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# Correlation effects in energy-band theory*

Sokrates T. Pantelides
*W. W. Hansen Laboratories of Physics and Department of Applied Physics, Stanford University, Stanford, California 94305*

Daniel J. Mickish
*Photo Products Department, Experimental Station Laboratories, E.I. duPont de Nemours and Company, Wilmington, Delaware 19898*

A. Barry Kunz
*Department of Physics and Materials Research Laboratories, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

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In this paper we study the effect of correlations on Hartree-Fock energy bands for solids. The band picture is retained, and we obtain rigorous and general expressions for the correlation corrections. These are then specialized to study insulators, and the range of validity of the approximations is discussed. Qualitative conclusions about the effects of correlation are obtained directly, without the need of model calculations. We recover the narrowing of the optical gap and the narrowing of the valence bands, which have been known through model calculations, and also show that the effect of correlation on x-ray-emission transition energies is less pronounced, almost negligible, due to a cancellation of correlation contributions. In the case of metals, we again obtain general results and discuss model calculations. We further address the problem of short-range correlations, which is best described in an alternative formalism, and give estimates of the corrections. We give specific and detailed results for MgO as illustration of all the concepts in this paper. Finally, we discuss the effect of correlation on wave functions and oscillator strengths, and, in an appendix, point out a comparison of correlation effects among free atoms, insulators, and metals.

## I. INTRODUCTION

During the last few years, self-consistent solutions of the Hartree-Fock equations with nonlocal exchange have been reported for a number of solids, mostly insulators,[1-5] but also a few semiconductors[6,7] and metals.[8,9] For nonmetals, these calculations confirmed earlier predictions[10] that the Hartree-Fock value for the optical gap would be *larger* than the experimental gap by 3–5 eV. These corrections have in the past been calculated using the semiclassical model of Mott and Littleton,[10,11] the parametrized polarization-potential model used by Dagens and Perrot,[5] the electronic-polaron model of Toyozawa[12,13] used by Kunz and co-workers, and the plasmon model of Hermanson.[14] Another model which has been used[1,2] in this context is based on the Coulomb-hole-plus-screened-exchange approximation of Hedin.[15] In this model, one constructs an effective one-electron potential which includes correlation in an approximate way.

In the case of metals, a model has been proposed by Overhauser[16] which calculates correlation corrections to the free-electron bands. This model was used by the present authors[8] to correct the Hartree-Fock bands of calcium.

Recently, it was found that the above models were not adequate to account for the discrepancies between Hartree-Fock theory and experiment in the case of LiF. Additional corrections were attributed to short-range correlations neglected by polaron-type models, and were estimated using atomic calculations.[17,18]

In this paper we give a unified treatment of energy-band theory beyond the Hartree-Fock approximation. We first formulate the problem using the configuration-interaction formalism and obtain rigorous expressions for the correlation corrections to Hartree-Fock bands. We then show that definite conclusions about the effects of correlation can be made without introducing a particular model, such as the electronic-polaron[12,13] or the plasmon model,[14,16] for the evaluation of the general expressions. We study the optical gap, where correlation effects are important,[10] and also x-ray-emission transition energies for which we find that correlation effects tend to cancel out, making Hartree-Fock theory quite accurate. The various models for calculations are identified, and their range of validity is discussed. We then show that these models neglect short-range correlation effects. We introduce an alternative formalism, and show how the new contributions to the correlation corrections may be estimated by neglecting overlaps. Throughout the paper, we do not consider electron-hole-interaction effects which go beyond band theory, leading to formation of excitons, resonances, etc.

The plan of the paper is as follows. In Sec. II we give the basic equations for the energy-band theory in the Hartree-Fock approximation, in order to establish notation and motivation. In Sec. III we give the general configuration-interaction formalism and define the correlated energy bands for an arbitrary solid. In Sec. IV we study the special case of insulators and wide-gap semiconductors. In Sec. V we discuss the special case of metallic crystals. In Sec. VI we address the problem of short-range correlations. In Sec. VII we discuss the effect of correlation on the Bloch functions calculated in the Hartree-Fock approximation. We close with concluding remarks in Sec. VIII.

## II. HARTREE-FOCK THEORY

The results of Hartree-Fock (HF) theory for a crystal are well known, but we summarize them here in order to establish notation and perspective for the main objective of this study.

In the HF approximation, the wave function of the $N$-electron system is approximated by an antisymmetrized product of one-electron functions $\psi^0_\alpha(r_i)$. This may be written

$$\Psi \simeq \Psi^0 = \mathcal{A} \prod_{\alpha=1}^{N} \psi^0_\alpha(r_i) , \qquad (1)$$

which is simply a Slater determinant. The best one-electron functions are then the eigenfunctions of the one-electron Fock operator $F$

$$F\psi^0_{n\vec{k}}(\vec{r}) = \epsilon^0_{n\vec{k}}\,\psi^0_{n\vec{k}}(\vec{r}) , \qquad (2)$$

where we have written a band index $n$ and a wave vector $\vec{k}$ instead of $\alpha$.[19] This is a consequence of the translational symmetry of the crystal (Bloch's theorem). The eigenvalues $\epsilon^0_{n\vec{k}}$ form the well-known Hartree-Fock energy bands. Their interpretation is given by Koopmans's theorem,[20] which states that

$$\epsilon^0_{n\vec{k}} = E^{(N)}_{\mathrm{HF}} - E^{(N-1)}_{\mathrm{HF}} \qquad (3a)$$

for a one-electron state which is occupied in the ground state of the system, and

