

Off-diagonal occupation numbers in local-density theory

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We introduce a new method for specifying the occupations of states in local-density theory by allowing "off-diagonal occupation numbers" (i.e., a generalized density matrix). We show that this technique has important applications to superlattice and slab geometries, allowing bonding-type interactions between defects, molecules, or surfaces to be effectively eliminated. Moreover, previously inaccessible charge states may now be studied. The method is shown to have the full sanction of local-density theory.

I. INTRODUCTION

In the theoretical study of aperiodic systems such as defects, molecules, and surfaces, the use of superlattice or slab geometries is frequently a crucial simplification. The philosophy is to model a truly isolated defect (or molecule or surface) by embedding it in a periodic matrix; one must then ensure that interactions between defect states (or molecular orbitals or surface states) are unimportant. It is the purpose of this paper to present a novel method which eliminates the dominant bonding-type interactions. In certain cases the method reduces to the obvious prescription of averaging over the Brillouin zone or over bonding and antibonding combinations of states. In other cases, however, it leads to a new and powerful technique which may, for example, be crucial to the theoretical study of charged defects in semiconductors.

The plan of the paper is as follows. In Sec. II we introduce the method with reference to a simple two-state model system. In Sec. III we show how the method can be applied in a realistic self-consistent local-density calculation; a sample calculation of this type is presented for illustrative purposes. In Sec. IV we demonstrate the validity of the method in the context of local-density theory. Finally, Sec. V contains a brief summary. Certain details of Sec. IV are deferred to the Appendix, which also contains a derivation of the expression for the Hellman-Feynman forces.

II. THE DENSITY MATRIX METHOD

By way of illustration, consider the simple model of Fig. 1. Here we have two defects, A and B , which would have defect gap states ψ_A and ψ_B with eigenvalues ϵ_A and ϵ_B if they were truly isolated. (We shall use the language of defects, though the discussion applies equally to molecules or surfaces.) Let us assume, moreover, that each defect is neutral when the gap state is singly occupied, as is typical for a dangling bond in a semiconductor. Now if the defects are not isolated, so that $V = \langle \psi_A | \hat{H} | \psi_B \rangle \neq 0$, one obtains bonding

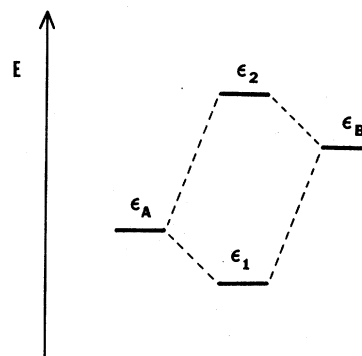


FIG. 1. Energy-level diagram for simple two-level system. ϵ_A and ϵ_B are the energy eigenvalues for isolated defects A and B , respectively; these interact to give the "bonding" and "antibonding" combinations ϵ_1 and ϵ_2 .

and antibonding states

$$\begin{aligned}\psi_1 &= \psi_A \cos\theta + \psi_B \sin\theta, \\ \psi_2 &= \psi_A \sin\theta - \psi_B \cos\theta,\end{aligned}\quad (1)$$

where θ defines a mixing angle. Let the energy zero be defined so that

$$\begin{aligned}\epsilon_A &= -\Delta, \\ \epsilon_B &= +\Delta.\end{aligned}\quad (2)$$

Then the solution of the Schrödinger equation gives

$$\tan 2\theta = -V/\Delta, \quad (3)$$

$$\epsilon_1 = -(\Delta^2 + V^2)^{1/2} = -\Delta \sec 2\theta, \quad (4)$$

$$\epsilon_2 = +(\Delta^2 + V^2)^{1/2} = +\Delta \sec 2\theta.$$

Note that we have implicitly assumed that ψ_A and ψ_B remain orthogonal in the interacting case; we shall return to this point at the end of this section.

