The matrix elements for the [111] defect are then (neglecting small contributions to the off-diagonal elements)

$$H_{11}=H_{77}=-\sigma_{12}+\sigma_{13}-\sigma_{23}\ ,\quad H_{22}=H_{88}=\sigma_{12}+\sigma_{13}+\sigma_{23}\ ,$$

$$H_{33}=H_{55}=-\sigma_{12}-\sigma_{13}+\sigma_{23}\ ,\quad H_{44}=H_{66}=\sigma_{12}-\sigma_{13}-\sigma_{23}\ .$$

All elements are multiplied by $\frac{2}{3}(\lambda_2-\lambda_1)$ and an integration factor which is approximately equal to unity.

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Electronic Polarons in Nonmetals*

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We use the techniques of perturbation theory and the electronic polaron to classify and obtain explicit formulas for electronic correlation in nonmetals. We consider explicitly the case in which the highest valence band is p type and the lowest conduction band is s type or vice versa, a situation which holds for all rare-gas solids, alkali halides, and most semiconductors of the types II-VI and III-V. We consider the case of an electron in a filled band as well as that of an electron in an otherwise empty band. In the case of the electron in an otherwise empty band our formulas are the expression found previously by Inoue, Mahutte, and Wang. Numerical results are presented for electrons both in occupied and otherwise empty bands for a number of crystals.

I. INTRODUCTION

The theory of the electronic properties of nonmetallic solids has been extensively investigated in recent years. Considerable progress has been made in understanding the electronic structure of rare-gas solids,[1] alkali halides,[2] and elemental and compound semiconductors[3] from *ab initio* calculations. It is seen that, if one adopts the Hartree-Fock point of view, considerable errors are introduced into calculations of such properties as optical band gaps.[4] There have been introduced two practical ways of including the effects of electron-electron correlation into energy-band calculations. In the first of these, due to Fowler,[4] one treats the conduction electron or valence hole as a static point charge. This formalism has the defect that dispersion in the correlation energy is neglected. The second formalism is due to Hedin[5] and was used by Brinkman[6] for silicon and by Lipari for rare-gas solids[1] and later by the author and Lipari for studies of NaCl, NaBr, and KCl.[2] This approach has two defects. One is that the theory is only useful for cases where the atomic subshells are completely occupied; hence in Si, Brinkman is unable to treat the correlation between valence states and the conduction electron correctly.[6] The second difficulty is a numerical one. In this formalism, it is necessary to perform a Hartree-Fock band-structure calculation first, and then one obtains from this parameters which define the $\vec{k}$-dependent dielectric function; finally one must resolve the entire band-structure problem using the $\vec{k}$-dependent dielectric function and the nonlocal self-energy operator. This method ignores correlation corrections for the core electrons.

There is a third formalism available for studying electron-electron correlations. This is the electron-polaron method introduced by Toyozawa.[7] This method has recently been used to compute correlation corrections for electrons at the bottom of the conduction band of several alkali-halide crystals by Inoue, Mahutte, and Wang.[8] This method has the disadvantage of having been developed for studies of conduction electrons alone and is not totally useful in that it neglects the correlation properties of the occupied levels.

These methods predict that the effect of electron-electron correlation is large. In fact, the effect upon the conduction electrons in a typical alkali halide is to alter the energy of the conduction band by several electron volts.

In this paper, we present a formal analysis of the problem of correlation in nonmetals using perturbation theory. This method has been thoroughly discussed by Sinanoğlu[9] and Nesbet[10] for studies of atomic or molecular structure. We define approximate pair correlations for the system and we use some of the results of Allen, Clementi, and Gladney[11] to simplify the resulting expressions. We then evaluate these expressions using the electron-polaron technique of Toyozawa[7] by second-order perturbation theory[8] for both the case of an electron in an otherwise empty band and for the case of a hole in an otherwise full band. The case of an electron in an otherwise empty band is exactly the same case treated by Toyozawa.[7] Finally, a series of numerical calculations are performed for both electrons and holes in a number of crystals. It is seen that the results are in fair agreement with those obtained by previous calculations.

II. FORMAL ANALYSIS

We wish to proceed as follows: We will include only that part of the electron-electron correlation which is included in terms of simple single-particle excitations and two-particle excitations. We will follow Toyozawa in assuming that the valence electrons are mostly responsible for the observed polarization properties.[7] We shall obtain our final results by means of second-order perturbation theory, and we shall neglect all correlations between electrons and the crystal lattice. We use nonrelativistic Schrödinger theory, and our Hamiltonian is

$$H=\sum_i\left[-\nabla_i^2-2\sum_i\left(Z_I/|\vec{R}_{Ii}|\right)+\sum_j{}'\left(1/|\vec{r}_{ij}|\right)\right] \quad . \tag{1}$$

H is in rydberg units; Z_I is the atomic number of the Ith nucleus, which is separated by $\vec{R}_{Ii}$ from the ith electron, and $\vec{r}_{ij}$ is the separation of the ith and jth electrons. The nuclei are assumed to be frozen into position. We desire to have approximate eigenvalues for H of Eq. (1). Thus, we wish to approximate the solution

$$H^{(N)}\psi_i^{(N)}(\vec{r}_1,\ \ldots,\ \vec{r}_N)=E_i^{(N)}\psi_i^{(N)} \quad . \tag{2}$$

Here the superscript refers to the number of electrons in the system and the subscript to the pertinent quantum numbers. In the future the subscript 0 refers to the ground state. If we ionize the system we will always order things so that the electron in the Nth orbital is removed, for the sake of convenience.

