formulate the constraints which should be imposed on a local-density treatment in order to ensure the internal consistency of the model. Throughout this paper we shall illustrate our findings by considering the case of the $A_1^2 T_2^2$ configuration in T_d symmetry.

We begin in Sec. II by discussing the Hartree-Fock treatment of this system, and its possible extensions. In Sec. III we apply local-density theory to the calculation of the total energy of single determinant states. We do this by using a second-order expansion of the energy in powers of the changes in occupation numbers with respect to a reference situation (which we take to be the symmetrically averaged state). This procedure has the advantage of reducing the problem to the calculation of the self-consistent change in energy

of the incompletely filled one-electron level (i.e., the localized state for defects in semiconductors). This change is expressed in terms of a few parameters. Considering the single determinantal energies as averages over the true multiplet states, we are able to express the multiplet splitting in terms of these parameters (Sec. IV). For degenerate multiplet states we finally obtain relations between these basic parameters by imposing the invariance of their energy with respect to any change in basis set. This reduces the number of parameters to two in the general $A_1^2T_2^2$ problem and to one in the atomic limit, as is also the case in conventional Hartree-Fock theory.

In Sec. V we show that it is possible to extend the previous treatment to the direct calculation of the energy of states which correspond to linear combinations of single Slater determinants. We devise a general method for expressing this energy as a linear combination of single determinantal energies. We then apply our self-consistent expansion of the energy to this situation and obtain modified energies for the multiplet states. We use this theory for the $A_1^2T_2^2$ case and show that it is the local-density analog of state-dependent Hartree-Fock theory.

In Sec. VI we write the wave functions as combinations of states belonging to different configurations. We extend the method derived in Sec. V and obtain in this way the local-density analog of a configuration-interaction treatment. Application is made to the free carbon atom.

II. THE HARTREE-FOCK TREATMENT OF THE $A_1^2T_2^2$ CASE IN T_d SYMMETRY

In this section we introduce the case of the $A_1^2T_2^2$ configuration in T_d symmetry which will illustrate the different steps of our analysis. This case represents, e.g., the neutral vacancy in silicon, but in a limiting situation it leads to the s^2p^2 configuration of the free carbon or silicon atom which was treated by von Barth² and represents a useful element for discussion.

We can define the problem as follows. We consider a defect whose one-electron Hamiltonian has full T_d symmetry and whose two highest-filled energy levels are the following: the lower one, corresponding to the irreducible representation A_1 , is nondegenerate with a wave function denoted v which is completely symmetric and we assume it to be filled with two electrons of opposite spin; the higher level corresponding to T_2 is triply degenerate with wave functions which are denoted x, y, z according to their symmetry properties, and we take this state to be incompletely filled with two electrons. In the case of the neutral

vacancy in silicon the A_1 state is found as a resonance in the valence band and the T_2 state as a deep level in the forbidden gap.¹¹⁻¹⁴ This case also corresponds to the s^2p^2 configuration of an atom in a tetrahedral crystal field while in zero field one recovers the free-atom situation.

To work out the many-electron problem for this $A_1^2T_2^2$ configuration in a Hartree-Fock treatment, we consider the completely filled valence-band states and the A_1 state itself as closed shells. We thus have only to determine the occupancy of the six spin orbitals $x, \bar{x}, y, \bar{y}, z, \bar{z}$ of the T_2 state (x has spin up, \bar{x} has spin down), and then to consider all possible Slater determinants, such as $|x\bar{x}\rangle$, for instance, where there is one electron in x and one in \bar{x} . The usual technique is first to obtain the spin orbitals as the self-consistent solutions of a symmetrized one-electron Hamiltonian. One then computes the matrix elements of the full many-electron Hamiltonian in the basis of the Slater determinants built from the available spin orbitals of the incompletely filled shell. Fortunately this complex problem can often be reduced by symmetry. This is because the full Hamiltonian is invariant under the symmetry operations of the point group (here T_d) and in our case does not depend on spin. Its eigenstates can be classified by the irreducible representations to which they belong and by their total spin. This completely defines the eigenstates which are given for our $A_1^2T_2^2$ case in Table I.¹⁵ We work out their relative energies by using rules derived in textbooks¹⁰ and obtain the multiplet structure of Fig. 1(a), which represents the most general result for this case. In this figure the difference in energies are written in terms of the Coulomb integrals $\langle ij|kl\rangle$ defined as

$$\langle ij|kl\rangle = \int e_i^*(1)e_j(1) \frac{1}{r_{12}} e_k^*(2)e_l(2) dr_1 dr_2. \quad (1)$$

In Fig. 1(b) we give the free-atom limit of the model. There, the 1A_1 level becomes 1S and 3T_1 becomes 3P . On the other hand, 1E and 1T_2 become degenerate to give 1D . This degeneracy imposes a relation between the Coulomb parameters, due to spherical symmetry, which is given by

$$\langle xx|xx\rangle - \langle xx|yy\rangle = 2\langle xy|xy\rangle. \quad (2)$$

This allows us to express the free-atom multiplet structure in terms of one parameter only as given in Fig. 1(b). In particular, one obtains the general relation

$$\frac{E(^1S) - E(^3P)}{E(^1D) - E(^3P)} = \frac{5}{2}. \quad (3)$$

The experimental ratio for carbon is found to be smaller,² i.e., 2.13. This is a measure of the

TABLE I. Eigenstates of the $A_1^2T_2^2$ configuration in T_d symmetry.

| | | | |
|-----------|--|--|--------------------|
| 1A_1 | $\frac{ x\bar{x}\rangle + y\bar{y}\rangle + z\bar{z}\rangle}{\sqrt{3}}$ | | |
| 1E | $\frac{2 x\bar{x}\rangle - y\bar{y}\rangle - z\bar{z}\rangle}{\sqrt{6}}$ | | |
| | $\frac{ y\bar{y}\rangle - z\bar{z}\rangle}{\sqrt{2}}$ | | |
| 1T_2 | $\frac{ y\bar{z}\rangle - z\bar{y}\rangle}{\sqrt{2}}$ | | |
| | $\frac{ z\bar{x}\rangle - x\bar{z}\rangle}{\sqrt{2}}$ | | |
| | $\frac{ x\bar{y}\rangle - y\bar{x}\rangle}{\sqrt{2}}$ | | |
| 3T_1 | $M_s = 1$ | $M_s = 0$ | $M_s = -1$ |
| | $ yz\rangle$ | $\frac{ y\bar{z}\rangle + z\bar{y}\rangle}{\sqrt{2}}$ | $ y\bar{z}\rangle$ |
| | $ zx\rangle$ | $\frac{ z\bar{x}\rangle + x\bar{z}\rangle}{\sqrt{2}}$ | $ z\bar{x}\rangle$ |
| | $ xy\rangle$ | $\frac{ x\bar{y}\rangle + y\bar{x}\rangle}{\sqrt{2}}$ | $ x\bar{y}\rangle$ |

strength of correlation effects and the interaction with states derived from higher configurations (such as $A_1T_2^3$ or T_2^4 , for instance) lowering preferentially the 1S state.

