

Quantum-mechanical cluster-lattice interaction in crystal simulation: Hartree-Fock method

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The problem of describing quantum mechanically a region of interest in an otherwise extended lattice is discussed for nonmetallic solids. A localizing potential to accomplish this is described, and its implications for the total-energy algorithm are analyzed. A spurious tunneling effect that may arise with a finite embedding lattice is also discussed.

I. INTRODUCTION

Lattice defects in crystalline materials, often in combinations that are difficult to resolve experimentally, determine many technologically important properties. Reliable computer simulation of such defects is therefore of potential value, and can be expected to contribute to fundamental understanding of the physical processes that determine the structure and properties of these materials. For point defects, an attractive approach is to use quantum mechanics to describe the response of the region near the defect to the defect and to embed this region in a potential similar to that of a perfect lattice. The lattice response of the embedding crystal lattice may then be described in terms of a much simpler model, applicable to a weakly perturbed perfect lattice, provided a reliable model of this type exists. In fact, such models do exist, or may be expected to emerge, for ionic, molecular, covalent, and simple-metallic crystals. In the present work, we refer specifically to nonmetals. In many of these materials the shell model,¹ based on classical point charges and masses, interacting by simply parametrized potentials, has been successful in correlating perfect-lattice equilibrium configurations, and static and dynamic elastic and dielectric properties within the harmonic approximation.² We shall therefore think of the embedding lattice in terms of the shell model. The region about the defect called the cluster will be referred to in terms of the unrestricted Hartree-Fock self-consistent-field approximation,³ augmented by explicit correlation corrections, although the main points apply to any approach based on the one-particle density, including the density-functional formulation.⁴ In this paper we consider only the independent-particle aspects.

For a cluster embedded in a classical lattice, special care must be taken to ensure that mathematical and physical consistency are maintained. This topic has been discussed by Kunz and Klein,⁵ who also introduced a formal procedure based on localizing potentials to deal with the short-range quantum-mechanical cluster-lattice interaction. The lowest-order term appropriate for an ionic-crystal was given by Kunz and Klein. The present work at the self-consistent-field level is an extension of

that of Kunz and Klein. In Sec. II the motivation and derivation of the Kunz-Klein localizing potential (KKLP) is given, and a specific implementation is described, which is believed useful for nonmetals.

Simulation of an infinite lattice containing a point defect represented by a cluster may be carried out by minimizing the total energy with respect to parameters that define the lattice configuration, including the defect. For shell-model ions, the configuration parameters are core and shell positions. For a cluster in the Hartree-Fock approximation they are variational parameters of the electronic wave function, and the nuclear positions. The one-electron Hartree-Fock functions are frequently based⁶ on a linear combination of atomic-type orbitals centered on ionic and other suitable sites, consisting of spherical harmonics with Gaussian radial dependences of given ranges. The variational parameters are then the linear coefficients of these atomic orbitals, and are obtained by matrix methods. States other than ground states may be analyzed by applying symmetry constraints to the calculation. Embedded molecular clusters representing segments of a perfect lattice may also be studied, and can provide a valuable test of the physical validity of the many-electron approximation being used.

The total-energy-minimization procedure described above is a practical proposition, and is, in fact, implemented in a general, user-friendly program, named ICECAP,⁷ for arbitrary host lattice, and for arbitrary point-defect composition and configuration. Recent applications⁸ of ICECAP, incorporating the KKLP, to color centers and to perfect-lattice clusters are demonstrating its versatility, and show that calculations in which lattice configuration and defect structure are simultaneously self-consistent are possible. Since the KKLP is based on a modified form of the Fock equation, the relationship of the resulting energy eigenvalues to the many-electron total energy is different from that arising from the original Fock equation. This point, and some practical points in solving the resulting equations are dealt with in Sec. III.^{9,10} These points are not considered in the original KKLP report or in subsequent work.

In Sec. IV, a spurious tunneling effect is described that may arise if the Coulomb sum, or the addition of short-

range interaction with the KKL P , are limited to too small a set of embedding-lattice ions.