$$\epsilon^0_{n'\vec{k}'} = E^{(N+1)}_{\mathrm{HF}} - E^{(N)}_{\mathrm{HF}} \qquad (3b)$$

for a one-electron state which is vacant in the ground state of the system. Here $E^{(M)}_{\mathrm{HF}}$ is the total energy of the $M$-electron system calculated in the HF approximation. In Eq. (3), the assumption is that during the removal or addition of an electron to the $N$-electron system, the $\psi^0_{n\vec{k}}(\vec{r})$ do not change appreciably. In this picture then, the excitations of the system are simple one-electron transitions from the state $\psi^0_{n\vec{k}}(\vec{r})$ to the state $\psi^0_{n'\vec{k}'}(\vec{r})$, and the excitation energy is

$$\hbar\omega^0 = \epsilon^0_{n'\vec{k}'} - \epsilon^0_{n\vec{k}} . \qquad (4)$$

We have written the excitation energy as $\hbar\omega^0$, as we visualize transitions via absorption or emission of a photon whose energy is given by Eq. (4). In view of Eq. (3), we see that such a *band-to-band* excitation consists of two *independent* processes: adding an extra electron to the $N$-electron system, and creating a hole in the $N$-electron system. The electron and the hole are not allowed to interact. The most significant feature of this picture is that it describes the various excitations by a unique band structure. This is illustrated schematically in Fig. 1. For the transitions $A$, $B$, and $C$, we have

$$\hbar\omega^0_C = \hbar\omega^0_A + \hbar\omega^0_B . \qquad (5)$$

Such a relation is extremely useful in deducing information from experiments. In what follows we will see how the band picture and Eq. (5) are retained beyond Hartree-Fock theory, as long as electron-hole-interaction effects (excitons) are not included.

## III. CORRELATION AND QUASIPARTICLE BANDS: GENERAL FORMALISM

In going beyond the Hartree-Fock approximation, one would like to retain the band picture so that excitation energies may be obtained directly from equations like (4), and so that relation (5) holds. Up to a point, this is possible and straightforward. By analogy to Eq. (3), we define band energies in terms of exact total energies as follows:

$$\epsilon_{n\vec{k}} = E^{(N)} - E^{(N-1)} , \qquad (6a)$$

$$\epsilon_{n'\vec{k}'} = E^{(N+1)} - E^{(N)} . \qquad (6b)$$

These are no longer one-electron energies. They are known as *quasi-particle* bands, for reasons that soon will become clear. If an excitation energy is defined as a difference in the new band ener-

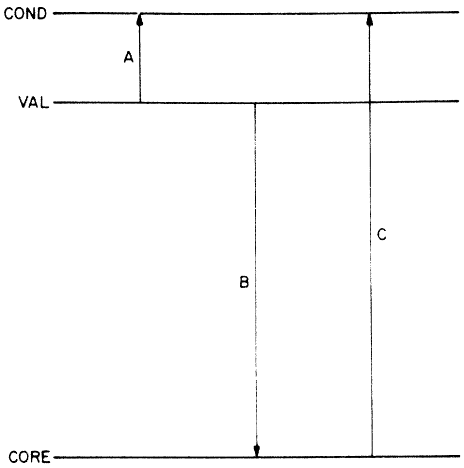

FIG. 1. Schematic band-to-band transitions in an insulator. $A$: valence-to-conduction-band optical absorption; $B$: valence-to-core-band x-ray emission; $C$: core-to-conduction-band x-ray absorption. Dispersion in $k$ is not shown, as it is of no interest to the present discussion.

gies by

$$\hbar\omega = \epsilon_{n\vec{k}} - \epsilon_{n'\vec{k}'} , \tag{7}$$

one can easily verify that a relation

$$\hbar\omega_C = \hbar\omega_A + \hbar\omega_B \tag{8}$$

analogous to Eq. (5) holds.

Clearly, the HF one-electron bands defined by Eq. (3) are a first approximation to the quasiparticle bands. In fact, definition (6) is useful only if one assumes that $E_{\mathrm{HF}}^{(M)}$ is a good approximation to the exact total energy $E^{(M)}$, so that contributions to $E^{(M)}$ beyond the HF approximation, the correlation energy, may be included by perturbation theory. Then one can write

$$E^{(M)} = E_{\mathrm{HF}}^{(M)} + E_C^{(M)} \tag{9}$$

for $M = N-1,\ N,\ N+1$, where the subscript $C$ stands for correlation energy.[21] By using Eq. (9) in (6) and comparing with Eq. (3), one then immediately obtains

$$\epsilon_{n\vec{k}} = \epsilon^0_{n\vec{k}} + (E_C^{(N)} - E_C^{(N-1)}) , \tag{10a}$$

$$\epsilon_{n'\vec{k}'} = \epsilon^0_{n'\vec{k}'} + (E_C^{(N+1)} - E_C^{(N)}) . \tag{10b}$$

In order to interpret Eq. (10), we proceed to introduce the configuration-interaction formalism used in Ref. 13. For convenience, from now on we will use a single index $i, j, k, \ldots$ to denote $n\vec{k}$ when the corresponding one-electron state is occupied in the HF ground state of the $N$-electron system; and a single index $a, b, c, \ldots$ to denote $n'\vec{k}'$ when the corresponding one-electron state is vacant. One can then show[22] that $E_C^{(N)}$ can be rigorously written as

$$E_C^{(N)} = \frac{1}{2} \sum_{j=1}^{N} \sum_{j'=1}^{N} e_{jj'}^{(N)} . \tag{11}$$