III. LOCAL-DENSITY CALCULATION FOR SINGLE DETERMINANTS

The basic result of the Hohenberg, Kohn, and Sham theory^{3,4} is that the ground-state energy is a functional of the electron density. A variational procedure can then be applied leading to one-particle equations whose eigenfunctions can be used to build the electron density in the usual manner. The procedure can be extended to the lowest-energy state of any *different* symmetry¹⁶ and could thus be used to calculate the multiplet structure. However, this is not useful here since one does not know the exact form of the exchange-correlation part of the energy and, in particular, not its symmetry dependence. In actual calculations one has to use approximations to this functional which could, e.g., be derived from the free-electron gas leading to the local-density treatment. The local-density calculation of the multiplet structure of free atoms has been shown to lead to inconsistencies and different authors^{1,2} have argued that local density is only valuable for calculating the total energy of states whose charge density corresponds to *single* Slater determinants. However, this is often not the case (in Table I only the 3T_1 state can be calculated that way). Ziegler, Rauk, and Baerends,¹ as well as von Barth,² have therefore

proposed that the energies of single determinants be considered as weighted averages over the true multiplet states. In this way, von Barth obtained an overdetermined set of numerical equations for the multiplet states of the s^2p^2 free atom. An approximate numerical solution gave the Hartree-Fock value of $\frac{5}{2}$ for the ratio of Eq. (3) and nu-

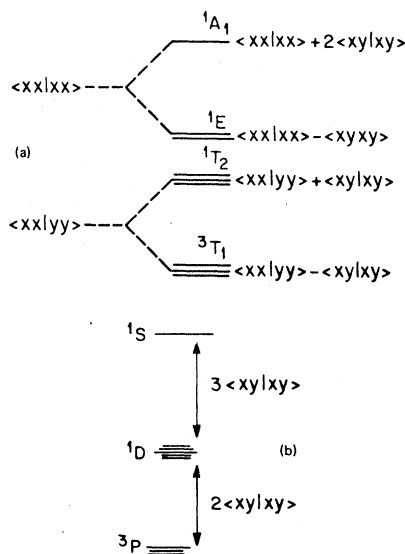


FIG. 1. (a) Hartree-Fock energy-level scheme of the $A_1^2T_2^2$ system in T_d symmetry and (b) Hartree-Fock energy-level scheme of the s^2p^2 free atom.

merical term values somewhat improved over Hartree-Fock.

Here we work in the same spirit, i.e., by applying local density only to single Slater determinants. However, we want to extend the theory to the more general case of *localized states in extended systems (for instance, deep levels in semiconductors)* which represents a more difficult problem. For this we derive a formalism relating the total energy to the calculation of the localized one-electron states only. This self-consistent treatment will allow us to write in analytical form the overdetermined set of equations and will thus lead to a reduction of the number of independent parameters. In this way we shall obtain the local-density analog of the Hartree-Fock treatment of Sec. II.

Let us assume that the one-electron local-density equations have been solved self-consistently for a symmetrically averaged electron density. In the $A_1^2 T_2^2$ situation this corresponds for the two electrons of the T_2 state to identical up and down spin densities ρ_0 , and ρ_0 , given by

$$\rho_0 = \rho_0 = \frac{x^2 + y^2 + z^2}{3}. \quad (4)$$

The corresponding one-electron Hamiltonian H_0 has the complete symmetry of the system. This defines our reference situation where the occupation number of the spin orbital $\psi_{i\sigma}$ (with orbital part ψ_i and spin σ) will be denoted $n_{i\sigma}^0$. For $A_1^2 T_2^2$, for instance, we have

$$n_x^0 = n_y^0 = n_z^0 = n_3^0 = n_2^0 = \frac{1}{3}. \quad (5)$$

We want to calculate the total energy $E(n_{i\sigma})$ of single Slater determinants belonging to the same configuration as a function of their occupation numbers $n_{i\sigma}$ and the value $n_{i\sigma}^0$ of the reference situation

$$E(n_{i\sigma}) = E(n_{i\sigma}^0) + \sum_{i,\sigma} \left(\frac{\partial E}{\partial n_{i\sigma}} \right)_0 \Delta n_{i\sigma} + \frac{1}{2} \sum_{i,j,\sigma,\sigma'} \left(\frac{\partial^2 E}{\partial n_{i\sigma} \partial n_{j\sigma'}} \right)_0 \Delta n_{i\sigma} \Delta n_{j\sigma'}. \quad (6)$$

The quantity $\partial E / \partial n_{i\sigma}$ can be partitioned as follows:

$$\frac{\partial E}{\partial n_{i\sigma}} = \left(\frac{\partial E}{\partial n_{i\sigma}} \right)_{\psi_{j\sigma'}} + \sum_{j\sigma'} \left(\frac{\partial E}{\partial \psi_{j\sigma'}} \right) \frac{\partial \psi_{j\sigma'}}{\partial n_{i\sigma}}. \quad (7)$$

As shown by Janak,¹⁷ if $E(n_{i\sigma})$ is obtained by a variational procedure, then the $\partial E / \partial \psi_{j\sigma'}$ are zero and Eq. (7) reduces to its first term which is nothing else but the eigenvalue $\epsilon_{i\sigma}$ of the one-electron equation giving $\psi_{i\sigma}$. The coefficient of the second-order term in (6) can thus be expressed as $(\partial \epsilon_i / \partial n_{j\sigma'})_0$. This allows one to express Eq. (6) in the form

$$E(n_{i\sigma}) = E(n_{i\sigma}^0) + \sum_{i\sigma} \epsilon_{i\sigma}^0 \Delta n_{i\sigma} + \frac{1}{2} \sum_{i\sigma} \Delta \epsilon_{i\sigma} \Delta n_{i\sigma}, \quad (8)$$

where we have used the fact that $\sum_{j\sigma'} (\partial \epsilon_i / \partial n_{j\sigma'})_0 \Delta n_{j\sigma'}$ is equal to $\Delta \epsilon_{i\sigma}$, the first-order change in the one-electron level $\epsilon_{i\sigma}$. In Eq. (8), for a given configuration ($A_1^2 T_2^2$, for instance) we consider changes $\Delta n_{i\sigma}$ only for the partly filled degenerate state (T_2 in our example). The energy $\epsilon_{i\sigma}^0$ is the same then in all states whose occupancy changes. It can then be factorized out. Because the total number of particles is conserved, the sum $\sum_{i\sigma} \Delta n_{i\sigma}$ vanishes, and therefore there is no first-order contribution. In the second-order term the quantity $\Delta \epsilon_{i\sigma}$ is the first-order change in the eigenvalue. That eigenvalue appears in the equation

$$\left(T + v_N + \int v(\vec{r}, \vec{r}') \rho(\vec{r}') d\vec{r}' + v_{xc}^\sigma(\rho_\uparrow, \rho_\downarrow) \right) \psi_{i\sigma} = \epsilon_{i\sigma} \psi_{i\sigma}, \quad (9)$$

where $T + v_N$ is the sum of the kinetic and nuclear potential energies; the third term is the Hartree potential and v_{xc}^σ is the exchange-correlation potential which is in general spin dependent. Expressing (9) in terms of the reference Hamiltonian H_0 , we can write to first order:

$$(H_0 + W^\sigma) \psi_{i\sigma} = \epsilon_{i\sigma} \psi_{i\sigma}, \quad (10)$$

where the first-order perturbative potential is defined by

$$W^\sigma(\vec{r}') = \int v(\vec{r}, \vec{r}') \Delta \rho(\vec{r}') d\vec{r}' + v_{xc}^{\sigma\uparrow}(\vec{r}) \Delta \rho_\uparrow(\vec{r}) + v_{xc}^{\sigma\downarrow}(\vec{r}) \Delta \rho_\downarrow(\vec{r}). \quad (11)$$