II. KKL P

In this section we begin by relating the problem of a small cluster in the Hartree-Fock approximation, containing N_A electrons, to the problem of the large crystal, containing N electrons. We then note that the cluster-Fock equation depends in part on occupied states of the embedding lattice. This dependence, in our formalism, is due to a subsidiary condition termed the Kunz-Klein localizing potential (KKL P). In the KKL P , this potential is chosen so that it cancels out the short-range part of the potential due to the lattice ions as seen by cluster electrons in so far as possible. It is in this sense that the KKL P is a localizing potential, because the cluster electrons end up seeing lattice ions as weak perturbing potentials and lattice periodicity is interrupted.

The short-range potential is evaluated once and for all for a given crystal lattice by applying the same localization condition to each ionic species in a perfect-lattice calculation. The use of a perfect-lattice short-range potential with a defect cluster is consistent with the idea that the cluster should contain all significant deviations from perfect-lattice electronic structure. Consider a large crystal containing N electrons. The N -electron Hamiltonian is

$$H = - \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{I=1}^N \sum_I \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I>J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} .$$

We obtain the Bohr-Rydberg atomic units used throughout this work by setting $e^2=2$, and $\hbar^2/2m=1$. We use a single Slater determinant to approximate solutions to the Hamiltonian and, the one-electron functions of the Slater determinant satisfy the Fock equation:

$$F(\underline{r})\psi_k(\underline{r}) = \epsilon_k \psi_k(\underline{r}), \quad k=1,2,\dots,N \quad (2.1)$$

where the Fock operator F is

$$F(\underline{r}) = -\nabla^2 - 2 \sum_j Z_j |\mathbf{r} - \mathbf{R}_j|^{-1} + 2 \int d\underline{r}' |\mathbf{r} - \mathbf{r}'|^{-1} \times \int d\underline{y} \delta(\underline{y} - \underline{r}') [1 - P(\underline{r}, \underline{y})] \rho(\underline{r}', \underline{y}), \quad (2.2)$$

$$\rho(\underline{r}', \underline{y}) = \sum_{k'=1}^N \psi_{k'}(\underline{r}') \psi_{k'}^*(\underline{y}), \quad (2.3)$$

where $\underline{r} \equiv (\mathbf{r}, s)$, \mathbf{r} is position and s is spin, \mathbf{R}_j and Z_j are nuclear positions and charges, and $P(\underline{r}, \underline{y})$ is the electron pairwise interchange operator. In the unrestricted Hartree-Fock approximation (UHF), ψ_k is a spin eigenstate only, and not an eigenstate of symmetry. In Eq. (2.3), ρ is the Fock-Dirac, one-particle density. Now consider a cluster A within the crystal, having N_A electrons. These N_A electrons are assumed to occupy a manifold of

states, denoted $k(A)$, localized in the cluster's vicinity, and chosen so that they will be adequate to describe physical properties, that are localized in and around the cluster. In practice, we may need to calculate initial and final states of a defect process such as optical absorption or diffusion activation. All spectroscopic details are obtained from total-energy considerations. The occupied states $k(A)$ satisfy a Fock equation that is obtainable by unitary transformation from the orthonormal set ψ_k of Eq. (2.1) (which becomes complete in the limit $N \rightarrow \infty$), to a new orthogonal basis, some of whose elements span the cluster manifold, including the N_A occupied states $k(A)$. The remaining $N_B = (N - N_A)$ new occupied basis functions, denoted $k(B)$, are orthogonal to the manifold $k(A)$. Thus

$$(F_A + U_A)\psi_k = \epsilon_k \psi_k, \quad k=1,2,\dots,N_A \quad (2.4)$$

where F_A is that part of F , Eqs. (2.1) and (2.2), that involves nuclei and electrons in the cluster, and V_A is due to those N_B electrons and the nuclei in the environment.⁵ Thus

$$F = F_A + V_A. \quad (2.5)$$

In Eq. (2.4), U_A clearly depends on $k(B)$. Now the purpose of using the cluster is so that we will not have to solve for the states $k(B)$ of the embedding lattice simultaneously with the states $k(A)$ of the cluster. The manifold $k(B)$, however, in general, need not be orthogonal to the occupied cluster manifold $k(A)$. In fact, we wish to maintain the full physical detail of our presumably careful choice of both cluster and lattice basis sets and yet incorporate properly this possible lack of orthogonality. In prior cluster considerations, the possibility of exploiting this degree of freedom was not used.