The quantities $e_{ij}^{(N)}$ are *pair correlation energies.* In second-order perturbation theory, they are given by[13,22]

$$e_{jj'}^{(N)} = \sum_{b>N} \sum_{b'>N} \frac{|\langle \psi_j^0 \psi_{j'}^0 | R | \psi_b^0 \psi_{b'}^0 \rangle|^2}{(\epsilon_j^0 + \epsilon_{j'}^0) - (\epsilon_b^0 + \epsilon_{b'}^0)} , \tag{12}$$

where

$$R = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} (1 - P_{12}) . \tag{13}$$

Here $P_{12}$ is the permutation operator. Now for the $(N-1)$-electron system, if we assume that $\psi_i^0$ is the state from which the electron was removed, we have

$$E_C^{(N-1)} = \frac{1}{2} \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{\substack{j'=1 \\ j'\neq i}}^{N} e_{jj'}^{(N-1)i} , \tag{14}$$

where $e_{jj'}^{(N-1)i}$ is as in Eq. (12), except that the sums over $b$ and $b'$ include the state $\psi_i^0$ as well. Similarly, for the $(N+1)$-electron system, if we assume that the extra electron is placed in state $\psi_a^0$, we have

$$E_C^{(N+1)} = \frac{1}{2} \sum_{j=1}^{N+1} \sum_{j'=1}^{N+1} e_{jj'}^{(N+1)a} , \tag{15}$$

where the $(N+1)$th term in the sum has $j = a$. The quantity $e_{jj'}^{(N+1)a}$ is as in Eq. (12), except that the sums over $b$ and $b'$ do not include $b = a$ or $b' = a$.

We can now determine the corrections to the HF bands as given by Eq. (10). We introduce a notation which will soon become clear, and write

$$\epsilon_i = \epsilon_i^0 + \mathcal{E}_i^{(N-1)}(h) + \mathcal{E}_i^{(N)}(e) , \tag{16a}$$

$$\epsilon_a = \epsilon_a^0 + \mathcal{E}_a^{(N)}(h) + \mathcal{E}_a^{(N+1)}(e) , \tag{16b}$$

where

$$\mathcal{E}_i^{(N)}(e) = \sum_{\substack{j=1 \\ j\neq i}}^{N} e_{ij}^{(N)} , \tag{17a}$$

$$\mathcal{E}_a^{(N+1)}(e) = \sum_{j=1}^{N} e_{ij}^{(N+1)a} , \tag{17b}$$

$$\mathcal{E}_i^{(N-1)}(h) = \frac{1}{2} \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{\substack{j'=1 \\ j\neq i}}^{N} (e_{jj'}^{(N)} - e_{jj'}^{(N-1)i}) , \tag{17c}$$

$$\mathcal{E}_a^{(N)}(h) = \frac{1}{2} \sum_{j=1}^{N} \sum_{j'=1}^{N} (e_{jj'}^{(N+1)a} - e_{jj'}^{(N)} . \tag{17d}$$

These expressions appear complicated, but they have a straightforward interpretation: $\mathcal{E}_x^{(M)}(e)$ is the self-energy of an electron when it occupies the one-electron HF state $x$, and the total number of electrons in the system is $M$. By analogy, $\mathcal{E}_x^{(M)}(h)$ is the total change in self-energies of the $M$ electrons when the electron occupying state $x$ is removed. It is thus referred to as the self-energy of a hole. In view of the definition of the quantities $e_{ij}^{(M)}$, it becomes clear that these self-energies arise from virtual scattering of an electron into the empty one-electron states (or hole into the occupied one-electron states), while another virtual excitation is created in order to conserve momentum. This yields the picture of an electron or hole which is dressed with virtual excitations of the electronic system, and which is called a *quasiparticle* (electronic polaron in ionic crystals). A significant feature of Eq. (16) is that, in general, any HF one-electron energy state, whether it is occupied or vacant in the HF ground state, must be corrected successively by the self-energy of an electron and then by a hole present in that state. Physically, this makes sense; the correlation energy is a sum of pair correlations [Eq. (11)]. We can think of the $e_{jj'}$ as correlation bonds between pairs of electrons. When an electron is removed, two things happen:

(i) all the bonds between this one electron and all the other electrons are broken. This is the electron self-energy in the $N$-electron system $\mathcal{E}_i^{(N)}(e)$; (ii) the bonds among all the $N-1$ electrons left behind change a little. All the changes together are the hole self-energy in the $(N-1)$-electron system, $\mathcal{E}_i^{(N-1)}(h)$. Similarly, when an electron is added, all the bonds it establishes constitute the electron self-energy in the $(N+1)$-electron system, and all the changes in the bonds of the $N$ electrons is the hole self-energy in the $N$-electron system. The number of electrons, $N$, $N+1$, or $N-1$ is very crucial, as we shall soon see.

There is one more point worth noting about Eqs. (16). To second order of perturbation theory, Eq. (16a) is exact for the ionization energy of an electron for a system of *any* size, whether it is an atom, molecule, or an insulating or metallic crystal. Similarly, Eq. (16b) gives the electron affinity for any system. In the next few sections, we will see how different approximations apply to different systems. For example, we find that for the ionization energy [Eq. (16a)], the electron self-energy is the dominant correction in atoms and small molecules. For wide-gap insulators, we have the other extreme, namely, only the hole self-energy is important. Finally, for metals, both corrections are equally important. We treat insulators in Sec. IV, and metals in Sec. V. Atoms and molecules are discussed in the Appendix.