Here $\Delta \rho(\vec{r})$ is the first-order change in electron density, $\Delta \rho_\uparrow$ and $\Delta \rho_\downarrow$ are its up and down spin components. The quantities $v_{xc}^{\sigma\uparrow}$ and $v_{xc}^{\sigma\downarrow}$ are the density derivatives of v_{xc}^σ with respect to ρ_\uparrow and ρ_\downarrow , respectively. The first-order change in $\Delta \epsilon_{i\sigma}$ can be computed by conventional first-order perturbation theory and expressed in the form

$$\Delta \epsilon_{i\sigma} = \langle \psi_{i\sigma}^0 | W^\sigma | \psi_{i\sigma}^0 \rangle, \quad (12)$$

the $\psi_{i\sigma}^0$ being the eigenstates of the reference Hamiltonian H_0 . Before proceeding to calculate W^σ it is important to notice that $\Delta \rho(\vec{r})$ is the sum of a bare part $\Delta \rho_b(\vec{r})$ given by

$$\Delta \rho_b(\vec{r}) = \sum_{i\sigma} \Delta n_{i\sigma} |\psi_{i\sigma}^0|^2 \quad (13)$$

due to the changes in occupation numbers alone, and of a self-consistent part $\Delta \rho_{sc}(\vec{r})$:

$$\Delta \rho_{sc}(\vec{r}) = \sum_{i\sigma} n_{i\sigma}^0 \delta |\psi_{i\sigma}^0|^2, \quad (14)$$

which is due to the changes in spin orbitals at fixed occupation numbers.

When performing a first-order treatment it is possible to separate completely pure electrostatic and pure spin-density fluctuations, defined by

$$\Delta\bar{\rho}(\mathbf{r}) = \frac{\Delta\rho_s(\mathbf{r}) + \Delta\rho_b(\mathbf{r})}{2}$$

and

$$\delta\Delta\rho(\mathbf{r}) = \frac{\Delta\rho_s(\mathbf{r}) - \Delta\rho_b(\mathbf{r})}{2}, \quad (15)$$

respectively. We can do the same for the perturbative potential W^0 in terms of \bar{W} and δW , the electrostatic and magnetic part. Equation (11) can thus be split into two parts:

$$\bar{W}(\mathbf{r}) = 2 \int v(\mathbf{r}, \mathbf{r}') \Delta\bar{\rho}(\mathbf{r}') d\mathbf{r}' + (v''_{\uparrow\uparrow} + v''_{\downarrow\downarrow}) \Delta\bar{\rho}(\mathbf{r}),$$

$$\delta W(\mathbf{r}) = (v''_{\uparrow\downarrow} - v''_{\downarrow\uparrow}) \delta\Delta\rho(\mathbf{r}). \quad (16)$$

On the other hand, the part $\Delta\rho_{sc}(\mathbf{r})$ is fixed by the perturbation potential and one can write

$$\Delta\rho_{sc}(\mathbf{r}) = \int K(\mathbf{r}, \mathbf{r}') \bar{W}(\mathbf{r}') d\mathbf{r}',$$

$$\delta\Delta\rho_{sc}(\mathbf{r}) = \int K(\mathbf{r}, \mathbf{r}') \delta W(\mathbf{r}') d\mathbf{r}', \quad (17)$$

where $K(\mathbf{r}, \mathbf{r}')$ is the linear response function, which is identical for up and down spins and thus also for electrostatic and magnetic response. From (16) and (17) it is then possible to obtain $\bar{W}(\mathbf{r})$ and $\delta W(\mathbf{r})$, using the decomposition of $\Delta\bar{\rho}$ and $\delta\Delta\rho$ into bare and self-consistent components. This allows us to write

$$\bar{W}(\mathbf{r}) = \int d\mathbf{r}' \{ 2v(\mathbf{r}, \mathbf{r}') + [v''_{\uparrow\uparrow}(\mathbf{r}) + v''_{\downarrow\downarrow}(\mathbf{r})] \delta(\mathbf{r} - \mathbf{r}') \} \left(\Delta\bar{\rho}_b(\mathbf{r}') + \int K(\mathbf{r}', \mathbf{r}'') \bar{W}(\mathbf{r}'') d\mathbf{r}'' \right),$$

$$\delta W(\mathbf{r}) = [v''_{\uparrow\downarrow}(\mathbf{r}) - v''_{\downarrow\uparrow}(\mathbf{r})] \left[\delta\Delta\rho_b(\mathbf{r}) + \int K(\mathbf{r}, \mathbf{r}') \delta W(\mathbf{r}') d\mathbf{r}' \right]. \quad (18)$$

These relations can be formally inverted to give

$$\bar{W}(\mathbf{r}) = \int \int d\mathbf{r}' d\mathbf{r}'' \epsilon_d^{-1}(\mathbf{r}, \mathbf{r}') \{ 2v(\mathbf{r}', \mathbf{r}'') - \delta(\mathbf{r}' - \mathbf{r}'') [v''_{\uparrow\uparrow}(\mathbf{r}') + v''_{\downarrow\downarrow}(\mathbf{r}')] \} \Delta\bar{\rho}_b(\mathbf{r}''),$$

$$\delta W(\mathbf{r}) = \int d\mathbf{r}' \epsilon_m^{-1}(\mathbf{r}, \mathbf{r}') [v''_{\uparrow\downarrow}(\mathbf{r}') - v''_{\downarrow\uparrow}(\mathbf{r}')] \delta\Delta\rho_b(\mathbf{r}'), \quad (19)$$

where $\epsilon_d^{-1}(\mathbf{r}, \mathbf{r}')$ and $\epsilon_m^{-1}(\mathbf{r}, \mathbf{r}')$ are the dielectric and magnetic screening matrices respectively which, in principle, can be calculated from the knowledge of $K(\mathbf{r}, \mathbf{r}')$ and the exchange correlation potential. We can now use result (19), combining it with (12) and (13) to show that the second term of equation (8) can be expressed as the difference of two contributions; the pure electrostatic

$$E_{\Delta\bar{\rho}_b} = \frac{1}{2} \int \Delta\bar{\rho}_b(\mathbf{r}) \bar{W}(\mathbf{r}) d\mathbf{r} \quad (20)$$

and the pure magnetic

$$E'_{\delta\Delta\rho_b} = -\frac{1}{2} \int \delta\Delta\rho_b(\mathbf{r}) \delta W(\mathbf{r}) d\mathbf{r}, \quad (21)$$

which can be rewritten as

$$E_{\Delta\bar{\rho}_b} = \frac{1}{2} \int \int \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \Delta\bar{\rho}_b(\mathbf{r}) \epsilon_d^{-1}(\mathbf{r}, \mathbf{r}') \{ 2v(\mathbf{r}', \mathbf{r}'') - \delta(\mathbf{r}' - \mathbf{r}'') [v''_{\uparrow\uparrow}(\mathbf{r}') + v''_{\downarrow\downarrow}(\mathbf{r}')] \} \Delta\bar{\rho}_b(\mathbf{r}'') \quad (22)$$

and

$$E'_{\delta\Delta\rho_b} = -\frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \delta\Delta\rho_b(\mathbf{r}) \epsilon_m^{-1}(\mathbf{r}, \mathbf{r}') [v''_{\uparrow\downarrow}(\mathbf{r}') - v''_{\downarrow\uparrow}(\mathbf{r}')] \delta\Delta\rho_b(\mathbf{r}'). \quad (23)$$

These are the self-consistently screened self-energies of the pure charge- and spin-density fluctuations induced by the changes in occupation numbers.