We wish to define an approximate process for constructing $\psi^{(N)}$ out of an expansion set of Slater determinants. Let us assume we have solved for the ground state of $H^{(N)}$ in the Hartree-Fock limit. We further assume this ground state to be nondegenerate. This is usually the case for a simple nonmetalic crystal. Thus the various bands are either completely filled or empty in the ground state. This produces a single Slater determinant $\psi_0^{(N)0}(\vec{r}_1,\ \ldots,\ \vec{r}_N)$ which has an energy E^0 and is

$$\psi_0^{(N)0}(\vec{r}_1,\ \ldots,\ \vec{r}_N)=(N!)^{-1/2}\det(\phi_i(\vec{r}_\alpha)),$$

or (3)

$$|\psi_0^{(N)0}\rangle=|\mathrm{vac}\rangle \quad .$$

We call the orbitals ϕ_i which occur in $\psi_0^{(N)0}$ occupied orbitals. The Hartree-Fock equations which define the ϕ's also contain solutions, not contained in $\psi_0^{(N)0}$, which are orthogonal to the occupied orbitals and are termed virtual orbitals. We shall use subscripts a, b, c, etc., to label virtual orbitals and i, j, k, etc., to label occupied orbitals. We order things such that $1\leqslant i\leqslant N<a$.

It is possible to form additional Slater determinants using these virtual orbitals. In doing this we follow the usage of Nesbet[10] and designate, for example, $\psi_i^{(N)0a}$ as that determinant where the ith occupied orbital has been replaced with the ath virtual orbital. Similarly, if orbitals i and j are replaced by orbitals a and b we denote this state as $\psi_{ij}^{(N)0ab}$. However, since we vary the number of particles we find second quantization useful here. If we limit ourselves to one- and two-electron excitations, we can represent $\psi_0^{(N)}$ and,[10] where $\alpha^\dagger$ and α are the fermion creation and annihilation operators, respectively,

$$|\psi_0^{(N)}\rangle = |\text{vac}\rangle + \sum_{i,a} A_i^{(N)0a}\,\alpha_a^\dagger\alpha_i\,|\text{vac}\rangle + \sum_{ijab} B_{ij}^{(N)0ab}\,\alpha_a^\dagger\alpha_b^\dagger\alpha_i\alpha_j\,|\text{vac}\rangle\,. \tag{4}$$

In principle we need to determine the values of the A's and B's by the variational method. In the case of our nondegenerate ground state, the A's turn out to be zero in the limit of second-order perturbation theory.[12] We can construct approximate excited states of the N-body system by replacing an occupied orbital with a virtual orbital in $\psi^{(N)0}$.

We also generate the ground state of the $(N-1)$-body system by removing the electron in the Nth orbital in the N-body system. This ground state is given to be

$$|\psi_{0N}^{(N-1)}\rangle = \alpha_N\,|\text{vac}\rangle + \sum_{i,a} A_i^{(N-1)a}\,\alpha_a^\dagger\alpha_i\alpha_N\,|\text{vac}\rangle + \sum_{ijab} B_{ij}^{(N-1)ab}\,\alpha_a^\dagger\alpha_b^\dagger\alpha_i\alpha_j\alpha_N\,|\text{vac}\rangle\,. \tag{5}$$

This wave function describes a nonmetalic solid with a hole produced in it.

In considering the case of an electron in the conduction band we desire to obtain the starting point of Toyozawa[7] and hence we consider the conduction electron to be an electron added to the N-body system. The wave function for this $(N+1)$-electron system in which we have added an electron in the ath state is designated

$$|\psi_0^{a(N+1)}\rangle = \alpha_a^\dagger\,|\text{vac}\rangle + \sum_{i,b}{}' A_i^{(N+1)b}\,\alpha_b^\dagger\alpha_i\alpha_a^\dagger\,|\text{vac}\rangle + \sum_{ijbc} B_{ij}^{(N+1)bc}\,\alpha_b^\dagger\alpha_c^\dagger\alpha_i\alpha_j\alpha_a^\dagger\,|\text{vac}\rangle\,. \tag{6}$$

In Eq. (6) by the prime we mean that in summing over the b and c we omit state a and that in summing over i, j, we include a.

The ϕ's in general satisfy the Hartree-Fock equation

$$F\phi_i(\vec{r}_\alpha) = \epsilon_i^0\,\phi_i(\vec{r}_\alpha) \tag{7}$$

and the eigenvalues ϵ_i have the usual meaning given by Koopmans's theorem.[13] It is the properties of these ϕ's which we wish to exploit. Finally, we will define the energy of the N-body system in its ground state and also for the $(N+1)$-body system as discussed above. These are seen to be

$$E_0^{(N)} = \int \psi_0^{(N)*} H \psi_0^{(N)}\,d\tau \Big/ \int \psi_0^{(N)*}\psi_0^{(N)}\,d\tau \tag{8}$$

and

$$E^{a(N+1)} = \int \psi_0^{a(N+1)*} H \psi_0^{a(N+1)}\,d\tau \Big/ \int \psi_0^{a(N+1)*}\psi_0^{a(N+1)}\,d\tau\,, \tag{9}$$

and the ionization energy for the Nth electron is

$$E_N^{(N-1)} - E_0^{(N)} = -\epsilon_N\,. \tag{10}$$

Now, we must define our correlation energy terms. We do this with respect to the energy of the base Hartree-Fock ground state. In so doing we rely on the content of Koopmans's theorem.[13] The energy of the N-body ground state to the accuracy of second-order perturbation theory is given as

$$E_0^{(N)} = E^0 + \sum_{i,a} \frac{(V_i^{(N)0a})^2}{\epsilon_i^0 - \epsilon_a^0} + \frac{1}{2}\sum_{i,j,a,b} \frac{(v_{ij}^{(N)0ab})^2}{\epsilon_i^0 + \epsilon_j^0 - \epsilon_a^0 - \epsilon_b^0 + v_{ij}^{ab}}\,. \tag{11}$$