## IV. INSULATORS AND WIDE-GAP SEMICONDUCTORS

In insulators, the following approximation to Eq. (16) has been implicitly assumed thus far[10,13]:

$$\epsilon_i = \epsilon_i^0 + \mathcal{E}_i^{(N-1)}(h)\,, \tag{18a}$$

$$\epsilon_a = \epsilon_a^0 + \mathcal{E}_a^{(N+1)}(e)\,. \tag{18b}$$

Toyozazawa's[12] electronic-polaron model has been shown by Kunz[13] to be a method for approximately evaluating $\mathcal{E}_i^{(N-1)}(h)$ and $\mathcal{E}_a^{(N+1)}(e)$. Hermanson's[14] plasmon model is an alternative model for evaluating the same terms.[23] Here we discuss the conditions of validity for Eq. (18), and arrive at some conclusions about Eq. (18) which are independent of the method used to calculate the self-energies.

We go back to Eq. (17) and the definitions of the quantities $e_{jj'}^{(M)}$. First we examine the self-energies that are retained in Eq (18) which become

$$\mathcal{E}_i^{(N-1)}(h) = \sum_{\substack{j=1\\ j\neq i}}^{N} \sum_{\substack{j'=1,\\ j'\neq i}}^{N} \sum_{b>N}^{N} \frac{|\langle jj'|R|ib\rangle|^2}{(\epsilon_b^0+\epsilon_i^0)-(\epsilon_j^0+\epsilon_{j'}^0)}\,, \tag{19a}$$

$$\mathcal{E}_a^{(N+1)}(e) = -\sum_{j=1}^{N} \sum_{\substack{b>N\\ b\neq a}} \sum_{\substack{b'>N\\ b\neq a}} \frac{|\langle ja|R|bb'\rangle|^2}{(\epsilon_b^0+\epsilon_{b'}^0)-(\epsilon_a^0+\epsilon_j^0)}\,. \tag{19b}$$

We first concentrate on the state $i$ being the top of the valence bands, and the state $a$ being the bottom of the conduction bands. In this case, we note that in both Eqs. (19a) and (19b) above, the smallest energy denominator is of the order of the Hartree-Fock energy gap $E_g^0$ between the valence and conduction bands. If we now examine the two self-energies which are dropped from Eq. (16) to Eq. (18), which are

$$\mathcal{E}_i^{(N)}(e) = -\sum_{\substack{j=1\\ j\neq i}}^{N} \sum_{b>N} \sum_{b'>N} \frac{|\langle ji|R|bb'\rangle|^2}{(\epsilon_b^0+\epsilon_{b'}^0)-(\epsilon_i^0+\epsilon_j^0)}\,, \tag{19c}$$

$$\mathcal{E}_a^{(N)}(h) = \sum_{j=1}^{N} \sum_{j'=1}^{N} \sum_{\substack{b>N\\ b\neq a}} \frac{|\langle jj'|R|ab\rangle|^2}{(\epsilon_b^0+\epsilon_a^0)-(\epsilon_j^0+\epsilon_{j'}^0)}\,, \tag{19d}$$

we note that in these two expressions, the smallest energy denominator is of the order of $2E_g^0$; the electron or the hole would have to scatter across the gap. Thus, if the terms (19b) and (19c) are dropped, then in calculating Eqs. (19a) and (19b) the electron or hole should be allowed to scatter only within an energy range less than $E_g^0$. (Note that this does not rule out interband scattering in general, but only scattering across the fundamental gap). This would allow a direct test of the validity of Eq. (18): If scattering of the electron or hole to energies larger than $E_g$ is computed and found to have a significant contribution to the self-energies in Eq. (18), the approximation (18) is not valid. One would expect this to happen in semiconductors with a small gap and, of course, in semimetals and metals where the gap vanishes. Even in insulators with a wide gap, however, approximation (18) cannot be expected to be altogether adequate. Clearly, if scattering by energies more than $E_g^0$ is omitted, the electrons in full core bands would not polarize when a hole is present in the valence band or in one of the core bands.

We conclude that approximation (18) is altogether bad for small-gap semiconductors and metals. For wide-gap insulators, it generally adequately describes correlation interactions with the electrons of the valence bands. It is not adequate for correlation interactions with core-band electrons. In this section, we confine our attention to the cases when approximation (18) is adequate. We study a number of general properties of the self-energy corrections to the HF energy bands which follow directly from this approximation, but we do not depend on any particular model for calculating them. Some of the results have been arrived at previously through specific *models*[12-14,24] which implicitly assumed approximation (18).

### A. Valence bands

We first examine the case in which the width of the HF valence bands is *less* than $E_g^0$. From the form of Eq. (19a) one immediately infers that, for all points in these bands, the energy denominator is *always* positive; the corresponding self-energy is, therefore, also positive, and the HF bands move *up* on the absolute energy scale.

As we noted earlier, for the top of the valence band, the smallest energy denominator is of order $E_g^0$. For points below the top, the energy denominators are less than $E_g^0$ for scattering to higher energies. Assuming that these terms dominate (the matrix element might alter this), we have the following consequence: as we move toward the bottom of the valence bands, the self-energies become larger and the HF levels move up more than the top levels. This is illustrated in Fig. 2. The net result is a narrowing of the valence bands. This is in agreement with results of actual calculations based on the electronic-polaron model, but we see here that it is a model-independent result. Matrix-element effects could, of course, alter the picture and result in smaller self-energies for the bottom of the valence band, the outcome being a net widening of the bandwidth. This seems to be unlikely, however.