IV. THE MULTIPLIET STRUCTURE FROM SINGLE DETERMINANTAL ENERGIES

Having obtained the energies of single determinants, the question remains of how to obtain in-

formation about the multiplet structure. Again we follow the proposal of Ziegler, Rauk, and Baerends,¹ and von Barth,² to consider each single determinant as a weighted average over multiplet states. Considering enough different single deter-

minants it should be possible, in most cases, to obtain enough equations between the multiplet energies to determine each of them separately and uniquely. However, as we shall see, one can also obtain an overdetermined set of equations, in which case incompatibilities may occur. This was already noticed by von Barth who found small numerical differences between states which, by symmetry, should have been strictly degenerate. Here we shall consider the constraints analytically and study their simultaneous solutions. We find a unique solution for the system $A_1^2 T_2^2$ which we treat here. However, unique solutions may not exist in more general cases. An investigation of such occurrences shall be discussed in a forthcoming paper.

We return to the system $A_1^2 T_2^2$ and consider, e.g., the single determinant $|x\bar{x}\rangle$ which is *not* an eigenstate of the problem (these are given in Table I). We notice that it can be expressed as a linear combination of the 1A_1 and 1E states. The assumption is then to write its energy as the corresponding weighted average of the 1A_1 and 1E energies, i.e., as

$$E(|x\bar{x}\rangle) = \frac{1}{3}(E_{1A_1} + 2E_{1E}). \quad (24)$$

On the other hand, we can evaluate its energy in terms of the integrals $E_{\Delta\bar{\rho}_b}$ and $E'_{\delta\Delta\rho_b}$ defined in Sec. III. For the determinant $|x\bar{x}\rangle$ both the up and

down spin densities are equal to x^2 , which gives for $\Delta\bar{\rho}_b$ and $\delta\Delta\rho_b$ defined by Eqs. (13) and (15):

$$\begin{aligned} \Delta\bar{\rho}_b &= x^2 - \frac{x^2 + y^2 + z^2}{3} \\ &= \frac{2x^2 - y^2 - z^2}{3} \end{aligned} \quad (25)$$

and

$$\delta\Delta\rho_b = 0, \quad (26)$$

respectively.

If we denote as $2\nu_1$ the function defined by (25), the energy of the determinant $|x\bar{x}\rangle$ then becomes equal to $4E_{\nu_1}$ since it is a quadratic function of $\Delta\bar{\rho}_b$. One can do a similar calculation for all possible single Slater determinants, the results of interest being given in Table II. In this table the density fluctuations are expressed in terms of symmetry functions which allows us to reduce the number of independent integrals E and E' to only five parameters E_ν , E_θ , E'_ν , E'_θ , and E'_{ρ_0} . The calculation of these is detailed in Ref. 18 for the neutral vacancy in silicon. Here we would like to stress the basic properties of the model which can be generalized to other systems.

One can see from Table II that, for the $A_1^2 T_2^2$ case, we have more equations (six) than there are multiplet levels (four, i.e., 1A_1 , 1E , 1T_2 , and 3T_1).

TABLE II. Table of single Slater determinants for V° . The charge and spin fluctuations (columns 2 and 3) are expressed in terms of the following symmetry components:

$$\nu_1 = \frac{2x^2 - (y^2 + z^2)}{6}, \quad \nu_2 = \frac{y^2 - z^2}{2\sqrt{3}}, \quad \rho_0 = \frac{x^2 + y^2 - z^2}{3}, \quad \theta_1 = yz, \quad \theta_2 = zx, \quad \theta_3 = xy.$$

There are no cross terms in $E_{\Delta\bar{\rho}_b}$ and $E'_{\delta\Delta\rho_b}$ between these elementary fluctuations. Owing to symmetry, one has $E_{\nu_1} = E_{\nu_2} = E_\nu$, $E_{\theta_1} = E_{\theta_2} = E_{\theta_3} = E_\theta$, and the same relations for E' .

| Determinant | $\Delta\bar{\rho}$ | $\delta\Delta\rho$ | Energy in terms of fundamental parameters | Energy as an average over multiplets |
|---|------------------------------|---------------------------------------|---|--------------------------------------|
| $ x\bar{x}\rangle$ | $2\nu_1$ | 0 | $4E_\nu$ | $\frac{1}{3}(E_{1A_1} + 2E_{1E})$ |
| $ y\bar{z}\rangle$ | $-\nu_1$ | $\sqrt{3}\nu_2$ | $E_\nu - 3E'_\nu$ | $\frac{1}{2}(E_{1T_2} + E_{3T_1})$ |
| $\left \frac{y+iz}{\sqrt{2}}, \frac{\bar{y}+i\bar{z}}{\sqrt{2}} \right\rangle$ | $-\nu_1$ | 0 | E_ν | $\frac{1}{2}(E_{1E} + E_{1T_2})$ |
| $\left \frac{y+iz}{\sqrt{2}}, x \right\rangle$ | $\frac{\nu_1}{2}$ | $-\frac{3}{2}\nu_1$ | $\frac{E_\nu}{4} - \frac{3}{4}E'_\nu$ | $\frac{1}{2}(E_{1T_2} + E_{3T_1})$ |
| $ y, z\rangle$ | $-\nu_1$ | $\rho_0 - \nu_1$ | $E_\nu - E'_{\rho_0} - E'_\nu$ | E_{3T_1} |
| $\left \frac{y+iz}{\sqrt{2}}, x \right\rangle$ | $\frac{\nu_1}{2}$ | $\rho_0 + \frac{\nu_1}{2}$ | $\frac{E_\nu}{4} - E'_{\rho_0} - \frac{E'_\nu}{4}$ | E_{3T_1} |
| $\left \frac{y+z}{\sqrt{2}}, x \right\rangle$ | $\frac{\nu_1 + \theta_1}{2}$ | $\rho_0 + \frac{\nu_1 + \theta_1}{2}$ | $\frac{E_\nu + E_\theta}{4} - E'_{\rho_0} - \frac{E'_\nu}{4} - \frac{E'_\theta}{4}$ | E_{3T_1} |

This means that, for the model to be coherent, relations should exist between the parameters E and E' . For instance, the three expressions for the 3T_1 state are compatible only if we have

$$\begin{aligned} E_\nu &= E'_\nu, \\ E_\theta &= E'_\theta. \end{aligned} \quad (27)$$

Since the same conditions hold for the other multiplet states of Table II a *unique solution* is possible. If these constraints are fulfilled, the number of independent parameters is reduced to two which we may choose to be E'_ν and E'_{ρ_0} . We thus obtain from Table II, the following expression for the multiplet states:

$$\begin{aligned} E_{3T_1} &= -E'_{\rho_0}, \\ E_{1E} &= 6E'_\nu - E'_{\rho_0}, \\ E_{1T_2} &= E'_{\rho_0} - 4E'_\nu, \\ E_{1A_1} &= 2E'_{\rho_0}. \end{aligned} \quad (28)$$

In this case the model is completely equivalent to the Hartree-Fock model, which leads to the multiplet structure of Fig. 1(a). The correspondence between the parameters is that $\langle xy | xy \rangle$ becomes equal to $E'_{\rho_0} - 2E'_\nu$ and $\langle xx | xx \rangle - \langle xx | yy \rangle$ to $6E'_\nu$. It is easy to show by integration over angles that in the atomic limit the parameter E'_{ρ_0} is equal to $5E'_\nu$, which gives the scheme of Fig. 1(b).