Now in most nonmetals, the electronic density of $k(B)$ is particularly well localized about lattice nuclei or possibly bond centers. In fact, in zeroth order, the lattice potential U_A has been thought of as a Madelung potential, arising from point-charge ions, as was shown by Kunz and Klein

$$\nabla_A^M = -2 \sum_{j(B)} I_j |\mathbf{r} - \mathbf{R}_j|^{-1}, \quad (2.6)$$

where $I_j \equiv Z_j - N_j$ is the ionic charge of ion j , and N_j is the number of electrons associated with ion j . The remainder of U_A is the short-range part V_A^S , arising from the quantum-mechanical nature of the electrons. Thus

$$U_A = V_A^M + V_A^S, \quad (2.7)$$

$$V_A^S = -2 \sum_{j(B)} N_j |\mathbf{r} - \mathbf{R}_j|^{-1} + 2 \int d\underline{r}' |\mathbf{r} - \mathbf{r}'|^{-1} \times \int d\underline{y} \delta(\underline{y} - \underline{r}') [1 - P(\underline{r}, \underline{y})] \rho_B(\underline{r}', \underline{y}). \quad (2.8)$$

A subsidiary condition can now be applied to the cluster-Fock equation (2.4) to modify the localization of V_A^S relative to the cluster. The term V_A^S was not explicit-

ly considered in prior work.

The procedure for applying a subsidiary condition to the Fock equation has been given generally by Gilbert.¹¹ It is based on the fact that the Fock-Dirac one-particle density operator ρ_A is a projection operator onto the manifold of occupied states $k(A)$:

$$\rho_A = \sum_{k'=1}^{N_A} |k'\rangle\langle k'|, \quad (2.9)$$

where $|k'\rangle$ is the state vector corresponding to orbital $\psi_{k'}(\underline{r})$. It follows that, for an arbitrary one-particle operator W

$$\rho_A W \rho_A |k\rangle = \begin{cases} \rho_A W |k\rangle & \text{if } k \text{ is occupied,} \\ 0 & \text{if } k \text{ is unoccupied.} \end{cases} \quad (2.10)$$

Using the theory due to Gilbert,¹¹ one may add Eq. (2.10) to Eq. (2.4) and obtain a modified Fock equation which leaves the total energy unchanged:

$$(F_A + U_A + \rho_A W \rho_A) |k\rangle = \pi_k |k\rangle, \quad k = 1, 2, \dots, N_A. \quad (2.11)$$

Unoccupied (virtual) orbitals $|k'\rangle$ are unaffected by the procedure.

It is not necessary to use the same W for all orbitals. However, if one changes W , a nonorthogonal solution set emerges.

Kunz and Klein⁵ have chosen $W = -\rho_A V_A^S \rho_A$ and argued that it would cancel the V_A^S term, yielding

$$(F_A + V_A^M) |k\rangle = \pi_k |k\rangle. \quad (2.12)$$

The term $-\rho_A V_A^S$ is called the KKLP. In this work both V_A^S and the KKLP receive explicit consideration. Thus the localizing effect is that KKLP selects an occupied cluster manifold $k(A)$ spanned by functions that see the lattice ions as weakly perturbed point charges, expressed by V_A^M , while leaving virtual cluster states to see the unmodified short-range lattice potential.

In a cluster calculation it is assumed that significant deviations from perfect-lattice electronic structure are included in the cluster, and therefore the electronic structure of the embedding lattice should be adequately represented in Eq. (2.11) by a perfect-lattice form of V_A^S . Now, in practice, we associate a set of orbitals with each ionic species in the lattice, so V_A^S , Eq. (2.8), may be written as a sum over lattice sites $j(B)$:

$$\rho_B = \sum_{j(B)} \rho_j, \quad \rho_j = \sum_{k'(j)} \psi_{k'}(\underline{r}) \psi_{k'}^*(\underline{y}), \quad (2.13)$$

where $k'(j)$ labels an orbital on site j . Thus the contribution to V_A^S from a given ionic species in a given perfect-lattice crystal can be determined by separate calculations that treat single ions of different species as the "cluster," surrounded by KKLP ions. The separate calculations can be iterated together to self-consistency, replacing an arbitrary set of initial lattice-site states in V_A^S by the cluster solutions for corresponding ions, and so on. This procedure has been described by Kunz.¹² The resulting contribution to V_A^S from each species is fitted to a set of