Here the quantity V is defined as

$$V_i^{(N)0a} = \langle\text{vac}\,|H\alpha_a^\dagger\alpha_i\,|\text{vac}\rangle$$

and

$$V_{ij}^{(N)0ab} = \langle\text{vac}\,|H\alpha_a^\dagger\alpha_b^\dagger\alpha_i\alpha_j\,|\text{vac}\rangle\,.$$

We note by Brillouin's theorem for our N-body ground state the $V_i^{(N)0a}$ are zero. The quantities v_{ij}^{ab} are given as[10]

$$v_{ij}^{ab} = -\langle ab\,|R\,|ab\rangle - \langle ij\,|R\,|ij\rangle + \sum_{k=i}^{j}\sum_{c=a}^{b}\langle ka\,|R\,|kc\rangle,$$

$$R = (1-P_{12})\,[e^2/(\vec{r}_{12})]\,.$$

In general, for Bloch-like states the v's tend to go as $1/N$ and are hence usually neglected in solid-state calculations. P_{12} is the operator which interchanges coordinates 1 and 2.

From this we identify part of the correlation energy and call it a "pair correlation" $e_{ij}^{(N)}$, which is seen to be

$$e_{ij}^{(N)} = \sum_{a>N} \frac{(V_i^{(N)0a})^2}{\epsilon_i^0 - \epsilon_a^0} + \sum_{a>N} \frac{(V_j^{(N)0a})^2}{\epsilon_j^0 - \epsilon_a^0} + \sum_{a>N}\sum_{b>N} \frac{(V_{ij}^{(N)0ab})^2}{\epsilon_i^0 + \epsilon_j^0 - \epsilon_a^0 - \epsilon_i^0}\,. \tag{12}$$

In terms of the "pair correlations" defined in Eq. (12) for the N-body case, which take on the appropriate form for the $(N-1)$- and $(N+1)$-body cases, [that is, one simply changes the upper limit of the sums in Eq. (12)], we have expressions for the total energy which are

$$E_0^{(N)} = E^0 + \frac{1}{2} \sum_{i,j=1}^{N}{}' e_{ij}^{(N)} \quad , \tag{13}$$

$$E_N^{(N-1)} = E^0 - \epsilon_N^0 + \frac{1}{2} \sum_{i,j=1}^{N-1}{}' e_{ij}^{(N-1)} \quad , \tag{14}$$

$$E^{a(N+1)} = E^0 + \epsilon_a^0 + \frac{1}{2} \sum_{i,j=1}^{N+1}{}' e_{ij}^{a(N+1)} \quad . \tag{15}$$

Here we add the superscript a to indicate that the orbital a has been occupied in Eq. (15). In the case where the electron in Nth orbital is removed from the system, we define its energy as being the negative of the ionization potential, and hence find that ϵ_N is given as

$$\begin{aligned} \epsilon_N &= E_0^{(N)} - E_N^{(N-1)} \ , \\ \epsilon_N &= \epsilon_N^0 + \frac{1}{2} \sum_{i,j=1}^{N-1}{}' (e_{ij}^{(N)} - e_{ij}^{(N-1)}) + \sum_{j=1}^{N-1} e_{Nj}^{(N)} \quad . \end{aligned} \tag{16}$$

We note that this expression for ϵ_N in Eq. (16) reduces to Koopmans's theorem result ϵ_N^0 when correlation is neglected. Similarly, we define the energy of the conduction electron as being the electron affinity of the solid, and hence ϵ_a is found to be

$$\begin{aligned} \epsilon_a &= E^{a(N+1)} - E_0^{(N)} \quad , \\ \epsilon_a &= \epsilon_a^0 + \frac{1}{2} \sum_{k,j=1}^{N} (e_{ij}^{a(N+1)} - e_{ij}^{(N)}) + \sum_{j=1} e_{(N+1)j}^{a(N+1)} \quad . \end{aligned} \tag{17a}$$

However, if we neglect the changes in correlation energy for the valence and core electrons, as does Toyozawa, due to the presence of the added electron in an empty band, we find that

$$\epsilon_a = \epsilon_a^0 + \sum_{j=1}^{N} e_{(N+1)j}^{a(N+1)} \ . \tag{17b}$$

It is noted that the approximation introduced by Toyozawa is consistent with the analysis of Allen, Clementi, and Gladney[11] and is also consistent with the results one may derive from Toyozawa's formalism.

Finally, in keeping with normal solid-state practice, it is useful to define a self-energy for the conduction electron and for the valence hole. These are called E_e and E_h, respectively, and are given as

$$E_e = \sum_{j=1}^{N} e_{(N+1)j}^{a(N+1)} \tag{18a}$$

and

$$E_h = \frac{1}{2} \sum_{i,j=1}^{N-1}{}' (e_{ij}^{(N)} - e_{ij}^{(N-1)}) + \sum_{j=1}^{N-1} e_{Nj}^{(N)} \ . \tag{18b}$$

At this point it is perhaps useful to discuss the use of second-order perturbation theory with some hope of understanding its reliability. It is also useful to discuss types of configurations which one includes in evaluating the correlation energies [Eqs. (12)–(18)]. We also note that for our $(N+1)$- and $(N-1)$-body system, single-particle excitations are included. These are necessary for two reasons. First, these configurations are not closed-shell configurations so that Brillouin's theorem doesn't exactly apply, and second, the one-electron orbitals used in the $(N+1)$- and $(N-1)$-body configurations do not satisfy exactly the Hartree-Fock equation for this system but satisfy the N-body Hartree-Fock equation (7).

One of the limitations of using second-order perturbation theory is that only the interactions of the excited configurations with the ground-state configuration are included. Thus the mutual interaction of the excited configurations, which may lie very close together in energy, is neglected. This question has been considered for the present types of systems by Inoue *et al.*[8] for the $(N+1)$-body case. They find the following: (a) Many-body corrections are exactly zero for odd orders of perturbation; (b) they give an explicit expression for fourth-order perturbation theory and evaluate this for a particular case. Inoue *et al.* find that the fourth-order perturbation correction is several orders of magnitude smaller than the second-order correction. The author concurs with this result and therefore believes that the use of second-order perturbation theory is not unreasonable.