We now investigate the questions of the nature of the constraints imposed by Eqs. (27) and of how they are fulfilled in actual systems. The first problem arises from the fact that a self-consistent local-density treatment in general leads to broken symmetry, for instance, the state $|xz\rangle$ leads to nonspherically symmetric density and Hamiltonian, the same being true for the equivalent states $|zx\rangle$ and $|xy\rangle$. Any linear combination of them which is still a single determinant (for instance, a combination of $|yz\rangle$ and $|xy\rangle$) would then lead to a different energy in the same local-density Hamiltonian. The process of imposing the constraints is thus equivalent in the present case to performing a symmetrical average over the Hamiltonian in Hartree-Fock theory, leading to the central-field approximation. It ensures the invariance of the energy of a degenerate multiplet level under any linear combination of its basis states.

To what extent are the constraints expressed by (27) obeyed in an actual LDF calculation? For the neutral vacancy it was shown that all parameters E_ν , E'_ν , E_θ , and E'_θ were small compared to E'_{ρ_0} , so that Eqs. (27) are trivially satisfied. Additional information comes from the numerical calculation made by von Barth² for the s^2p^2 configuration of the free carbon and silicon atoms. In the atomic case it turns out that self-consistency is not an

important effect, so that the integrals E and E' were evaluated with ϵ_d^{-1} and ϵ_m^{-1} equal to unity. For carbon, the difference between the two 3P calculations corresponding to $\frac{3}{4}(E_\nu - E'_\nu)$ is found to be -0.01 eV. This shows that (27) is satisfied practically within numerical accuracy using self-consistent LDF results.

V. DIRECT EXPRESSION OF THE MULTIPLET STATES IN TERMS OF SINGLE DETERMINANTS

There is an implicit assumption underlying the method used in Sec. IV, where the energy of single determinants was considered to be a weighted average over the true multiplet levels. This assumption is that the single determinantal energies of local-density theory are related to the true multiplet states exactly as they are for the full many-electron Hamiltonian. In other words, the knowledge of the diagonal terms in the determinantal basis automatically should give the nondiagonal terms by the same relations which exist for the full many-electron Hamiltonian. This suggests that we could directly write the energy of each multiplet level as a given combination of single determinantal energies, and then minimize this energy with respect to the spin orbitals.

Let us introduce the method considering the simple example of the 1A_1 state of the $A_1^2T_2^2$ configuration. From Table I, the multiplet state is the following combination of single Slater determinants:

$$\Psi({}^1A_1) = \frac{1}{\sqrt{3}} (|x\bar{x}\rangle + |y\bar{y}\rangle + |z\bar{z}\rangle). \quad (29)$$

If we evaluate its energy from the full many-electron Hamiltonian, taking symmetry into account, we have

$$E({}^1A_1) = \langle x\bar{x} | H | x\bar{x} \rangle + 2\langle x\bar{x} | H | y\bar{y} \rangle. \quad (30)$$

The first term is the average energy of a single determinant and we know that it can be calculated from local-density theory. The second term is a matrix element between different Slater determinants for which we shall be trying to find rules to calculate using local-density theory. For this purpose we rewrite the matrix element¹⁰ as

$$\langle x\bar{x} | H | y\bar{y} \rangle = \langle xy | xy \rangle, \quad (31)$$

i.e., in terms of the Coulomb integrals defined by (1). However, that particular Coulomb integral can also be written as

$$\langle xy | xy \rangle = \langle x\bar{y} | H | x\bar{y} \rangle - \langle xy | H | xy \rangle, \quad (32)$$

which is the difference between the energies of two single Slater determinants. This means that we

can exactly write

$$E({}^1A_1) = \langle x\bar{x} | H | x\bar{x} \rangle + 2(\langle x\bar{y} | H | x\bar{y} \rangle - \langle xy | H | xy \rangle). \quad (33)$$

Each of the three terms in (33) can be evaluated by local-density theory. We shall thus calculate the energy of the 1A_1 state in local-density theory from the expression

$$E({}^1A_1) = E(|x\bar{x}\rangle) + 2[E(|x\bar{y}\rangle) - E(|xy\rangle)]. \quad (34)$$

Similar arguments can be applied to the other multiplet levels and if we use the determinantal energies given in Table II, with the constraints (27), we immediately obtain the results of Sec. IV. One obvious advantage of the present formulation is that it directly eliminates certain inconsistencies already pointed out by von Barth.² This is particularly clear for the 3T_1 state. Calculating its local-density energy from the single determinant $|xy\rangle$ of $S_z=1$, gives $E(|xy\rangle)$. Had we made a direct application of local-density theory to the $S=0$ state $(1/\sqrt{2})(|x\bar{y}\rangle + |\bar{x}y\rangle)$ we would have obtained $\frac{1}{2}[E(|x\bar{y}\rangle) + E(|\bar{x}y\rangle)]$ which, using Table II, gives a completely different value. The method discussed above, however, gives for this $S_z=0$ state

$$E\left(\frac{|x\bar{y}\rangle + |\bar{x}y\rangle}{\sqrt{2}}\right) = \langle x\bar{y} | H | x\bar{y} \rangle + \langle \bar{x}y | H | \bar{x}y \rangle. \quad (35)$$

The second term of (35) can be expressed as the difference between $\langle xy | H | xy \rangle$ and $\langle x\bar{y} | H | x\bar{y} \rangle$, yielding a local-density expression:

$$E\left(\frac{|x\bar{y}\rangle + |\bar{x}y\rangle}{\sqrt{2}}\right) = E(|x\bar{y}\rangle) + E(|xy\rangle) - E(|x\bar{y}\rangle) = E(|xy\rangle). \quad (36)$$

Having obtained individual expressions for the multiplet states we are in a position to apply a variational procedure to each of them separately. For this we write the total energy of each multiplet state as a linear combination of single determinantal energies $E(|\alpha\rangle)$, analogous to the case of the 1A_1 state (34),

$$E = \sum_{\alpha} c_{\alpha} E(|\alpha\rangle). \quad (37)$$

The corresponding coefficients c_{α} are given in Table III for each multiplet state. An important property is that

$$\sum_{\alpha} c_{\alpha} = 1. \quad (38)$$

We now apply a variational procedure to calculating each of the multiplet states. Again we shall do this by second-order self-consistent perturbation theory. Each energy $E(|\alpha\rangle)$ occurring in Eq.