Gaussians using a fitting procedure due to Keegstra.¹³ Then the KKLP becomes

$$\rho_A V_A^S \rho_A = \sum_{\substack{k(A) \\ k'(A)}} \psi_k(\underline{r}) \psi_{k'}^*(\underline{r}) \int d\underline{r}' \psi_{k'}^*(\underline{r}') V_A^S(\underline{r}') \psi_k(\underline{r}'), \quad (2.14)$$

in which the integrals are straightforward for a Gaussian basis. Thus one has obtained both the KKLP and V_A^S in a computationally convenient form. Thus we now solve

$$(F_A + V_A^M + V_A^S - \rho_A V_A^S \rho_A) |k\rangle = \pi_k |k\rangle. \quad (2.15)$$

What is substantially new here is easy to describe. In the original paper presenting a rigorous approach to cluster formalisms, by Kunz and Klein,⁴ a basic extension of the concept of chemical building blocks for an extended system was made. This extension provides the formal base used here. However, specific development of a general computational formalism was not undertaken. The principal effect of localization was argued, on formal grounds, to be the embedding of the cluster in a point-ion lattice. This has proven to be useful for some problems.¹⁰ Clearly, however, the use of an embedding point-ion field limits the usefulness to ionic solids alone, and to ionic systems in which orbital overlaps are negligible at that. Our experiences with energy-band theory⁹ indicates that alkali halides are described well in this way, but not oxides.

This contention is trivially seen by following two series of calculations contained in Ref. 9. The first is the calculation for NaCl. Initially, the local orbitals were reported for NaCl by Kunz in 1971 and used to obtain NaCl energy bands by Lipari and Kunz. These local orbitals were found using a simple single-center localization rather than a full KKLP procedure. This procedure was fully criticized by Gilbert and Kunz. Later Kunz (1982) used the full, general KKLP multicenter localization procedure to study the electronic structure of 12 alkali halides including NaCl. The essential band-structure features were unchanged between the approximate localization procedure and the general one. Furthermore, the band results for NaCl were tested by Himpfel and Steinman in 1978 using angle-resolved photoemission. These tests established the essential correctness of the NaCl results. Importantly, the initial calculations preceded the measurement by several years. Thus by this measure the alkali halides are rather insensitive to boundary details. Such has not been the case for oxides. Jennison and Kunz performed a calculation for TiO in 1977 using single-center localization, a prescription slightly better than simple point-ion field termination, and failed to obtain accurate band results for TiO due to the failure of the O^{2-} orbitals to properly localize. This was discussed in the 1982 alkali halide paper by Kunz. Thus one finds rather different success for alkali halides and oxides. Even for better localized oxides such as NiO, use of simple point-ion fields around clusters yields qualitative accuracy, but quantitative results are not as good as for alkali halides. This is very well presented in the work of Grunes *et al.*

The present formulation imposes no such limitation. It simply assumes that there is some distance away from a defect such that the first-order density matrix for atoms, ion, and molecules (building blocks) located farther from the defect than this distance are, in the Hartree-Fock limit, the same as for the perfect system. This assumption is certainly reasonable, and conventional methods can be used to obtain the solution, just as in the energy-band problem.⁹ The method we use here is the most recently developed and includes a multicenter approach to localization. It does not depend on smallness of interatomic overlap or systematic elimination of small but persistent diffuse orbital basis functions as did some early approaches to obtaining local orbitals. In this regard the solution for the distant region is obtained to the state of the art. Having obtained this solution the long- and short-range parts of the potential surrounding the cluster are known.