One of the reasons that the higher-order perturbation-theory corrections are small is that some attention was given to the choice of how one constructs the excited configurations which go into Eqs. (4)–(6). The utility of a proper choice of excited configuration has long been recognized in atomic calculations.[10] In our discussion we have said the orbitals used are solutions to Fock's equation (7). If one applies the proper boundary conditions this produces a unique set of occupied orbitals. However, the spectrum of virtual orbitals is quite arbitrary and in practice any set of orbitals, orthogonal to the occupied orbitals, will serve to construct the excited-state configurations. For any such set of orbitals the formulas presented in this section remain valid.[10] This arbitrariness of the virtual Fock orbitals is discussed in the Appendix and a "generalized" definition of the Fock operator used in Eq. (7) is presented.

We now briefly discuss which configurations are to be included and how they are chosen. In doing this we restrict the explicit discussion to the $(N+1)$-body wave function Eq. (6), understanding that the extension of the discussion to the other cases is simply formal and trivial. The possibilities for single-particle excitation are twofold: (i) An electron can scatter internal to its own band; (ii) an electron can scatter to another band. Case (i) doesn't contribute to the correlation energy because the excited determinant belongs to a different irreducible representation of the translation group than the ground-state wave function and hence the matrix element coupling them is zero. Case (ii) is explicitly contained in Toyozawa's formalism and the particular choice of excited orbital is an excitonic one rather than a band function.[7] That this is included is clear from Eq. (22) of Inoue *et al.*[8] by noting the summation includes the term $\vec{q}=0$. One can evaluate the specific contribution of this type of excitation,and it is small compared with the two electron excitations.

For the two-electron excitations one has three possibilities: (a) Two particles are scattered internal to their band; (b) two particles are excited to other states; (c) one particle is scattered internal to its band and one particle is excited to another state. Process (a) does not occur here since we have at most one particle free to scatter internal to its own band. Process (b) can be included, but an evaluation of this process based upon the Toyozawa formalism shows that its influence is small compared to process (c). That this is so can be deduced from the formulas presented in Sec. III of this paper. Thus we must consider process (c) carefully. If the configurations chosen are based upon the Bloch type of solutions to Eq. (7), one may anticipate difficulties in the use of second-order perturbation theory since there are clearly an infinite number of possible excited states nearly degenerate in energy which correspond to the same irreducible representation of the translation group as the base determinant and one may expect the mutual interaction of these states to be non-negligible. This difficulty is avoided making use of the arbitrariness of the Fock virtual orbitals. Following Toyozawa[7] one choses a Bloch function for the orbital of the electron scattered internal to its band. However, rather than represent the excited electron by a Bloch function one forms an excitonic wave function, in which both electron and hole are represented by localized functions in a given determinantal wave function, and linear combinations of such determinantal wave functions are formed which satisfy the periodic properties of the lattice. This is discussed in Sec. III and, as we noted previously, seems to avoid the difficulties which could occur due to the neglect of the mixing of the excited configurations.

III. EVALUATION OF CORRELATION ENERGY

In this section we obtain approximate expressions for Eqs. (18a) and (18b). To accomplish this, we follow the work of Toyozawa.[7] Since the method appears in full in Toyozawa's paper, we will sketch the derivation here, emphasizing the physical arguments. We begin by looking at part of (17) or (18), that is, for example ,

$$\sum_{j=1}^{N-1} e_{ij}^{(N)} \quad .$$

We restrict our attention to i or j being those electrons in the valence band or those electrons in the same band as the electron in question. We shall restrict our attention to those configurations which lie closest in energy to the state of interest. This will be partly justified later.

We wish to consider the interaction between the ith electron and the M electrons in the band with the jth electron. We assume here the jth electron is in the valence band for simplicity. This interaction is

$$U(\vec{r};\vec{r}_1,\ldots,\vec{r}_M)=\sum_{j=1}^{M} e^2/|r-\vec{r}_j| \quad , \tag{19}$$

and the total Hamiltonian is represented as

$$H=H_0(\vec{r})+H_c(\vec{r}_1,\ldots,\vec{r}_M)+U(\vec{r};\vec{r}_1,\ldots,\vec{r}_M) \; . \tag{20}$$

H_0 includes the kinetic energy and the interaction of the electron with the core electrons and with the nuclei. H_c is the equivalent Hamiltonian for the valence electrons. The c system in the independent-particle limit has excited states in which some electrons are in the conduction bands and some valence holes. In the next limit we find some excitations (i.e., spatially correlated electrons and holes). We assume the energy needed to create such an exciton is $\epsilon_{n\kappa}$ and is independent of κ, the exciton translational quantum number. We specify the eigenstates of the system by the number of excitons of each $\vec{\kappa}$ and n present (the excitons are considered to be bosons). We find (dropping the subscript $\vec{\kappa}$)

$$H_c\psi(\ldots,n_{\vec{\kappa}'i},\ldots,n_{\vec{\kappa}j},\ldots;\vec{r}_1,\ldots,\vec{r}_M)=\Big(E_0+\sum\nolimits_m \epsilon_m \sum\nolimits_\kappa n_{\vec{\kappa},m}\Big)\psi(\ldots,n_{\vec{\kappa}'i},\ldots,n_{\vec{\kappa}j},\ldots;\vec{r}_1,\ldots,\vec{r}_M) \; . \tag{21}$$