Now suppose one is modeling the system A^0B^0 containing two neutral defects. A naive calculation of the ground state would place two electrons in the bonding orbital ψ_1 (i.e., occupation numbers $n_1=2, n_2=0$). However, this introduces two serious errors compared to the case of isolated defects: (i) The system energy is lowered by

$$\begin{aligned}\Delta E &= 2\epsilon_1 - \epsilon_A - \epsilon_B \\ &= -2(\Delta^2 + V^2)^{1/2},\end{aligned}\quad (5)$$

and (ii) because ψ_1 has more weight on ψ_A , there is a charge transfer from B to A of a fraction

$$2|\langle \psi_A | \psi_1 \rangle|^2 - 1 = \cos 2\theta \quad (6)$$

of an electron. Moreover, in the limit of weak interaction $V \rightarrow 0$, we obtain two electrons in ψ_A and none in ψ_B , which rather models the case A^-B^+ .

Luckily, for the case of neutral defects A^0B^0 , there is a simple prescription which solves the problem. We just specify that the two electrons be shared between ψ_1 and ψ_2 :

$$n_1 = 1, \quad n_2 = 1. \quad (7)$$

Then the energy difference is

$$\epsilon_1 + \epsilon_2 - \epsilon_A - \epsilon_B = 0, \quad (8)$$

and the charge transfer is

$$|\langle \psi_A | \psi_1 \rangle|^2 + |\langle \psi_A | \psi_2 \rangle|^2 - 1 = 0. \quad (9)$$

Thus the effects of the interaction V are effectively eliminated. Moreover, one obtains the correct limit as $V \rightarrow 0$. In a superlattice calculation with one de-

fect per supercell, one can similarly eliminate the effects of interactions between all pairs of defect states by integrating over all k vectors in the Brillouin zone; with two or more defects per supercell, one must explicitly average over two or more bands as well.

Consider now the charged configuration A^-B^+ . Again, one would like to have a prescription for populating ψ_1 and ψ_2 in such a way that the total energy and charge transfer are independent of the interaction V . However, the sum of the occupation numbers n_1 and n_2 is constrained, so that one has only a single degree of freedom with which to fit two criteria. Worse, even if one were to abandon an attempt to satisfy the total energy constraint, there is no choice of n_1 and n_2 which will transfer all charge from ψ_B to ψ_A .

In order to provide ourselves with sufficient degrees of freedom to satisfy both the energy and charge constraints, we must generalize from the specification of n_1 and n_2 to the specification of a 2×2 density matrix.¹ Herein lies the heart of our method. The density matrix can be written

$$n_{ij}^H = \langle \psi_i | \hat{n} | \psi_j \rangle \quad (i, j = 1, 2), \quad (10)$$

where the superscript H denotes the fact that the matrix is written in the *Hamiltonian eigenstate* representation, in which the basis vectors are the eigenstates of the interacting system. In this representation, we can make the connection

$$\begin{aligned}n_1 &\rightarrow n_{11}^H, \\ n_2 &\rightarrow n_{22}^H,\end{aligned}\quad (11)$$

from the traditional occupation numbers. The specification of n_{12}^H gives us the additional degree of freedom we need.

To choose \hat{n} we make use of the *local* representation of the density matrix, in which the basis vectors are ψ_A and ψ_B themselves. We then simply require that the density matrix in this representation,

$$n_{\alpha\beta}^L = \langle \psi_\alpha | \hat{n} | \psi_\beta \rangle \quad (\alpha, \beta = A, B), \quad (12)$$

be diagonal with the occupations of ψ_A and ψ_B along the diagonal, e.g.,

$$n^L = \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix}, \quad (13)$$

for the case A^-B^+ . Transforming to the eigenstate representation, we find

$$n^H = \begin{bmatrix} 1 + \cos 2\theta & \sin 2\theta \\ \sin 2\theta & 1 - \cos 2\theta \end{bmatrix}, \quad (14)$$

where use has been made of Eq. (1). The total energy is now

$$E = \text{tr}(\hat{n}\hat{H}) = \sum_{\alpha} n_{\alpha\alpha}^L \epsilon_{\alpha} = -2\Delta. \quad (15)$$