We now need a correct algorithm for the total energy of the embedded cluster, and this is given in Sec. III. In addition, for nonionic solids, such as rare-gas crystals or molecular solids, the presence of van der Waals forces necessitates the inclusion of correlation effects. How this is done rigorously in embedded-cluster calculations has not been given in the literature, and is covered in a separate work. The unrestricted Hartree-Fock (UHF) solutions form a basis for the correlation treatment. Finally, we note that the UHF eigensolution need not be an eigenfunction of spin. For spectroscopy this is potentially a problem, but symmetry projections onto spin eigenfunctions are trivially accomplished.¹⁰

III. TOTAL ENERGY

Let us examine how the total energy of an infinite crystal containing a molecular cluster is related to the modified cluster-Fock equation (2.11). We first note the well-known result that from the original cluster-Fock equation (2.4) the total energy E is

$$E = \bar{E} + V_I, \quad (3.1)$$

where V_I is the classical part of the energy:

$$\begin{aligned} V_I = & \sum_{j(A) > j'(A)} 2Z_j Z_{j'} |\mathbf{R}_j - \mathbf{R}_{j'}|^{-1} \\ & + \sum_{j(A), j'(B)} 2Z_j I_{j'} |\mathbf{R}_j - \mathbf{R}_{j'}|^{-1} \\ & + \sum_{j(B) > j'(B)} [2I_j I_{j'} |\mathbf{R}_j - \mathbf{R}_{j'}|^{-1} + V_B^S(\mathbf{R}_j, \mathbf{R}_{j'})], \end{aligned} \quad (3.2)$$

where V_B^S is the pairwise short-range ion-ion interaction energy, with other terms representing nuclear-nuclear, nuclear-ion, and ion-ion Coulomb interactions for nuclei of the cluster and ions of the lattice. In Eq. (3.1), \bar{E} is the many-electron energy of the cluster in the Hartree-Fock approximation

$$\bar{E} = \frac{1}{2} \sum_{k(A)=1}^{N_A} (\epsilon_k + f_k), \quad (3.3)$$

where f_k is the one-particle part of ϵ_k :

$$f_k = \left\langle k \left| \left[-\nabla^2 - 2 \sum_{j(A)} Z_j |\mathbf{r} - \mathbf{R}_j|^{-1} + U_A \right] \right| k \right\rangle. \quad (3.4)$$

Note that

$$\epsilon_k = f_k + \sum_{k'(A)} \langle k, k' | \{ |\mathbf{r} - \mathbf{r}'|^{-1} [1 - P(\underline{r}, \underline{r}')] \} | k, k' \rangle. \quad (3.5)$$

For U_A we use Eq. (2.7), $U_A = V_A^M + V_A^S$, with V_A^S determined as described in Sec. II. Now between Eq. (2.4) for ϵ_k and Eq. (2.11) for π_k , there has been a unitary transformation in the cluster manifold $k(A)$, so ψ_k in Eq. (2.4) does not correspond to $|k\rangle$ in Eq. (2.11). Nevertheless, the trace is invariant, so it follows that

$$\begin{aligned} \sum_{k(A)} \epsilon_k &= \sum_{k(A)} \langle k | (F_A + U_A) | k \rangle \\ &= \sum_{k(A)} (\pi_k + \langle k | V_A^S | k \rangle), \end{aligned} \quad (3.6)$$

where we have used the projection property of ρ_A on $k(A)$. By combining Eqs. (3.1)–(3.6) we have a tractable means of evaluating E in terms of the eigenvalues π_k , and other quantities that will have been evaluated in the course of solving Eq. (2.11).

These results may also be derived as an approximation, starting from the N -electron description of the whole crystal, Eqs. (2.1)–(2.3). The derivation is outlined in the Appendix. This raises another aspect of cluster-lattice consistency, namely the question of whether the quantum-mechanical and shell-model descriptions of perfect-lattice features (in this case short-range interionic potentials) are compatible. Some details of this problem have been discussed formally by Harding *et al.*,⁷ and some preliminary results have been reported,^{8,14} but much remains to be done.

IV. FINITE LATTICE

In this section we discuss the practical question of how far into the embedding lattice one need carry the localization procedure.