Naturally, Eq. (21) holds only if $\sum_m\sum_\kappa n_{\kappa m} \ll M$. We need the matrix elements of U with respect to the solutions of Eq. (21). We shall use the linear-combination-of-atomic-orbitals (LCAO) method for the one-electron orbitals. The integral I which we must evaluate is

$$I=\langle(\ldots,n_{\vec{\kappa}'i},\ldots,n_{\vec{\kappa}j},\ldots;\vec{r}_1,\ldots,\vec{r}_M)$$

$$\times \left|U\right|(\ldots, n_{\vec{\kappa}'i}, \ldots, n_{\vec{\kappa}j}, \ldots; \vec{r}_1, \ldots, \vec{r}_M)\rangle \; . \tag{22}$$

This integral is nonzero in three cases. We have case (1): $n = n'$ for all $\vec{\kappa}$ and j and the electrons excited coincide; case (2): $n = n'$ for all $\vec{\kappa}$ and j but 1 and here $n+1 = n'$ and the excited electrons coincide for the cases where $n = n'$; case (3): the reverse of case (2).

In studying these cases, we consider, as does Toyozawa, only changes in the total charge and in dipole moment. In case (1), where there is neither change in total charge nor dipole moment, we can essentially use the Fock potential due to the valence electrons in the ground state. We call, in this case,

$$I = U_0(r) \quad . \tag{23}$$

In either case (2) or (3), we find

$$I = e\phi_{m'n}(r) \quad , \tag{24}$$

where $\phi_{m'n}(r)$ is the dipole potential due to the dipole moment μ on the m'th atom when it is excited to the state n;

$$\mu_n = \int \phi^{g*}(r)\, e r \phi_n^e(r)\, dr \quad , \tag{25}$$

where we use ground and excited atomic Slater determinants here. These expressions are further simplified by Toyozawa for the case in which the valence-band function is s- or p-like.

In principle we must evaluate (25) for each excited state of the atom in question. This is clearly a difficult, if not impossible, task. However, we see that Eq. (25) is related to the transition oscillator strength for the transition $0 \rightarrow n$ of the atom. We shall use this fact to simplify our problem. We shall replace the spectrum of the atom by a single excited level which is ϵ above the ground state. We therefore have unit oscillator strength per electron for transitions from the ground to excited state. Hence, we may use this fact to obtain a value for μ; we drop the subscript since there is now only one excited state. As we shall see, the exact value in ϵ is not very critical. We have done what Toyozawa assumes; that is, we replace the spectrum by a single effective exciton band of energy ϵ. If we do this, then Eqs. (24) and (25) simplify immediately to the result originally given by Toyozawa. Again we stress that the exciton we introduce here is not the one which one sees experimentally but is an averaged representation of an entire spectrum.

If we follow the example of Toyozawa and introduce boson creation and annihilation operators $b_k^\dagger$, b_k for the exciton, we find that

$$U(\vec{r}; \vec{r}_1, \ldots, \vec{r}_M) = U_0(\vec{r}) - e\phi(\vec{r}) \; , \tag{26}$$

$$\phi(\vec{r}) = (\alpha/V^{1/2}) \sum \; (i/|\vec{K}|)\, (b_{\vec{K}}\, e^{i\mathrm{K}\cdot\vec{r}} - b^\dagger_{\vec{K}}\, e^{-i\vec{K}\cdot\vec{r}}) \; , \tag{27}$$

$$\alpha^2 = 2\pi\epsilon(1 - 1/\epsilon_\infty) \quad . \tag{28}$$

In Eq. (27), V is the volume of the solid, and in Eq. (28), ϵ_∞ is the optical dielectric constant. Therefore,

$$H = [H_0 + U_0(\vec{r})] + (E_\rho^0 + \epsilon {\textstyle\sum_{\vec{k}}} b^\dagger_{\vec{k}} b_{\vec{k}}) - e\phi(\vec{r}) \; . \tag{29}$$

Here E^0 is the energy of the system when there is no conduction electron. It is the term $e\phi(\vec{r})$ which contains the effect of pair correlation here.

Now we generate the final form for $e\phi(\vec{r})$ following the method of Inoue, Mahutte, and Wang. We use a Bloch function formed from localized functions as the one-electron orbital for the electron in question, that is,

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{N^{1/2}} \sum_{\mu=1}^{N} e^{i\vec{k}\cdot\vec{R}_\mu}\, \phi(\vec{r} - \vec{R}_\mu) \quad . \tag{30}$$

We must evaluate $\int \phi^*_{\vec{k}}(\vec{r}) e(\vec{r}) \phi_{\vec{k}'}(\vec{r})\, dr$. If we work to lowest order in interatomic overlap, one has[8]

$$-\int \phi^*_{\vec{k}}(\vec{r})\, e\phi(\vec{r}) \phi_{\vec{k}'}(\vec{r}) = \sum_{\vec{k}\vec{K}} V_{\vec{K}}(0)\, (b^\dagger_{-\vec{K}} - b_{\vec{K}})\, \alpha^\dagger_{\vec{k}-\vec{K}}\, \alpha_{\vec{k}} \; , \tag{31}$$

$$V_{\vec{K}}(0) = e\left(\frac{2\pi\epsilon(1 - 1/\epsilon_\infty)}{V}\right)^{1/2} \frac{i}{|\vec{K}|} \int \phi^*_n(\vec{r} - \vec{R}_\mu) \times e^{i\vec{K}\cdot\vec{r}}\, \phi_m(\vec{r} - \vec{R}_\mu)\, dr \quad . \tag{32}$$

Here we introduce the electron creation and annihilation operators $\alpha^\dagger_{\vec{K}}$ and $\alpha_{\vec{K}}$. If the one-electron orbitals about site $\vec{R}_\mu$ are orthogonal and if $|\vec{K}|^{-1}$ is large compared to the size of an orbital ϕ, we find

$$V_{\vec{K}}(0) = e\left(\frac{2\pi\epsilon(1 - 1/\epsilon_\infty)}{V}\right)^{1/2} \frac{i}{|\vec{K}|} \times \int \phi_n(\vec{r} - \vec{R}_N)\, e^{-i\vec{k}\cdot\vec{r}}\, \phi_m(\vec{r} - \vec{R}_N)\, dr\, \delta_{nm} \quad . \tag{33}$$