TABLE III. Table of energies of the multiplet states in terms of single determinantal energies, according to Eq. (34).

| Multiplet state | c_{xx} | c_{xy} | c_{xy} | $\Delta \bar{\rho}_b$ | $\delta \Delta \rho_b$ |
|-----------------|----------|----------|----------|-----------------------|-------------------------------------|
| 1A_1 | 1 | 2 | -2 | $2\nu_1$ | $2(\sqrt{3}\nu_2 - \rho_0 + \nu_1)$ |
| 1E | 1 | -1 | 1 | $2\nu_1$ | $-(\sqrt{3}\nu_2 - \rho_0 + \nu_1)$ |
| 1T_2 | 0 | 2 | -1 | $-\nu_1$ | $2\sqrt{3}\nu_2 - \rho_0 + \nu_1$ |
| 3T_1 | 0 | 0 | 1 | $-\nu_1$ | $\rho_0 - \nu_1$ |

(37) can be viewed as some function $E(n_{i\sigma}^{\alpha})$ of the occupation numbers $n_{i\sigma}^{\alpha}$ of the spin orbitals $\psi_{i\sigma}$. The total energy is then some function of these $n_{i\sigma}^{\alpha}$, which has to be a minimum for any variation of the $\psi_{i\sigma}$. This condition can be written as usual in the form of a one-electron-like equation for any $\psi_{i\sigma}$, i.e., as

$$\left(T + v_N + \frac{\sum_{\alpha} c_{\alpha} [v_H(\rho^{\alpha}) + v_{xc}^{\alpha}(\rho^{\alpha})]}{\sum_{\alpha} c_{\alpha} n_{i\sigma}^{\alpha}}\right) \psi_{i\sigma} = \epsilon_{i\sigma} \psi_{i\sigma}, \quad (39)$$

where v_H and v_{xc}^{α} are the Hartree and exchange-correlation potential for the determinant $|\alpha\rangle$ leading to the electron density

$$\rho^{\alpha} = \sum_{i\sigma} n_{i\sigma}^{\alpha} |\psi_{i\sigma}|^2. \quad (39')$$

If we now expand E to second order in powers of the quantities $\Delta n_{i\sigma}^{\alpha} = n_{i\sigma}^{\alpha} - n_{i\sigma}^0$ where, as before, $n_{i\sigma}^0$ defines some reference state, we obtain an expression similar to (6), except that there is one more index α in the expansion. Each first-order derivative $\partial E / \partial n_{i\sigma}^{\alpha}$ can be written as in (7). Again the term $\partial E / \partial \psi_{i\sigma}$, vanishes and $\partial E / \partial n_{i\sigma}^{\alpha}$ can be evaluated as the following quantity:

$$\frac{\partial E}{\partial n_{i\sigma}^{\alpha}} = c_{\alpha} \epsilon_{i\sigma}^{\alpha}, \quad (40)$$

with $\epsilon_{i\sigma}^{\alpha}$ given by

$$\epsilon_{i\sigma}^{\alpha} = \langle \psi_{i\sigma} | T + v_N + v_H(\rho^{\alpha}) + v_{xc}^{\alpha}(\rho^{\alpha}) | \psi_{i\sigma} \rangle. \quad (41)$$

We can now write the second order expansion in a manner analogous to Eq. (8)

$$E = E(n_{i\sigma}^0) + \sum_{\alpha} c_{\alpha} \sum_{i\sigma} \epsilon_{i\sigma}^0 \Delta n_{i\sigma}^{\alpha} + \frac{1}{2} \sum_{\alpha} c_{\alpha} \sum_{i\sigma} \Delta \epsilon_{i\sigma}^{\alpha} \Delta n_{i\sigma}^{\alpha}. \quad (42)$$

Here $\epsilon_{i\sigma}^0$ is the common zeroth-order value of all $\epsilon_{i\sigma}^{\alpha}$ in the reference situation, where the average density is ρ^0 . It is also equal to the eigenvalue of Eq. (39) for that reference situation, since in that case all $n_{i\sigma}^0$ are equal to $n_{i\sigma}^0$, ρ^{α} is equal to ρ^0 , the sum of c_{α} being unity.

In situations derived from a single configuration,

the first-order term disappears and we have only to evaluate the first-order changes in the $\epsilon_{i\sigma}^\alpha$. It is easy to show that

$$\Delta\epsilon_{i\sigma}^\alpha = \langle \psi_{i\sigma}^0 | W_\alpha^\sigma | \psi_{i\sigma}^0 \rangle, \quad (43)$$

where W_α^σ is given by expression (11) in terms of $\Delta\rho^\alpha$, $\Delta\rho_r^\alpha$, and $\Delta\rho_b^\alpha$, which are the differences between the corresponding densities in the determinantal state $|\alpha\rangle$ and in the reference state. Each $\Delta\rho^\alpha$ can be split into a bare component $\Delta\rho_b^\alpha$ given by (13) using $\Delta n_{i\sigma}^\alpha$ and into a self-consistent part $\Delta\rho_{sc}^\alpha$ which, as defined in (14), does not depend on α since the $\psi_{i\sigma}$ are the eigenfunctions of the average equation (39). The calculation of the self-consistent part of the density $\Delta\rho_{sc}$, i.e., of $\delta|\psi_{i\sigma}|^2$, requires the resolution of Eq. (39) to first order. This equation is, to that order, equivalent to Eq. (10) with W^σ given in the form

$$W^\sigma = \sum_\alpha c_\alpha W_\alpha^\sigma. \quad (44)$$

Thus, the self-consistent part of the electron density is given by the average perturbation potential defined by (44). The calculation of the energy now proceeds along the same lines as in Sec. III. We split all quantities into pure electrostatic and pure spin components and obtain Eqs. (16) and (17) for the average potential defined by (44) and $\Delta\rho_{sc}$. Equations (18) and (19) remain valid if we define $\overline{\Delta\rho_b}(\vec{r})$ and $\delta\Delta\rho_b(\vec{r})$ as the corresponding averages

$$\begin{aligned} \overline{\Delta\rho_b}(\vec{r}) &= \sum_\alpha c_\alpha \overline{\Delta\rho_b^\alpha}(\vec{r}), \\ \delta\Delta\rho_b(\vec{r}) &= \sum_\alpha c_\alpha \delta\Delta\rho_b^\alpha(\vec{r}). \end{aligned} \quad (45)$$

Similarly, from (42) and (43), the second-order term in the energy can be written as the difference of two contributions

$$\begin{aligned} \overline{\Delta E} &= \frac{1}{2} \sum_\alpha c_\alpha \int \overline{\Delta\rho_b^\alpha}(\vec{r}) W_\alpha(\vec{r}) d\vec{r}, \\ \delta\Delta E &= -\frac{1}{2} \sum_\alpha c_\alpha \int \delta\Delta\rho_b^\alpha(\vec{r}) \delta W_\alpha(\vec{r}) d\vec{r}, \end{aligned} \quad (46)$$

which are the analog of Eqs. (20) and (21). In these expressions \overline{W}_α and δW_α are given by expressions (18) where on the right-hand side, $\Delta\rho_b$ and $\delta\Delta\rho_b$ are replaced by $\overline{\Delta\rho_b^\alpha}$ and $\delta\Delta\rho_b^\alpha$, while the term involving \overline{W} and δW is kept unchanged. Multiplying these equations by c_α and summing over α yields expression (19) for the average potential \overline{W} and δW . From this equation one can now calculate the energies given by (46) and write them in the form

$$\begin{aligned} \overline{\Delta E} &= \sum_\alpha c_\alpha F_{\overline{\Delta\rho_b^\alpha}} + E_{\overline{\Delta\rho_b^\alpha}} - F_{\overline{\Delta\rho_b^\alpha}}, \\ \delta\Delta E &= \sum_\alpha c_\alpha F'_{\delta\Delta\rho_b^\alpha} + E'_{\delta\Delta\rho_b^\alpha} - F_{\delta\Delta\rho_b^\alpha}, \end{aligned} \quad (47)$$

where the $E_{\overline{\Delta\rho_b^\alpha}}$ and $E'_{\delta\Delta\rho_b^\alpha}$ are the self-consistently screened self-energies given by (22) and (23) while the quantities F and F' are the corresponding unscreened quantities, i.e., with ϵ_d^{-1} and ϵ_m^{-1} equal to unity.