Any Madelung sum can be carried to infinity using Ewald's summation method,¹⁵ but if that is not done, certain precautions should be observed. First, a finite summation may get the Coulomb potential at the origin accurately, but unless quite a large number of ions is included it will not be accurate throughout the cluster region. For example, 500 ions give an error of 0.1 eV at a distance of two nearest-neighbor spacings from the origin in MgO.¹⁶ Second, if the finite set of ions has a net charge, the possibility of spurious tunneling-type UHF solutions arises. This can happen as follows. Suppose the UHF cluster is bound by a potential well in the infinite crystal. Now suppose only a finite number of ions is used, in an approximately spherical region centered on the cluster. If these ions have a net positive charge, it will all reside at or near their outer boundary, and will be uniformly dis-

tributed. In a continuum approximation, the potential is simply raised uniformly within the finite crystal by this uniform spherical surface charge, and tails off to zero at infinity outside the sphere according to Coulomb's law. The resulting combination of elevated potential well and Coulomb tail now represents a potential barrier of finite thickness for states that were previously bound inside the well. Electrons in these positive-energy states can tunnel out, and will do so if represented by basis sets of sufficient range, such as may seem variationally appropriate, particularly for excited and/or weakly bound states. For example, with 2000 ions, as in the present version of ICECAP, the boundary radius is about eight nearest-neighbor spacings. Thus basis functions that either singly or in combination have significant amplitude at this distance or greater cannot be used with confidence. Ensuring that the set of ions is uncharged, as with the Evjen method,¹⁷ will overcome this problem.

A similar effect can occur with the KKL_P which inevitably extends short-range interactions only to a finite distance. One can see this if V_A^S is thought of as an effective positive potential due to Pauli repulsion. Then, in the infinite crystal it extends to infinity, but in practice it extends only to a finite distance, beyond which there is a potential drop. The result is an effective potential barrier of finite thickness through which spurious tunneling may occur. In the following paper extensions to include correlation corrections and also results for the Cu impurity in NaF are given.

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APPENDIX

In this appendix we consider a crystal containing N electrons, divided into cluster (A) and embedding (B) regions, with N_A electrons in the cluster, occupying a manifold $k(A)$, and $N_B = (N - N_A)$ electrons in the embedding lattice, occupying manifold $k(B)$. The total energy E_N is

$$E_N = \sum_{k(A+B)} \langle k | f_0 | k \rangle + \frac{1}{2} \sum'_{k,k'(A+B)} \langle kk' | g(1-P) | kk' \rangle + V_{nn}, \quad (\text{A1})$$

where

$$f_0 = \left[-\nabla^2 - 2 \sum_{j(A+B)} Z_j | \mathbf{r} - \mathbf{R}_j |^{-1} \right], \quad (\text{A2})$$

$$g = 2 | \mathbf{r} - \mathbf{r}' |^{-1}, \quad (\text{A3})$$

$$V_{nn} = \sum_{j > j'(A+B)} 2Z_j Z_{j'} | \mathbf{R}_j - \mathbf{R}_{j'} |^{-1}. \quad (\text{A4})$$

To obtain the cluster states we rewrite Eq. (2.4) using Eqs. (2.5), (2.6), (A2), and (A3):

$$\left\{ f_0 + \sum_{k'(A+B)} \langle k' | g(1-P) | k' \rangle \right\} | k \rangle = \epsilon_k | k \rangle, \quad k = 1, 2, \dots, N_A. \quad (\text{A5})$$

As in Eq. (3.3), we introduce the cluster-electron energy \bar{E} . Now from Eq. (A5),

$$\epsilon_k = \langle k | f_0 | k \rangle + \sum_{k'(A+B)} \langle kk' | g(1-P) | kk' \rangle. \quad (\text{A6})$$

From Eqs. (3.4) and (2.6),

$$f_k = \langle k | f_0 | k \rangle + \sum_{k'(B)} \langle kk' | g(1-P) | kk' \rangle. \quad (\text{A7})$$

Thus from Eqs. (A6) and (A7):

$$\begin{aligned} \bar{E} &= \frac{1}{2} \sum_{k(A)} (\epsilon_k + f_k) \\ &= \sum_{k(A)} \left\{ \langle k | f_0 | k \rangle + \sum_{k'(B)} \langle kk' | g(1-P) | kk' \rangle \right. \\ &\quad \left. + \frac{1}{2} \sum'_{k'(A)} \langle kk' | g(1-P) | kk' \rangle \right\}. \end{aligned} \quad (\text{A8})$$