Of course, we could have obtained the same result by evaluating the trace in the eigenvector representation instead, but the use of the local representation in Eq. (15) makes explicit the fact that the energy is now independent of the interaction V . Similarly, the charge density

$$\begin{aligned} \rho(r) &= \sum_{ij} n_{ij}^H \psi_i^*(r) \psi_j(r) \\ &= \sum_{\alpha\beta} n_{\alpha\beta}^L \psi_{\alpha}^*(r) \psi_{\beta}(r) \end{aligned} \quad (16)$$

is most easily evaluated in the local representation, giving

$$\rho(r) = 2 |\psi_A(r)|^2, \quad (17)$$

which is also manifestly independent of V . Note that evaluating in the eigenstate representation leads to

$$\begin{aligned} \rho(r) &= n_{11}^H |\psi_1(r)|^2 + n_{22}^H |\psi_2(r)|^2 \\ &\quad + 2 \text{Re}[n_{12}^H \psi_1^*(r) \psi_2(r)]. \end{aligned} \quad (18)$$

It is the last term on the right side which allows us to transfer additional charge from ψ_B to ψ_A .

Thus, our density-matrix (DM) method says simply to specify the occupations in the local representation, then transform to the usual energy eigenstate representation to obtain a density matrix containing off-diagonal occupation numbers; the energy and charge are then given by Eqs. (15) and (16). (For a superlattice calculation containing two defects per cell, we must also average over all k vectors, using the density matrix method to specify the band occupation at each k point.) Note that in the case of neutral defects $A^0 B^0$, one has

$$n^L = n^H = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Thus the prescription given earlier in Eq. (7) is seen to follow as a special case of the density-matrix method.

Finally, let us return to the question of nonorthogonality. If $S = \langle \psi_A | \psi_B \rangle \neq 0$, then the eigenvalues ϵ_1 and ϵ_2 are renormalized by the factors $(1 \pm S \sin 2\theta)^{1/2}$, respectively. Then the evaluation of $\text{tr}(\hat{n}\hat{H})$ in the Hamiltonian eigenvector representation leads to an error in the energy,

$$\delta E = -2SV + O(S^2), \quad (19)$$

for the neutral and charged cases alike. This is small compared to the error in Eq. (5) for which the density matrix successfully corrects.

III. APPLICATION TO A REALISTIC CALCULATION: DANGLING BONDS IN Se

In the previous section we saw how the DM method can be used to effectively eliminate the interaction between the gap states on neighboring defects. In a realistic calculation, however, an added complication arises: The local basis orbitals (the ψ_A and ψ_B of the preceding section) are not known *a priori*. As we shall see shortly, this problem is easily overcome. It is then a simple matter to calculate the $\rho(r)$ via Eq. (16), and from ρ the usual Hartree and exchange-correlation potentials with which the next iteration is set up. When self-consistency is achieved, ρ is also used to calculate the total energy via the usual prescription of local-density theory.²

Let us consider a concrete example. Suppose we wish to investigate the different possible charge states (D^- , D^0 , D^+) of the dangling bond in selenium. A pair of dangling bonds can easily be made by creating a vacancy in crystalline (trigonal) Se; this vacancy structure can then be repeated in a superlattice configuration. With the correct choice of lattice vectors, it is easy to construct a supercell with one vacancy for every eight atoms along each chain, and with no two vacancies side-by-side on neighboring chains. Because all the Coulomb energies diverge unless the supercell is net neutral, we are restricted to the charge configurations $D^0 D^0$ and $D^- D^+$.