An additional comment of interest is that for the *top* of the valence band, scattering near the top is dominant, so that an effective-mass expansion of the band energy of the form $\hbar^2k^2/2m^*$ (or equivalent anisotropic forms) may be adequate. On the other hand, for the *bottom* of the valence band, scattering near the *top* is again dominant and an effective-mass expansion would not be appropriate at all.

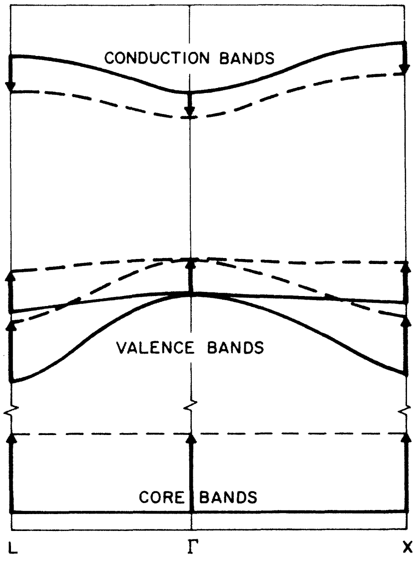

FIG. 2. Effect of correlation on the Hartree-Fock energy bands (solid lines) in an insulator. The dashed lines are the correlated bands.

Finally, we examine the case of HF valence bands for which the bandwidth is *larger* than $E_g^0$. In this case, the self-energy expressions blow up for points which lie an energy $\geq E_g^0$ below the top; the energy denominator can be zero. This simply means that the form of perturbation theory we used is inadequate to describe such cases. In fact, approximation (18) itself is on shaky grounds. One might still expect similar qualitative results such as narrowing of bands. By simulating the excitation spectrum of the crystal with a "model" spectrum, one might even be able to avoid the singularity. We will see how this can be done in Sec. IV E below, and in Sec. V, which is on metals.

### B. Core bands

The core bands are very simple because they are generally flat, i.e., the bandwidth is negligible compared with $E_g^0$. The self-energy corrections are similar to the case of valence bands which are narrower than $E_g^0$, and hence they are always positive. Because of their flatness, and the fact that they are farther than $E_g^0$ from other bands, their self-energy corrections will in general be *larger* than those of the top of the valence band. In both cases the smallest energy denominators are equal to $E_g^0$, but there are *more* of them in the case of a flat band. (Flatter bands have larger effective masses, and thus the result "larger effective mass implies larger self-energies" is again model-independent, barring unexpected matrix-element effects. Hermanson[14] arrived at this conclusion with his model calculation of self-energies.)

### C. Conduction bands

Conduction bands, of course, form a continuum. From any particular point in these bands, scattering can again be allowed within a range extending less than $E_g^0$ on both sides, in accordance with the conditions of approximation (18). For the bottom of the conduction band and for points within a distance $E_g^0$ from the bottom, Eq. (19b) reveals again that the energy denominators are always positive. This makes the self-energy corrections always negative, which means that these conduction bands always move down on the energy scale. Again, this result is familiar from model calculations of self-energies.[12–14,24] For the conduction bands of higher energies, the perturbation expressions blow up again. A "model" might again save the day, and one can argue that the self-energies at high energies go to zero (Sec. V).

For the bottom of the conduction band, the smallest energy denominator is equal to $E_g^0$ as it was for the top of the valence band. Ignoring matrix-element effects again, we can conclude that the self-energy correction is larger when the minimum is flat than when it is steep. Since, in general, conduction-band effective masses are smaller than valence-band effective masses (valence bands are flatter), electron self-energies would in general be smaller. This has again been borne out from model calculations.[12–14,24]

For points above the minimum, scattering to the neighborhood of the minimum is again more important (energy denominators are smaller than $E_g^0$) so that, for example, the flatness of the band at $L$ might not determine the relative size of the self-energy correction at $L$ (assuming a minimum at $\Gamma$). If matrix-element effects do not change the picture radically, we would again expect that points of higher energy have larger self-energy corrections, as illustrated in Fig. 2. This cannot be altogether true, of course, since at very high energies self-energies ought to vanish. Matrix elements may be the ones to bring about the switch. The fact that a switch from increasing to decreasing self-energy corrections *must* occur, lends support to the speculation that electron self-energies don't vary appreciably over the range of energies of interest. Overhauser's[16] model for metals (Sec. V) shows that electron self-energies for the empty bands increase for a while, and then make a fairly abrupt switch and start decreasing, heading toward zero. A similar effect is more likely to happen in insulators. In fact, Toyozawa's electronic-polaron model shows that the effective mass of an electron is *enhanced* by self-energy effects. This means that the band minimum becomes flatter, in agreement with our general result that points of higher energy move down *more* than the minimum. We can thus end this subsection with the conclusion that the general Eq. (19a) would indicate a downward movement of the conduction bands, with points of higher energy moving more than the minimum. Only particular calculations can show whether the movement is essentially rigid or not. So far, model calculations seem to favor almost rigid motion of conduction bands, at least for the energies of interest.

### D. Interband transitions

We have thus far studied the general trends of correlation corrections on HF bands. We now examine the effect of these corrections on interband transitions. There are two cases of interest: (i) excitation of an electron from an occupied band (core or valence) to the empty conduction bands; and (ii) transition of an electron from a valence band to a state in a core that happens to be vacant. If we choose to think in terms of transitions caused by interactions with an electromagnetic radiation field, (i) corresponds to the absorption of photons and (ii) to the emission of photons.