Identifying corresponding terms in Eq. (A1), we obtain

$$\begin{aligned} E_N &= \bar{E} + \sum_{k(B)} \langle k | f_0 | k \rangle \\ &\quad + \frac{1}{2} \sum'_{k,k'(B)} \langle kk' | g(1-P) | kk' \rangle + V_{nn}. \end{aligned} \quad (\text{A9})$$

Finally, we wish to identify terms in V_{nn} , Eq. (A9), with terms in V_I , Eqs. (3.1) and (3.2). Now,

$$\begin{aligned} \sum_{k(B)} \langle k | f_0 | k \rangle &= \sum_{k(B)} \langle k | -\nabla^2 | k \rangle \\ &\quad - 2 \sum_{k(B)} \sum_{j(A+B)} Z_j \langle k | | \mathbf{r} - \mathbf{R}_j |^{-1} | k \rangle. \end{aligned} \quad (\text{A10})$$

If we imagine that $k(B)$ consists of orthogonal basis functions $k(j)$ associated with individual ions $j(B)$, then in Eq. (A10)

$$\begin{aligned} \sum_{k(B)} \sum_{j(A+B)} Z_j \langle k | | \mathbf{r} - \mathbf{R}_j |^{-1} | k \rangle \\ = \sum_{j(B)} \sum_{j'(A+B)} \sum_{k(j')} \langle k(j') | | \mathbf{r} - \mathbf{R}_j |^{-1} | k(j') \rangle. \end{aligned} \quad (\text{A11})$$

We now approximate the right-hand side of Eq. (A11) by

$$\sum_{j(A+B)} \sum_{j'(B)} N_{j'} | \mathbf{R}_{j'} - \mathbf{R}_j |^{-1}, \quad (\text{A12})$$

where $N_{j'}$ is the number of electrons on ion j' . Similarly, using Eq. (A3), we assume that in Eq. (A9)

$$\frac{1}{2} \sum'_{k,k'(B)} \langle kk' | g | kk' \rangle \approx \sum'_{j,j'(B)} N_j N_{j'} | \mathbf{R}_j - \mathbf{R}_{j'} |^{-1}. \quad (\text{A13})$$

Combining Eqs. (A12) and (A13) with V_{nn} , Eq. (A4), and using the relation $Z_j = (I_j + N_j)$ for $j(B)$, we reduce Eq. (A9) to the form of Eqs. (3.1) and (3.2), provided we identify

$$\frac{1}{2} \sum'_{j,j'(B)} V_B^S(\mathbf{R}_j, \mathbf{R}_{j'}) = \frac{1}{2} \sum'_{k,k'(B)} \langle kk' | gP | kk' \rangle, \quad (\text{A14})$$

where $\sum'_{kk'(B)}$ omits terms in which $k(B)$ are for the same ion. The identification is clear if we think in terms of the basis set $k(j)$, so that

$$\sum_{k(B)} = \sum_{j(B)} \sum_{k(j)}.$$

Equation (A14) represents an approximation in which ion-ion short-range interaction arises only from ex-

change. The resultant form of Eq. (A9) is therefore the same as that of Eq. (3.1), except that it has an extra quantum-mechanical ionic self-energy consisting of electronic kinetic energy from Eq. (A10) and intraionic exchange, left over from Eq. (A14). Thus the self-energy is

$$\sum_{j(B)} \left[\sum_{k(j)} \langle k(j) | -\nabla^2 | k(j) \rangle + \frac{1}{2} \sum_{k,k'(j)} \langle k(j)k'(j) | gP | k(j)k'(j) \rangle \right]. \quad (\text{A15})$$

In practice, where the functions $k(j)$ with $j(B)$ are fixed, this does not contribute to interionic short-range interaction.

¹B. G. Dick, Jr., and A. W. Overhauser, *Phys. Rev.* **112**, 90 (1958); see also, for example, W. Cochran, *The Dynamics of Atoms in Crystals* (Arnold, London, 1973).

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