Each of the two defects has a dangling-bond gap state near midgap.³ When we diagonalize the Hamiltonian at a given k point, we obtain two eigenvectors ψ_1 and ψ_2 corresponding to the weakly bonding and antibonding combinations of these states. If we were really interested in modeling the vacancy in Se, we would doubly occupy the bonding orbital to get the true ground state:

$$n^H = \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix}. \quad (20a)$$

If we want to model *distant neutral* defects ($D^0 D^0$), we use

$$n^H = n^L = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (20b)$$

In both cases, the dangling bonds are each neutral.

If we want to model *distant charged defects* (D^-D^+), however, we need

$$n^L = \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix}. \quad (20c)$$

For the latter case, we need to know the 2×2 unitary transformation that connects the "local" basis functions ψ_A and ψ_B to the eigenstates ψ_1 and ψ_2 . That is, we need to "find" the ψ_A and ψ_B corresponding to the energy eigenstates of the isolated systems A and B .

To do so, we write the local state as a linear combination of the two eigenstates

$$\psi = \alpha_1 \psi_1 + \alpha_2 \psi_2, \quad (21)$$

and then require that ψ_A be given by the ψ which maximizes

$$\frac{\langle \psi | \hat{P} | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (22)$$

where \hat{P} is a difference of two projection operators

$$\hat{P} = \int_{\Omega_A} d\vec{r}' |\vec{r}'\rangle \langle \vec{r}'| - \int_{\Omega_B} d\vec{r}' |\vec{r}'\rangle \langle \vec{r}'|, \quad (23)$$

with the volumes Ω_A and Ω_B being, e.g., spheres of radius $1-2 \text{ \AA}$ centered about defects A and B , respectively. Similarly, ψ_B is defined to be the ψ which minimizes Eq. (22); in fact, the appropriate α 's are given by the eigenvectors

$$\sum_j P_{ij} \alpha_j = \lambda \alpha_i \quad (i, j = 1, 2), \quad (24)$$

of the matrix

$$P_{ij} = \langle \psi_i | \hat{P} | \psi_j \rangle. \quad (25)$$

Physically, ψ_A is that linear combination of ψ_1 and ψ_2 which has the most character on Ω_A and the least on Ω_B , and vice versa for ψ_B . As long as ψ_A and ψ_B are weakly overlapping states, the exact definition of ψ_A and ψ_B in terms of ψ_1 and ψ_2 will only be very weakly dependent upon the geometry of Ω_A and Ω_B .

This scheme provides a natural way to find the unitary transformation which connects the local and eigenstate basis; this must be done for each k point on each iteration. In a plane-wave calculation, the matrix elements P_{ij} are given by

$$P_{ij} = \sum_G P(\vec{G}) \rho_{ij}(-\vec{G}), \quad (26a)$$

$$P(\vec{r}) = \int_{\Omega_A} d\vec{r}' \delta(\vec{r} - \vec{r}') - \int_{\Omega_B} d\vec{r}' \delta(\vec{r} - \vec{r}'), \quad (26b)$$

$$\rho_{ij}(\vec{r}) = \psi_i^*(\vec{r}) \psi_j(\vec{r}). \quad (26c)$$

The Fourier transform of (26b) can be done analytically, while that of (26c) involves no more effort than is usual in constructing the charge density.

The total energy is evaluated in practice by summing the band-structure energy in the usual way except for the substitution of Eq. (11):

$$\sum_i \epsilon_i \rightarrow \text{tr}(\hat{n} \hat{H}) = \sum_i n_{ii}^H \epsilon_i. \quad (27)$$

The correction due to overcounting of Hartree and exchange-correlation terms is calculated from ρ in the usual way [see, e.g., Eq. (31)].

We have carried out this approach for the selenium defects D^0D^0 and D^-D^+ using a self-consistent pseudopotential approach. The nonlocal pseudopotential of Hamann, Schluter, and Chiang⁴ and the Wigner exchange correlation formula⁵ were employed. For illustrative purposes it is sufficient to use one special k point⁶ and cutoffs of 2.5 Ry and 8.33 Ry for the Hamiltonian and Lowdin⁷ basis sets, respectively.