That is, the electron is scattered internal to its own band and in part justifies our prior statements relating to which configurations are needed. This is the form given by Inoue *et al.*[8] We complete the second quantization of our Hamiltonian subtracting out the energy of the ground-state Hartree-Fock determinant, except for the orbital in question, and find it to be

$$H = \sum_{\vec{k}} \epsilon_{\vec{k}}\, \alpha^\dagger_{\vec{k}} \alpha_{\vec{k}} + \epsilon \sum_{\vec{K}} b^\dagger_{\vec{K}} b_{\vec{K}} + \sum_{\vec{k}\vec{K}} V_{\vec{K}}(0)\, (b^\dagger_{-\vec{K}} - b_{\vec{K}})\, \alpha^\dagger_{\vec{k}-\vec{K}}\, \alpha_{\vec{k}} \quad . \tag{34}$$

In the ground state we have no excitons and hence we see that the first term on the right-hand side of (34) is just what we get from Hartree-Fock for the electron in question, while the last term is the effect of correlating the electron with all the valence electrons. We proceed from here to find the self-energy for the electrons and the hole. In the case of the electron, we have the result of Inoue *et al.*[8] Thus, we find that (18a) and (18b) become

$$E_e(\vec{k}) = \sum_{\vec{K}} \frac{|V_{\vec{K}}(0)|^2}{\epsilon(\vec{k}) - \epsilon - \epsilon(\vec{k} - \vec{K})} \tag{35}$$

and

$$E_h(\vec{k}) = \sum_{\vec{K}} \frac{|V_{\vec{K}}(0)|^2}{\epsilon + \epsilon(\vec{k}) - \epsilon(\vec{k} - \vec{K})} \;. \tag{36}$$

Again we stress that we have included only the lowest exciton band and we restrict the scattering of the electron to its own band.

We can make several qualitative statements about (35) and (36). First, if the bands are flat, there is no dispersion in E_e or E_h and the expressions are independent of $\vec{k}$. Second, if the bandwidth is less than ϵ, as it usually is, E_e is negative and E_h is positive. Finally, the expressions are such that the effect of correlation is to narrow the bands. This narrowing is proportional to the width of the band. These qualitative judgments are mostly consistent with the previous calculations.[1,2] The sign of the effect is consistent with the work of Fowler.[4] We note that the extension of Eqs. (35) and (36) to the case of degenerate bands is simple. We simply sum Eqs. (35) and (36) over the degenerate bands.

IV. NUMERICAL CALCULATIONS

Our task is to evaluate Eqs. (35) and (36) for several cases. In order to do this we need several pieces of information. These are expressions for $\epsilon(\vec{k})$, ϵ, ϵ_∞, the lattice constant, and Wannier functions for the band in question. We restrict ourselves to s-like bands in fcc solids and use the simple-tight-binding value for $\epsilon(\vec{k})$; this is[14]

$$\epsilon(\vec{k}) = E_0 + V_{ss}\,(\cos\tfrac{1}{2}k_x a \cos\tfrac{1}{2}k_y a + \cos\tfrac{1}{2}k_x a \cos\tfrac{1}{2}k_z a + \cos\tfrac{1}{2}k_y a \cos\tfrac{1}{2}k_z a)\,. \tag{37}$$

The values of a and ϵ_∞ are gathered from standard sources. The value for ϵ is not critical as one can see from Eqs. (32), (35), and (36), since as the bandwidth goes to zero, the values for E_e and E_h become independent of ϵ. In most cases we consider, the value for ϵ is large compared to the bandwidth and hence the choice of ϵ is not critical. In principle, one should not use an experimental value for ϵ, but should evaluate it from wave functions used in the calculation to define the exciton band. Such a calculation is difficult in practice. The author evaluates ϵ as follows. Use the Hartree-Fock energy bands, when they are available. If they are not available, such energy bands as are available are used. From this, one can estimate the exciton binding energy by the effective-mass approximation. This value when subtracted from the band gap yields the value for ϵ. In the case of the core levels we obtain the correct Wannier functions from local-orbitals calculations.[15] For the conduction bands we get approximate hydrogenic tight-binding functions using the quantum-defect method. The value of the electron self-energy is found to be nearly independent of the wave function used.

In Table I, we give values for $E_e(\vec{k})$ at $\vec{k} = (0, 0, 0)$, $(2\pi/a)\,(1, 0, 0)$, and $(\pi/a)\,(1, 1, 1)$, or Γ, X, and L, for the lowest conduction band of MgO,[16] KI,[17] KCl,[18] NaCl,[19], LiCl, Ar, ZnS,[20] and InAs.[20] In Table II, we give values for $E_h(\vec{k})$ for core levels in MgO, KI, LiCl, and CaF_2. These values are found to be $\vec{k}$ independent. We also give values for E_e and E_h from other sources when available. We see in Table I that our values for E_e are in fair agreement with those from other sources except that in the case of KCl there is substantial disagreement between the present work and that of Ref. 8. This is surprising inasmuch as both works use

TABLE I. Values of $-E_e(\vec{k})$ at Γ, X, and L are given using Eq. (35) for the lowest conduction band of several solids. Also given are the values for $E_e(\vec{k})$ obtained from other sources whenever possible. Results are in eV.