The energies given by Eqs. (47) correspond to the case in which asymmetrical as well as symmetrical density fluctuations are screened. However, the model as it stands, is unnecessarily complex. For instance, the terms $E - F$ occurring in (47) depend upon the choice of the basis state through $\Delta\rho_b$ and $\delta\Delta\rho_b$. If we want results corresponding to a fully symmetric Hamiltonian it is clear that we have only to retain the screening of symmetrical fluctuations in $E - F$. This simplifies the form of $E - F$ and ensures the invariance of this term to changes in basis set.

We can now work out the results for the $A_1^2 T_2^2$ configuration. For this we simply evaluate the first term on the right of (47), using the c_α given in Table III and the determinantal energies given in Table II. We replace the expressions E, E' of Table II by F, F' and we use the fact that the determinants $|x\bar{y}\rangle, |xy\rangle$ have the same energies as $|y\bar{z}\rangle, |yz\rangle$. For the second and third terms on the right-hand side of (47) we give the expression of $\Delta\rho_b$ and $\delta\Delta\rho_b$ in Table III, but only retain the symmetrical contribution due to ρ_0 for $E - F$, for the reasons we have discussed above. We also impose symmetry constraints analogous to (27) on F and F' , i.e.,

$$\begin{aligned} F_\nu &= F'_\nu, \\ F_\theta &= F'_\theta. \end{aligned} \quad (48)$$

Taking into account these parameter symmetrizations, we get the following results for the multiplet levels:

$$\begin{aligned} E(^1A_1) &= 2F'_{\rho_0} - 4(E'_{\rho_0} - F'_{\rho_0}), \\ E(^1E) &= 6F'_\nu - F'_{\rho_0} - (E'_{\rho_0} - F'_{\rho_0}), \\ E(^1T_2) &= -4F'_\nu + F'_{\rho_0} - (E'_{\rho_0} - F'_{\rho_0}), \\ E(^3T_1) &= F'_{\rho_0} - (E'_{\rho_0} - F'_{\rho_0}). \end{aligned} \quad (49)$$

This is formally a similar result as was obtained in expression (28) of Sec. IV but where the quantities E are replaced by F . In addition the 1A_1 level has been lowered by $3(E'_{\rho_0} - F'_{\rho_0})$ with respect to the other levels. In the free-atom limit this gives rise to the structure of Fig. 2. The ratio $[E(^1S) - E(^3P)]/[E(^1D) - E(^3P)]$ is no more given by the Hartree-Fock value $\frac{5}{2}$ but is replaced by $\frac{5}{2}\{1 - [(E'_{\rho_0}/F'_{\rho_0}) - 1]\}$. We can evaluate the corrected value from the numerical values given by von Barth,² noting that $E'_{\rho_0} - F'_{\rho_0}$ is the energy difference between self-consistent and non-self-consistent spin-unrestricted calculations which he

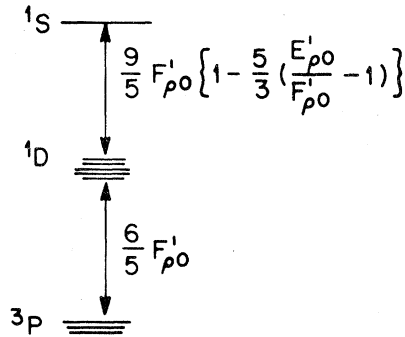


FIG. 2. Local-density (LDF) analog of the term-dependent Hartree-Fock result for the $s^2 p^2$ free atom.

finds to be 0.04 eV. This reduces the ratio to 2.4 for carbon, still significantly different from the experimental value of 2.13.

The results we have obtained here parallel term-dependent Hartree-Fock theory for free atoms, where the radial part of the spin orbitals is varied for each multiplet state separately. In that case too [see (2)] the multiplet ratio is decreased to about 2.4. However, the absolute values of the splittings are in much better agreement with experiment using local-density theory rather than Hartree-Fock.

VI. THE LOCAL-DENSITY-THEORY ANALOG OF CONFIGURATION INTERACTION

We have seen in Sec. V how local density can be used directly to calculate the energy of states which are linear combinations of single Slater determinants. However, we had restricted these combinations to the ground-state configuration which in our example, was the $A_1^2 T_2^2$ configuration. We shall now extend the treatment to states which are combinations of single determinants not only of the ground-state configuration but also of excited-state configurations. This leads to a more flexible wave function and through the variational principle, to an improved description of the multiplet structure of the ground-state configuration. The procedure is then completely analogous to configuration interaction, except that we are working with effective electron-electron interactions given by local-density theory. Let us then recall the procedure to be followed.

(i) The diagonal energies in a Slater determinantal basis are directly expressed in the local-density formulation.

(ii) The nondiagonal matrix elements are taken to be related to the diagonal elements by the same relations as given for the full many-electron Hamiltonian.

This completely defines the Hamiltonian matrix

and allows its complete calculation by local-density theory. Again, symmetry constraints analogous to those expressed by Eq. (27) have to be imposed in order for the effective Hamiltonian matrix to have the full symmetry of the system.

The total energy of a multiplet state is now given by

$$E = \sum_{i,\alpha} C_{\alpha i} E(|\alpha i\rangle), \quad (50)$$

where $E(|\alpha i\rangle)$ is the energy of a single determinantal state $|\alpha i\rangle$, while the sum over i is performed over different possible configurations. As in Sec. V this energy has to be minimized with respect to the spin orbitals $\psi_{i\alpha}$. A new feature is that it must also be varied with respect to the coefficients of the total wave function, since it is now expanded in terms of components belonging to different configurations. This part is equivalent to performing a diagonalization of the corresponding Hamiltonian matrix. Self-consistency could in principle be incorporated into the formulation in a way similar to what was done in Sec. V. However, the equations become much more involved and we shall not go through the whole procedure here. In fact, we expect that in most cases configuration interaction will have a small effect which can be described by second-order perturbation theory. This correction will be evaluated with the self-consistent spin orbitals obtained from a calculation using the reference Hamiltonian for the ground-state configuration. The error in the configuration-interaction correction due to the neglect of the self-consistent change in the spin orbitals is a higher-order effect which we shall not take into account.