The resulting charge densities for the defect states are plotted in Figs. 2(a) and 2(b), respectively. In the neutral case, we see that the dangling-bond p states of each defect are equally occupied. For D^-D^+ , however, it is clear that we have succeeded in transferring an entire electron from one defect state to the other. (Of course, much of this

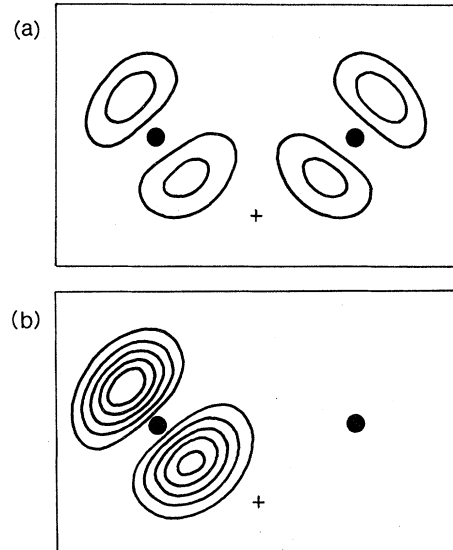


FIG. 2. Charge-density plots for the defect bands at a vacancy in Se. (a) D^0D^0 . (b) D^-D^+ . The plane of the plot contains the two defect sites (left and right) marked by solid circles, and vacancy site (bottom center) marked by the + sign. The contour interval is arbitrarily chosen.

charge is screened by other states in the system, so the defects do not really have the full charge of $\pm e$. This is to be expected considering the large dielectric constant of these materials.) It is now straightforward to obtain the Coulomb "correlation" energy $E(D^-D^+) - E(D^0D^0)$, for example, which we find to be 0.44 eV for this geometry. We should emphasize, however, that there are two classes of interdefect "interactions" which are *not* eliminated by using the DM method.

Firstly, there are the Coulomb interactions between charged defects. In the D^-D^+ example above, we must recognize that we are calculating properties of the D^- or D^+ in the electric field of other nearby defects, and that $E(D^-D^+)$ contains the Coulomb energy of the lattice of charges. In solids, these effects will be greatly reduced by dielectric screening.

Secondly, there are the overlap interactions typical of closed-shell systems, which are usually characterized as repulsion due to Pauli exclusion. As a somewhat artificial example, suppose we wished to model atomic bromine by applying the DM approach to the diatomic molecule Br_2 . The use of the DM approach will eliminate the strong bonding interaction, in which two holes are shared in a σ_p^* orbital. As a result, the DM version of Br_2 will behave like a pair of closed-shell, i.e., noble gas, atoms. The calculation of the overlap interaction has previously been extended to open-shell systems⁸; the interaction is found to be quite weak down to distances comparable to the molecular bond length. Note, however, that the fact that only two states near ϵ_f are included in the DM may give rise to a larger error in a few cases. For example, if one wished to model atomic sodium by applying the DM method to the diatomic molecule Na_2 , s - p hybridization would still give rise to substantial bonding despite the "filled s shell" character. For any realistic calculation, of course, it is the theorist's responsibility to control for the above effects, whether by trying larger and larger unit cells, or by compensating for the interaction by ap-

propriate modeling.

Finally, one might question whether the effects of Coulomb and exchange-correlation interactions within a given defect (i.e., the effects of self-consistency) are properly accounted for in the context of local-density theory. In the following section, we dispel this concern by developing the method in the local-density formalism.