	Γ			X			L		
Substance	This work	Other values		This work	Other values		This work	Other values	
MgO	3.21	···	···	4.13	···	···	3.83	···	···
KI	1.72	2.18[a]	2.38[b]	2.28	2.18[a]	···	2.09	2.18[a]	
KCl	1.70	1.96[a]	2.75[b]	2.04	1.96[a]	2.09[c]	1.94	1.96[a]	2.05[c]
NaCl	2.02	2.43[a]	2.41[d]	2.28	2.43[a]	2.27[d]	2.21	2.43[a]	2.39[d]
LiCl	2.36	3.14[a]	···	2.73	3.14[a]	···	2.62	3.14[a]	···
Ar	1.44	1.10[a]	2.19[e]	1.57	1.10[e]	2.20[e]	1.53	1.10[a]	2.20[e]
ZnS	3.08	···	···	4.56	···	···	4.02	···	···
InAs	1.60	···	···	2.05	···	···	2.93	···	···

[a] Reference 4.

[b] Reference 8.

[c] Reference 18.

[d] References 2 and 19.

[e] Reference 1.

TABLE II. Values of $E_h(\vec{k})$ are given for some s-like core states of several crystals using Eq. (36). Values are also given according to Fowler (Ref. 4) wherever possible. Results are in eV.

Substance	Level	Present work	Ref. 4
MgO	Mg 2s	4.31	
KI	I 1s	2.52	1.44
KI	I 2s	2.52	1.44
KI	I 3s	2.51	1.44
KI	I 4s	2.48	1.44
KI	K 1s	2.52	2.18
KI	K 2s	2.51	2.18
KI	K 3s	2.41	2.18
LiCl	Li 1s	3.41	3.14
CaF_2	Ca 2s	2.75	···

the same expression for E_e. The difference is not due to different choices of parameters in the two calculations, for when the author used the parameters stated in Ref. 8 the agreement became worse. Lipari has also evaluated Eq. (35) for the case of KCl and is in agreement with the results of this present work.[21] We are not able to understand the exact reasons for the disagreement between the present result and that of Inoue *et al.*

There are other trends to observe here. One is that the present results for $E_e(\vec{k})$ seem to have greater dispersion than previous work. In the case of Ref. 4 this is easy to understand, since Fowler treates the electron as a static charge and neglects the translational symmetry of the solid and hence omits any dispersion. It is not possible to explain the lack of substantial dispersion in the other results considered.

In the case of the formation of the hole, we see from Table II that the self-energy E_h is essentially independent of which hole is created in a given solid. This may be unreasonable. This is likely to occur here, since our final model includes only the relaxation of the valence levels and the levels from which an electron is removed. Thus we expect this to be most accurate for the outer levels only since the relaxation of levels between the level in question and the valence levels is neglected. In general, the agreement between our present model and that of Ref. 4 is poor. It is possible to understand why this is so.

In the Fowler model, it is assumed that the hole exists as a positive point charge on the lattice site about which it is created. This positive point charge then polarizes the charge clouds on the surrounding atoms and ions. Using a Mott-Littleton[22] approach, Fowler is able to compute the amount of energy involved in polarizing the surrounding ions. This model entirely neglects two other contributions which may be of importance in this case. These are that the correlation energy between the electron removed and the other electrons in the ion from which it is removed is neglected, as is the energy associated with the relaxation of the wave functions on this ion in the Hartree-Fock source when the electron is removed. We can estimate these effects in a simple model.

We obtain the correlation energy for a hole on a Li$^+$ ion in LiCl from Fowler,[4] and it is 3.14 eV. The correlation between 1s electrons contributes -1.19 eV.[11] We compute the relaxation energy from the difference between the ionization energies for Li$^+$ to Li^{++} computed by Koopmans's theorem and by self-consistent Hartree-Fock techniques. This contribution is 1.52 eV. The final self-energy for the hole in LiCl's Li$^+$ 1s shell is then 3.57 eV, which agrees well with the value of 3.41 eV obtained in the present calculation.

V. CONCLUSIONS

In this paper, we have used simple perturbation theory to investigate the correlation energy associated with a lone electron in the conduction band of a nonmetal and also to understand the correlation energy associated with an electron in a filled shell of a nonmetal. In both cases our model permits us to obtain expressions of these self-energies, using the method of Toyozawa, which are easy to evaluate using an electronic digital computer. These models have been evaluated for the lowest conduction band and also for several core levels of a number of solids. These solids include ionic insulators, a rare-gas solid, and a II-IV and a III-IV semiconductor. We see that the effect of correlation is to narrow the bands. We also find the self-energy for conduction electrons to be negative and the self-energy for holes to be positive. This feature is in good agreement with previous work. The magnitude of these corrections is sizable, about 2 eV, and this also is in agreement with previous work.

It is useful to relate these results to the results of standard energy-band calculations. These calculations fall into two categories. These are those calculations which use adjustable parameters and those which do not. Only the latter are useful here. These also fall into two classes. These are those which use a local exchange approximation and those which use the nonlocal Fock exchange. Calculations of the former type are most numerous. Those substances with reasonable Fock types of calculations are Ar,[1] Kr,[1] LiCl,[2] LiBr,[23] NaCl,[2] NaBr,[24] and KCl.[25] The observed band gaps[26,27] and the computed Hartree-Fock band gaps are given in Table III for these solids, as are the band gaps obtained using local exchange approximations with no adjustable parameters.[28] The trends are obvious. The Hartree-Fock calculations consistently overestimate the observed band gaps by several

TABLE III. Values of band gaps are given for several crystals. In column 1 we specify the solid, in column 2 the Hartree-Fock gap is given, in column 3 the local exchange gap is given (see Ref. 28), and in column 4 we give the experimental gap. Results are in eV.

1	2	3	4
Ar	16.20	7.08	14.3
Kr	15.1	11.3	11.8
LiCl	11.47	8.7	9.4
LiBr	12.10	7.4	7.6
NaCl	12.08	7.4	8.75
NaBr	11.03	6.4	7.1
KCl	11.76–10.1	6.5–6.3	8.7

eV, whereas the use of local exchanges produces band gaps which are smaller than experiment. The error in the Hartree-Fock gaps is consistent with the results of the present calculation.