In the case of absorption, the transition energy is given by

$$\hbar\omega_{\text{abs}} = \epsilon_a - \epsilon_i , \tag{20}$$

so that

$$\hbar\omega_{\text{abs}} = (\epsilon_a^0 - \epsilon_i^0) + (\mathcal{E}_a(e) - \mathcal{E}_i(h)) , \tag{21}$$

where we dropped the superscripts on the self-energies for simplicity. This is the expression originally discussed by Fowler[10] for the optical gap. Since we have found $\mathcal{E}_a(e) < 0$ and $\mathcal{E}_i(h) > 0$, we recover the well-known result that HF absorption thresholds are reduced by correlation effects.

We now turn to the emission process during which an electron drops from a valence-band level to a core-band level. Both these levels belong to the occupied space of the HF manifold so, according to approximation (18), both are corrected by *hole* self-energies. Using $\epsilon_{i_v}$ and $\epsilon_{i_c}$ for the valence- and core-band levels, respectively, we get

$$\hbar\omega_{\text{emis}} = \epsilon_{i_v} - \epsilon_{i_c} , \tag{22}$$

so that

$$\hbar\omega_{\text{emis}} = (\epsilon_{i_v}^0 - \epsilon_{i_c}^0) + (\mathcal{E}_{i_v}(h) - \mathcal{E}_{i_c}(h)) . \tag{23}$$

We note an important new result. Since the two-hole self-energies are both positive, they will tend to cancel each other. This means that correlation corrections to emission energies may not be significant. As we saw earlier, core-hole self-energies are likely to be larger, in which case the HF transition energy is reduced by correlation. It is conceivable, however, that core-hole self-energies may be smaller, in which case the HF transition energy is increased by correlation.

Finally, we observe that by writing the corresponding expressions for $\hbar\omega_A$, $\hbar\omega_B$, and $\hbar\omega_C$ of Fig. 1 using Eqs. (21) and (23), relation (8) is satisfied.

### E. Models

Equations (19a) and (19b) have not been evaluated in real cases. Examination of Eq. (19b), for example, reveals that it can be interpreted as an interaction energy, to second order, between the electron and a collection of virtual particles which can take on energies equal to $\epsilon_p = \epsilon_{b'}^0 - \epsilon_j^0$, and whose wave functions are given by the products $\psi_{b'}^0 \psi_j^0 = \psi_p$. The electron can scatter from state $\epsilon_a^0$ to states $\epsilon_b^0$ via the creation of a virtual particle. Equation (19b) becomes

$$\mathcal{E}_a(e) = -\sum_{\substack{b>N \\ b\neq a}} \sum_p \frac{\langle ja|R|bb'\rangle}{\epsilon_b^0 + \epsilon_p - \epsilon_a^0} . \tag{24}$$

By imposing conservation of crystal momentum, and recalling that $a$ and $b$ stand for $nk$ and $l, k+q$, $p$ is found to stand for a band index (let $p$ denote this band index) and a wave vector which must be $q$. Hence

$$\mathcal{E}_{nk}(e) = -\sum_{l}\sum_{p}\sum_{\substack{q \\ (l,\,k+q \neq nk)}} \frac{|V_{lp}(q)|^2}{\epsilon^0_{l,k+q} + \epsilon_{pq} - \epsilon^0_{nk}}\,, \qquad (25)$$

where we have written $V_{lp}(q)$ for the matrix element. In a similar manner, the following expression is found for a hole self-energy:

$$\mathcal{E}_{nk}(h) = \sum_{l}\sum_{p}\sum_{\substack{q \\ (l,\,k+q \neq nk)}} \frac{|V_{lp}(q)|^2}{\epsilon^0_{l,k+q} - \epsilon_{pq} - \epsilon^0_{nk}}\,. \qquad (26)$$

In Eq. (25) the sum over $l$ is over empty bands; in Eq. (26) the sum over $l$ is over occupied bands.

The electronic-polaron model of Toyozawa[12] and Kunz[13] takes the virtual particles to be longitudinal excitons, and restricts attention to one band with no dispersion. Hermanson's model takes the virtual particles to be plasmons. In both of these models, virtual excitations of only the valence electrons are included; these are handled adequately by linear response (dielectric theory). Virtual excitation of core electrons (resulting in core polarizations) are entirely neglected, and in fact are not calculable by linear-response theory. As we saw earlier, they don't even fall within the validity limits of approximation (18). They will be discussed in detail in Sec. VI.

The details of the two models may be found in the respective papers.[12–14,24] In both cases, the coupling matrix elements are determined so as to reproduce the dielectric properties (in the linear limit) of the insulator. One prediction of the electronic-polaron model[12,13,24] deserves more attention here. As we mentioned in passing earlier, it predicts a definite enhancement of the particle's effective mass, which means that the band minimum becomes flatter. Toyozawa finds this enhancement to be by a factor of $\frac{1}{6}\alpha$ where $\alpha$ is the polaron coupling constant. In alkali halides $\alpha$ is $\sim 0.5$,[12] so that the mass enhancement is about 10%. This means that levels slightly above the conduction-band minimum move down by as much as 10% more than the minimum. It seems likely then, that levels farther away from the minimum at $\Gamma$ (say), as we go toward $X$ or $L$, would move down by over 10% more than the minimum. Such a result is evident in the calculations of Ref. 13. This calls for more accurate calculations of correlation corrections to the conduction bands.