IV. THE DENSITY MATRIX IN LOCAL-DENSITY THEORY

We begin with a brief review of local-density functional theory,² where one assumes the exchange-correlation energy of an N -electron system may be written as a local functional of the charge density. Thus the total electronic energy is

$$E[\rho] = T[\rho] + \int d\vec{r} \rho(\vec{r}) \{ V_{\text{ext}}(\vec{r}) + \epsilon_H[\rho(\vec{r})] + \epsilon_{\text{xc}}[\rho(\vec{r})] \}, \quad (28)$$

where T is the kinetic energy, V_{ext} the external potential (e.g., the ion pseudopotential), and ϵ_H and ϵ_{xc} are the Hartree and exchange-correlation energy functionals. The ground-state problem reduces to finding the ρ which minimizes E in Eq. (28); it is given by a self-consistent solution of

$$\bar{H} = T + V_{\text{ext}} + \mu_H(\rho) + \mu_{\text{xc}}(\rho), \quad (29a)$$

$$\bar{H}\psi_i = \epsilon_i\psi_i, \quad (29b)$$

$$\rho(\vec{r}) = \sum_i^N |\psi_i(\vec{r})|^2, \quad (29c)$$

where the potentials μ_H and μ_{xc} are related to ϵ_H and ϵ_{xc} via

$$\mu = \epsilon + \rho \frac{\partial \epsilon}{\partial \rho}, \quad (30)$$

and where the ψ_i are the N lowest eigenstates of the mean-field Hamiltonian \bar{H} . The total energy can then be recast as

$$E = \sum_i^N \epsilon_i + \int d\vec{r} \rho(\vec{r}) \{ \epsilon_H[\rho(\vec{r})] - \mu_H[\rho(\vec{r})] + \epsilon_{\text{xc}}[\rho(\vec{r})] - \mu_{\text{xc}}[\rho(\vec{r})] \}. \quad (31)$$

If we express ρ in terms of the density matrix as in Eq. (16), then the ground-state solution is given by

$$\hat{n} = \sum_i^N |\psi_i\rangle \langle \psi_i|. \quad (32)$$

In other words, \hat{n} and \bar{H} are simultaneously di-

agonalizable, with \hat{n} being simply a projection operator which projects onto the N -dimensional subspace spanned by the ψ_i .

Now in a traditional excited-state calculation,

$$\rho(\vec{r}) = \sum_i n_i |\psi_i(\vec{r})|^2, \quad (33)$$

i.e.,

$$\hat{n} = \sum_i n_i |\psi_i\rangle\langle\psi_i|. \quad (34)$$

Whereas one had $n_i = \theta(\epsilon_f - \epsilon_i)$ for the ground state, n_i can now be used to arbitrarily populate the excited eigenstates. However, one can only construct a *tiny fraction* of all excited-state configurations in this way, because one is still restricting \hat{n} to be simultaneously diagonalized with \bar{H} . The configuration A^-B^+ of Sec. II is a trivial example of an excited state which can only be reached by relaxing this restriction. The crux of our DM argument is to posit an *arbitrary* density operator, which can be diagonalized as

$$\hat{n} = \sum_j n_j |\phi_j\rangle\langle\phi_j|. \quad (35)$$

It corresponds to occupying each state ϕ_j with n_j electrons; in general the ϕ_j need *not* be eigenstates of \bar{H} . Moreover, we have an unambiguous prescription for calculating the total energy of such an excited state, i.e., Eqs. (35), (16), and (28).

In principle, this generalized DM approach allows us to study an infinite number of previously inaccessible excited-state configurations. In practice, however, the utility of this approach in the study of excitations is limited for two reasons.

Firstly, one is usually physically interested in the excited *eigenstates* of the true many-body system; in general it can be argued that this corresponds to occupying excited one-electron *eigenstates* in the local-density picture. Thus the traditional approach is usually adequate. (There are occasional exceptions; consider, for example, an electron excited into a localized state weakly coupled to the continuum. As long as the lifetime of such a resonance is long, it is physically correct to do the self-consistent solution with one electronic charge in the localized state, despite the fact that the traditional approach would give zero charge there.)