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APPENDIX: VIRTUAL ORBITALS IN HARTREE-FOCK THEORY

In this Appendix we discuss the virtual orbitals of the Hartree-Fock equation. The Hartree-Fock equation results from minimizing the energy of the many-body Hamiltonian with respect to a determinantal wave function. The usual form for this equation is

$$F\phi_i = \epsilon_i \phi_i = \left(-\nabla^2 - 2\sum_I \frac{Z_I}{|\vec{R}_I - \vec{r}|} + 2\int \frac{\rho(\vec{r}\,', \vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\,' - \frac{2\rho(\vec{r}, \vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \right)\phi_i , \quad \text{(A1)}$$

where

$$\rho(\vec{r}, \vec{r}\,') = \sum_{i=1}^{N} \phi_i(\vec{r})\,\phi_i^\dagger(\vec{r}\,') \quad . \quad \text{(A2)}$$

In this Appendix we use the nomenclature established in the text.

We now introduce an operator $A^{1\text{-}F}$ which was originally suggested by Gilbert[29] and whose use has been explored by Huzinaga and Arnau[30] and by Kunz.[31] This operator is defined to be

$$A^{1\text{-}F} = (1-\rho)A(1-\rho) , \quad \text{(A3)}$$

and has the properties

$$A^{1\text{-}F}\phi_i \equiv 0, \qquad i \leq N \quad \text{(A4)}$$

$$A^{1\text{-}F}\phi_a = A\phi_a - \rho A\phi_A , \quad N < a \quad \text{(A5)}$$

or

$$A^{1\text{-}F}\phi_a = \textstyle\sum_b c_b\, \phi_b , \qquad N < a, b \quad . \quad \text{(A6)}$$

These results hold for any well-behaved Hermitian operator A. Thus, we see that the effect of $A^{1\text{-}F}$ operating on a virtual orbital is to produce a linear combination of other virtual orbitals. It is clear from Eq. (A4) that if we introduce $A^{1\text{-}F}$ into F the Hartree-Fock ground state is unchanged. Thus we define a "general" Hartree-Fock equation of the form

$$(F + A^{1\text{-}F})\phi_i = \epsilon_i \phi_i \ . \quad \text{(A7)}$$

As has been discussed by Gilbert[29] for the closely related operator $A^F = \rho A \rho$, one can, in general, produce a quite arbitrary spectrum for Eq. (A7). It is clear that for the purposes of configuration-interaction calculations any equation of the form (A7) produces an equally valid set of one-electron orbitals. What is also clear is that some sets are quite a bit preferable to other sets for the purposes of actual calculations. Several aspects of this question are discussed by Huzinaga and Arnau[30] and by Kunz.[31]

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Quenching of Tb^{3+} Luminescence by Direct Transfer and Migration in Aluminum Garnets

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The relative emission per ion and the lifetime have been obtained as a function of Tb concentration for the $^5D_4$ to ^7F_J transitions in $(Y_{1-x}Tb_x)_3Al_5O_{12}$ crystals. At 297 °K both are concentration independent for $x < 0.3$ and decrease as $x^{4.6\pm0.2}$ for $x > 0.4$ up to about a factor 10^2 for $Tb_3Al_5O_{12}$. From the time dependence of the intrinsic $Tb_3Al_5O_{12}$ luminescence the initial nonexponential portion of the decay is shown to be consistent with direct dipolar transfer to nonradiative sinks. The later part of the decay is exponential and involves resonant Tb^{3+}-Tb^{3+} migration to the sinks. The direct transfer is found to be relatively temperature insensitive, but migration is not. There is little migration at low temperatures but for $T > 8$ °K, where the higher-energy $^5D_4$ levels begin to be populated, the migration rate increases rapidly. The temperature dependence of the migration constant D was calculated using the level populations and oscillator strengths. The migration contribution to the exponential decay is proportional to $D^{3/4}$ indicating the Tb^{3+}-Tb^{3+} transfer also involves dipolar interactions. Impurity-perturbed Tb^{3+} emission is observed for $T < 12$ °K. These ions are mainly populated by direct dipole transfer from the intrinsic ions. Multiple-ion-decay processes involving the deexcitation of an ion in the $^5D_4$ state and the simultaneous excitation of three or more neighboring Tb^{3+} ions are shown to be negligible at low temperatures.

I. INTRODUCTION

It is well known that the radiative-emission efficiency of most luminescent materials is reduced at high activator concentrations. The additional nonradiative decay results from direct multipolar or exchange interactions between like- or unlike-ion pairs or clusters,[1,2] and from the migration of the excitation to nonradiative quenching centers.[3,4] A considerable effort has been expended to elucidate the quenching mechanism from the *concentration dependence* of the radiative yield and the transient decay curves.[5,6] An alternative technique involves the detailed analysis of the transient luminescence decay of the concentrated crystal following pulsed excitation.[3] The latter is of particular value in cases, such as organic materials, where dipolar interactions are known to be important, and quenching can occur by direct transfer or involve migration to a sink.[7]

Both methods have been used to study the $^5D_4$ to ^7F_J ($J = 1-6$) emission of Tb^{3+} in the garnet series $(Tb_xY_{1-x})_3 Al_5O_{12}$ with $0.1 \leq x \leq 1$. The $^5D_4$ level is separated from $^7F_0$ by ~14 000 cm^{-1} (Fig. 1), and energy conservation makes the multipolar and exchange decay mechanisms between Tb^{3+} ions a high-order process. To quench an ion in the $^5D_4$ state requires that it and at least two of its neighbors be excited to $^7F_0$ plus the emission of 3500 cm^{-1} of phonons; alternatively, three neighbors