Finally, we note one interesting difference in the two models. In the electronic polaron, the minimum excitation energy is the optical exciton, i.e., it is of order $E_g$. We recall that if the Hartree-Fock valence band were wider than $E_g$, the perturbation expression blows up when applied to correct the bottom of the band. In the plasmon model, the minimum excitation energy is the plasma frequency, which is of order $1.5\,E_g$. Thus, through the artifice of the model, one can use the perturbation expressions for valence bands which are wider than $E_g$. This same artifice proves to be extremely valuable in the case of metals (Sec. V).

## V. METALS

The situation in metals is entirely different. There is no gap separating occupied states from virtual states. First, this makes approximation (18) completely bad; both terms in Eqs. (16a) and (16b) must be taken into account on an equal footing. Second, disaster occurs in all cases, because there are always energy denominators in Eq. (19) which vanish. This is a well-known problem.[25] The singularity is found to be logarithmic.

One can get around this difficulty by the artifact used in Overhauser's model[16]: One can go ahead and interpret the expressions for the self-energies as interactions with a set of virtual particles and write equations like (25) and (26) for all four of the self-energies of interest appearing in Eq. (16). Then, if one assumes that these imaginary particles can take on nonzero energies larger than a finite energy, the singularity is removed. Overhauser's model takes these particles to be plasmons[26] whose smallest energy is given by $\hbar\omega_p$, where $\omega_p$ is the plasma frequency. The model works well. In Fig. 3 we show the results for a number of metallic densities to energies high enough to illustrate the point we made earlier: electron self-energies at first keep getting larger in absolute magnitude, but a switch occurs at some energy, so that, finally, the correlation correction goes to zero at very high energies.

There are a few interesting observations to be made. First we note that *if* approximation (18) were to be valid, it would mean that the top of occupied levels (Fermi level $\epsilon^0_F$) moves up while the bottom of empty levels (infinitesimally above $\epsilon^0_F$) moves down. Thus a level at $\epsilon^0_F - \delta$ would undergo a positive correction, and a level at $\epsilon^0_F + \delta$ would undergo a negative correction. In the limit $\delta \to 0$, the correction would have to go to zero, since in normal metals no gap exists at the Fermi level. Thus the expression for the correlation energy would go through zero at $\epsilon^0_F$. We don't expect this to be so, however, because Eq. (18) is not valid; both occupied and vacant states can move either up or down in principle. This is borne out by Overhauser's model. The Fermi level is seen to move down by about 1–1.5 eV. This is a measure of how much Eq. (18) breaks down in that case. We also note that the bottom of the band at $k = 0$ moves up for a net *narrowing* of the HF band. The Overhauser model has been

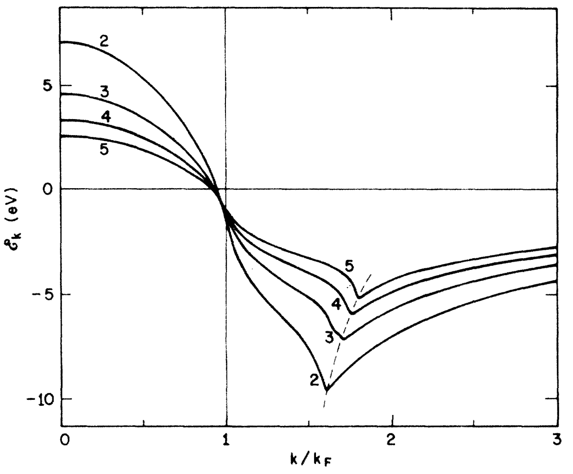

FIG. 3. Correlation correction to Hartree-Fock bands for metals in the free-electron limit using Overhauser's model (Ref. 16). The number on each curve is the value of $r_s$, the radius of an average spherical volume per electron in Bohr units. Note that at some point at energies above the Fermi level, the correlation energy turns up toward zero.

used by the present authors to correct the *ab initio* HF bands for metallic calcium with a fair amount of success.[8]

## VI. SHORT-RANGE CORRELATIONS

Under the category of short-range correlations we will study effects that go beyond the approximations which lead to the polaron and plasmon models discussed in Secs. IV and V. These are predominantly polarizations of core-band electrons resulting from virtual excitations with energy denominators larger than $E_g^0$. For such processes, approximation (18) ceases to be appropriate. We call these short-range effects because the models used to calculate the correlation interactions with valence-band electrons neglect scatterings of short wavelengths. This is clearly true for the electronic-polaron model: only one band of excitons is included, and thus $q$ is restricted in the range of the first Brillouin zone. Larger $q$'s—short wavelengths—are left out; if $q$ is allowed outside the first zone, it would correspond to more than one band of excitons. In the case of the plasmon model, some kind of short-range effects are included through the dispersion of the dielectric function. Such a correction could be included in the polaron model as well. In either case, one would conclude that dispersion in the dielectric function would make the coupling constant and, hence, the self-energies *smaller*. Use of effective mass in the plasmon model means that only small values of $q$ are sampled anyway, so that short-wavelength effects are again excluded. Dispersion in the dielectric function would thus not alter the self-energies appreciably.

We might note, before we begin, that long-range correlation corrections calculated by the electronic polaron method have generally been adequate to account for the shifts of the HF valence and conduction bands, and produce agreement with experimental values of optical gaps. In the case of LiF, this was not true; core-electron polarizations were estimated by atomic models, and agreement with experiment was obtained. In this section we present a formal study of these corrections.