Secondly, the Hohenberg-Kohn theorem⁹ of density-functional theory states that the density-functional total energy is equal to the true many-body total energy *only* for the ground state of the system. Thus, the DM and the traditional approaches both lack the sanction of this theorem when applied to excited systems. We do not know how seriously to take this objection; it may turn out to be unimportant, particularly for the lowest excited state of a given symmetry.

Thus, the applicability of the generalized DM method to the study of excited systems is still to be explored. In this paper, our approach is different.

We restrict ourselves to the case of modeling noninteracting subsystems (e.g., defects or molecules) in terms of weakly interacting ones. The discussion which follows, and that of Secs. II and III, apply to this latter case.

Consider, then, two subsystems A and B with interaction V . In the limit of infinite separation ($V \rightarrow 0$), the application of the DM method on the entire system is *identical* to separate *ground-state* calculations on the isolated systems A and B . Thus the total energy is guaranteed to reflect the true many-body energy. Of course, this is true only insofar as the local density functional is a good approximation to the true density functional. For example, one might object that a straightforward calculation of the ground state of the entire AB system ought also to reflect the true many-body energy. For the special case of two identical defects (with degenerate levels), the result is indeed identical to the DM result. (We still assume infinite separation.) On the other hand, for two different defects, self-consistency will generally give rise to a charge transfer between A and B , which proceeds until $\epsilon_A = \epsilon_B$. Thus, the result is manifestly *different* from that of the DM. The extent to which the two approaches differ is one measure of the error introduced by the local-density approximation. In any case, the DM result is equally as valid as the "ground-state" result, and has the physical appeal of requiring integral occupation numbers of A and B , and allowing various charge states to be studied.

Suppose now that we introduce an interaction V between the states of the two defects in the DM approach. We show in the Appendix that the charge density ρ and the total energy E are *independent* of V , under a set of assumptions which are equivalent to neglecting the Coulomb and overlap effects discussed at the end of Sec. III. Thus for small but finite V , the DM approach gives us the "best" way to model the true many-body ground-state energy of the *isolated* subsystems A and B .

V. SUMMARY AND CONCLUSIONS

We have introduced a generalized method for specifying the occupations of the states in local-density theory by allowing "off-diagonal occupation numbers" (i.e., a general density matrix). We have shown that this technique has important applications for modeling noninteracting systems in terms of weakly interacting ones, and have present-

ed a sample calculation on defects in Se for illustrative purposes. Finally, we have demonstrated that the method has the same sanction as the usual local-density theory.

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APPENDIX

We formulate a generalized version of the DM method as follows. Consider an isolated subsystem A in its ground state, with eigenstates ϕ_i^A , Hamiltonian H_0^A , and a density matrix n_0^A which is diagonal in the ϕ_i^A representation. Now we allow A to interact with subsystem B (with eigenstates ϕ_i^B , Hamiltonian H_0^B , and density matrix n_0^B) and take the unperturbed $\{\phi_i^A \cup \phi_i^B\}$ to be our "local" basis. In this basis, we have

$$n_0 = \begin{pmatrix} n_0^A & 0 \\ 0 & n_0^B \end{pmatrix}, \quad (\text{A1})$$

in the DM method for the noninteracting case.

Now let A and B interact via

$$V = \alpha \begin{pmatrix} 0 & v \\ v^T & 0 \end{pmatrix}, \quad (\text{A2})$$

where α is a small parameter describing the strength of the interaction. In general, one would have block-diagonal as well as block-off-diagonal elements in Eq. (A2), and nonzero overlaps $\langle \phi_i^A | \phi_j^B \rangle$. As pointed out in Sec. III, however, the DM method does not aspire to eliminate Coulomb and closed-shell overlap interactions, and we will therefore assume a "pure bonding" interaction as in Eq. (A2).