With this simplification the problem becomes very easy to solve. We have simply to write the Hamiltonian matrix for a multiplet state of given symmetry in the basis formed by the wave functions of different configurations. Let us discuss this procedure in detail in the example of the 1A_1 state. We know that the wave function for the ground-state configuration $A_1^2 T_2^2$ is $\psi_1({}^1A_1)$ given by (Table I)

$$\psi_1({}^1A_1) = \frac{|v\bar{v}x\bar{x}\rangle + |v\bar{v}y\bar{y}\rangle + |v\bar{v}z\bar{z}\rangle}{\sqrt{3}}, \quad (51)$$

where we have now specified that the spin orbitals v and \bar{v} are occupied. We look for 1A_1 states belonging to higher-excited configurations. For $A_1 T_2^3$ there is no 1A_1 state, but there is one for the T_2^4 configuration, whose wave function is given by (see Ref. 10)

$$\psi_2({}^1A_1) = \frac{|x\bar{x}y\bar{y}\rangle + |y\bar{y}z\bar{z}\rangle + |z\bar{z}x\bar{x}\rangle}{\sqrt{3}}. \quad (52)$$

For the diagonal energy of $\psi_2({}^1A_1)$ the most im-

portant part comes from the difference in one-electron energies $\epsilon(T_2) - \epsilon(A_1)$ between the one-electron states of the reference Hamiltonian [this corresponds to the first-order term in Eq. (6)].

The nondiagonal matrix elements of the full many-electron Hamiltonian H between $\psi_1(^1A_1)$ and $\psi_2(^1A_1)$ have the form

$$\begin{aligned} \langle \psi_1(^1A_1) | H | \psi_2(^1A_1) \rangle &= 2 \langle v\bar{v}x\bar{x} | H | y\bar{y}x\bar{x} \rangle \\ &= 2 \langle vy | vy \rangle \end{aligned} \quad (53)$$

in terms of Coulomb integrals defined by Eq. (1). As was done in Sec. V [Eq. (32)], we can express Eq. (53) as the difference between the energies of two Slater determinants, i.e.,

$$\langle \psi_1(^1A_1) | H | \psi_2(^1A_1) \rangle = 2 [E(|x\bar{x}v\bar{v}\rangle) - E(|x\bar{x}vy\rangle)]. \quad (54)$$

This quantity can now be evaluated by local-density theory. For this we simply use the second-order expansion, developed previously in its non-self-consistent version which leads to parameters $F_{\Delta\bar{p}}$ and $F'_{\Delta\bar{p}}$.

We now consider the remaining 1E , 1T_2 , and 3T_1 states, using the configurations $A_1^2T_2^2$, $A_1T_2^3$, and T_2^4 , respectively. The corresponding combinations of Slater determinants are given in Ref. 15 and we here only give the 3×3 matrices corresponding to the three configurations under study. For second-order perturbation theory only the matrix elements H_{12} and H_{13} between the ground-state configuration and the excited-state configurations are needed. These are for the full many-electron Hamiltonian

$$\begin{aligned} ^1E &\Rightarrow H_{12} = \sqrt{6} \langle vx | yz \rangle, \quad H_{13} = \langle vy | vy \rangle, \\ ^1T_2 &\Rightarrow H_{12} = \sqrt{2} \langle vx | yz \rangle, \quad H_{13} = -\langle vy | vy \rangle, \\ ^3T_1 &\Rightarrow H_{12} = \sqrt{2} \langle vx | yz \rangle, \quad H_{13} = \langle vy | vy \rangle. \end{aligned} \quad (55)$$

In all three cases the diagonal energies H_{22} and H_{33} of the excited configurations are Δ and 2Δ , respectively, where Δ is the excitation energy $\epsilon(T_2) - \epsilon(A_1)$. Following our procedure we have to reduce (55) to linear combinations of single determinantal energies. For $\langle vy | vy \rangle$ the procedure was given for the 1A_1 state in (53) and (54). For the term $\langle vx | yz \rangle$ this can also be done but in a more complicated manner. However, in the atomic limit this term exactly vanishes by symmetry which is also true for its local-density expression. We are then left with the only parameter $\langle vy | vy \rangle$. Evaluating it from (54) and the second-order non-self-consistent expansion, we obtain

$$\langle vy | vy \rangle = F'_{(v^2+y^2)/2} - F'_{(v^2-y^2)/2}. \quad (56)$$

Applying second-order perturbation theory to all cases we obtain for the 1A_1 state a downwards en-

TABLE IV. Comparison of experiment and calculated multiplet splittings using configuration interaction and different local-density approximations (LDX, LD). For explanation of quantities see text. Energies in eV.

| | LDX | LD | Experiment |
|---------------------------|--------|--------|------------|
| F'_{ρ_0} | 1.325 | 1.108 | |
| $\Delta[E(^1S) - E(^3P)]$ | -0.329 | -0.230 | |
| $E(^1D) - E(^3P)$ | 1.59 | 1.33 | 1.26 |
| $E(^1S) - E(^3P)$ | 3.52 | 2.95 | 2.68 |

ergy shift given by

$$\Delta E(^1A_1) = -\frac{2 |\langle vy | vy \rangle|^2}{\Delta} \quad (57)$$

and for the 1E , 1T_2 , and 3T_1 states shifts given by

$$\begin{aligned} \Delta E(^1A_1) &= \Delta E(^1T_2) \\ &= \Delta E(^3T_1) = -\frac{|\langle vy | vy \rangle|^2}{2\Delta}. \end{aligned} \quad (58)$$

This means that the 1A_1 state is lowered with respect to the group of the three other multiplet levels by an amount equal to $(3/2\Delta) |\langle vy | vy \rangle|^2$. To estimate this amount we assume that for carbon (or silicon) the states v and y have similar radial parts, in which case (56) simply reduced to F'_{ρ_0} . This is known numerically for carbon from the work of von Barth² and calculated in two cases, pure exchange local density (LDX) and exchange-correlation local density (LD). The results for F'_{ρ_0} are given in Table IV for the two cases. We have taken in both cases $\Delta = 8$ eV, which results from the calculations of Ref. 10. Table IV shows the shift $\Delta[E(^1S) - E(^3P)]$ calculated as $(-3/2\Delta) |F'_{\rho_0}|^2$ both in the LDX and LD approximations. It also shows the corrected splitting $E(^1S) - E(^3P)$ where the correction obtained here (i.e., -0.12 eV) is added to that obtained in Sec. V. We see that there is good improvement, especially with LD where most of the discrepancy with experiment has been removed.

VI. CONCLUSION

We have systematically analyzed how certain multiplet structures can be obtained from local-density theory by simply evaluating the energy of single Slater determinants. We have first considered such determinants as weighted averages over multiplet states and evaluated their energies by a second-order expansion in the occupation numbers. This leads to a set of equations for the multiplet-term values which may or may not be overdetermined. For certain cases like the $A_1^2T_2^2$ system a unique solution can be found which estab-

lishes relationships between fundamental energy parameters. These relationships are found to be well satisfied for numerical results for the lattice vacancy in silicon and for the free carbon atom. We have then extended the method to the direct calculation of multiplet states within a given configuration. Finally, we have generalized this pro-

cedure to include configuration interaction and have obtained substantial improvement of calculated term splittings when applying the procedure to the free carbon atom. Work is in progress to see if the techniques developed here can be extended to the description of d electrons associated with transition-metal atoms.

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