In a traditional calculation of the ground state, we would vary n away from (A1) until the total energy

$$E = \text{tr}(nH), \quad (\text{A3})$$

given from

$$H = T + V_{\text{ext}} + \epsilon_H(\rho) + \epsilon_{\text{xc}}(\rho) + V, \quad (\text{A4})$$

is minimized. Suppose this occurs at n'_0 for $\alpha=0$;

then the driving force for an $n \neq n'_0$ at $\alpha \neq 0$ must come from the possibility of the new term

$$\text{tr}(nV) \quad (\text{A5})$$

lowering the total energy.

In the generalized DM approach, however, we require that n remain block diagonal

$$n = \begin{pmatrix} n^A & 0 \\ 0 & n^B \end{pmatrix}, \quad (\text{A6})$$

with

$$\begin{aligned} \text{tr}(n^A) &= N^A, \\ \text{tr}(n^B) &= N^B, \end{aligned} \quad (\text{A7})$$

fixed, while E is minimized. Thus, a variational principle still obtains. Within these constraints, n_0 itself minimizes E for $\alpha=0$. Now, however,

$$\text{tr}(nV) = 0, \quad (\text{A8})$$

because V is block-off-diagonal while n is block diagonal. Thus, within the new constraints (A6) and (A7), n_0 remains the solution even at nonzero α , and the total energy (and charge density) remain independent of α .

Physically speaking, without the DM constraint, eigenfunctions from subspace A pick up components in B to order $\delta\psi = O(\alpha)$, giving rise to $\delta E = O(\alpha^2)$ by the variational principle. The use of the DM method forbids this, so that E is independent of α .

Of course, the method as presented in Sec. III only includes two states (those in the vicinity of ϵ_f^A and ϵ_f^B) in the DM. In this case, eigenstates from below ϵ_f^A in A develop components from above ϵ_f^B in B , so that

$$\delta E = O(\alpha^2/E_g), \quad (\text{A9})$$

with E_g being the smallest energy denominator, i.e., the band gap. For most cases of interest, the error is negligible.

We turn finally to a discussion of the Hellman-Feynman forces. The momentum-space expression for the forces has been worked out previously for the usual ground-state case.¹⁰ The electronic contribution to the i th component of the force on atom μ can be written

$$\begin{aligned} F_i^\mu &= - \frac{dE}{dR_i^\mu} \\ &= - \left. \frac{\partial E}{\partial R_i^\mu} \right|_{n \text{ const}} - \frac{\partial E}{\partial n} \frac{\partial n}{\partial R_i^\mu}. \end{aligned} \quad (\text{A10})$$

The first term represents the explicit dependence of E upon R_l^μ , while the second represents the implicit dependence via n (i.e., via the wave functions). The fact that E is a variational minimum with

respect to the allowed n in the DM method implies $\partial E / \partial n = 0$; i.e., the second term in Eq. (A10) vanishes as usual. The explicit dependence then gives

$$\bar{F}^\mu = -i\Omega_{\text{at}} \sum_{\vec{k} \vec{m} \vec{m}' \vec{G} \vec{G}'} (\vec{G}' - \vec{G}) \exp[i(\vec{G}' - \vec{G}) \cdot \vec{R}^\mu] n_{mm'}^H \psi_m^*(\vec{k} + \vec{G}) \psi_m(\vec{k} + \vec{G}') U_{\text{ps}}(\vec{k} + \vec{G}, \vec{k} + \vec{G}'), \quad (\text{A11})$$

where m and m' are band indices and U_{ps} is an arbitrary (e.g., nonlocal) ion pseudopotential. Equation (A11) reduces to the usual ground-state expression¹⁰ in the case where the density matrix is diagonal in the basis of energy eigenstates ψ_m .

¹Although the formalism is similar, this is not the statistical density matrix. Rather, it is an effective one-electron density matrix used to specify the occupied states of a many-Fermion system. See J. M. Ziman, *Elements of Advanced Quantum Theory* (Cambridge University Press, London, 1969), p. 140ff.

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