The configuration-interaction formalism used in the previous sections, though good in principle, is not very suitable for the effects of interest here. They are, instead, conveniently described by a formulation similar in spirit to the formalism introduced by Frenkel[27,28] for exciton states in insulators. In this approach, the ground state of the system is written

$$\Psi_g = \mathfrak{A}\prod_{\mu=1}^{N_A} \phi_\mu^0 , \tag{27}$$

where $\phi_\mu^0$ is the ground-state many-electron wave function of the $\mu$th atom, and $N_A$ is the total number of atoms. If the $\phi_\mu^0$ are taken to be free-atom wave functions, $\Psi_g$ for the crystal would have to be a linear combination of functions like Eq. (27). On the other hand, the $\phi_j^0$ may be thought to be built from Wannier functions of the crystal, in which case Eq. (27) is adequate. We will have this in mind, but will use the term "atomic" for simplicity and clarity in the motivation.

The ground-state energy of the crystal containing $N$ electrons can then be written

$$E^{(N)} = \langle \Psi_g | H^{(N)} | \Psi_g \rangle , \tag{28}$$

where $H^{(N)}$ is the $N$-electron Hamiltonian. For the Frenkel exciton, one then proceeds to construct an *excited* state of the *N-electron* system. In the problem of interest here, as is clear from Eq. (6), we instead construct the *ground* states of the ($N$ + 1)-*and* ($N$ − 1)-*electron* systems, in order to describe the bottom of the conduction band and top of the valence band, respectively. For example, for the ($N$+ 1)-electron system, we first define

$$\Phi_\nu^- = \mathfrak{A}\,\phi_\nu^- \prod_{\mu\neq\nu} \phi_\mu^0 , \tag{29}$$

where $\phi_\nu^-$ is the total wave function of the ground state of a negatively charged ion at the $\nu$th site. Then, in order to satisfy crystalline symmetry, we construct the Bloch-sum-type state

$$\Psi_{a\vec{k}'} = \frac{1}{\sqrt{N_A}} \sum_{\nu=1}^{N_A} e^{i\vec{k}'\cdot\vec{R}_\nu} \Phi_\nu^- , \tag{30}$$

so that

$$E^{(N+1)} = \langle \Psi_{a\vec{k}'} \,|\, H^{(N+1)} \,|\, \Psi_{a\vec{k}'} \rangle . \tag{31}$$

The index $a$ labels conduction bands. Finally, from Eq. (6b) we get

$$\epsilon_{a\vec{k}'} = \langle \Psi_{a\vec{k}'} \,|\, H^{(N+1)} \,|\, \Psi_{a\vec{k}'} \rangle - \langle \Psi_g \,|\, H^{(N)} \,|\, \Psi_g \rangle . \tag{32}$$

Similarly, for the $(N-1)$-electron system, we define

$$\Phi_\lambda^+ = \mathcal{A}\, \phi_\lambda^+ \sum_{\mu \neq \lambda}^{N_A} \phi_\mu^0 , \tag{33}$$

where $\phi_\lambda^+$ is the wave function of a positively charged ion at the $\lambda$th site. Then

$$\Psi_{i\vec{k}} = \frac{1}{\sqrt{N_A}} \sum_{\lambda=1}^{N_A} e^{i\vec{k}\cdot\vec{R}_\lambda} \Phi_\lambda^+ , \tag{34}$$

where $i$ labels valence or core bands. Finally, from Eq. (6a),

$$\epsilon_{i\vec{k}} = \langle \Psi_g \,|\, H^{(N)} \,|\, \Psi_g \rangle - \langle \Psi_{i\vec{k}} \,|\, H^{(N-1)} \,|\, \Psi_{i\vec{k}} \rangle . \tag{35}$$

The first thing we must show for the above formalism is that, if we neglect polarization, we recover the Hartree-Fock approximation and Koopmans's theorem. We do this for the case of the extra electron. If we neglect polarization of the occupied orbitals, we can write

$$\bar{\phi}_\nu^- = \chi_\nu(\vec{r})\, \phi_\nu^0 , \tag{36}$$

where $\chi_\nu(\vec{r})$ is the Wannier function at the bottom of the conduction band (first virtual orbital of the atom described by $\phi_\nu^0$). The bar on $\bar{\phi}_\nu^-$ denotes that polarization is not included. Using Eq. (36) into (29), and then in Eq. (30), and comparing with Eq. (27), we can write the *unpolarized* equivalent of Eq. (30) as

$$\bar{\Psi}_{a\vec{k}'} \simeq \psi_{a\vec{k}'}^0(\vec{r})\, \Psi_g , \tag{37}$$

where

$$\psi_{a\vec{k}'}^0(r) = \frac{1}{\sqrt{N_A}} \sum_\nu e^{i\vec{k}'\cdot\vec{R}_\nu} \chi_\nu(\vec{r}) , \tag{38}$$

is clearly the HF Bloch function of the extra electron in the conduction band. With Eq. (37) in Eq. (32), we see that everything reduces to the Koopmans theorem and thus

$$\epsilon_{a\vec{k}'} = \epsilon_{a\vec{k}'}^0 . \tag{39}$$

The proof for the hole state is analogous, but slightly more involved.

Having shown this, we immediately conclude that the electron-band energy is given by

$$\epsilon_{a\vec{k}'} = \epsilon_{a\vec{k}'}^0 + \mathcal{E}_{a\vec{k}'}^0 , \tag{40}$$

where, from Eq. (32),

$$\begin{aligned}\mathcal{E}_{\vec{k}'} = {} & \langle \Psi_{a\vec{k}'} \,|\, H^{(N+1)} \,|\, \Psi_{a\vec{k}'} \rangle \\ & - \langle \bar{\Psi}_{a\vec{k}'} \,|\, H^{(N+1)} \,|\, \bar{\Psi}_{a\vec{k}'} \rangle .\end{aligned} \tag{41}$$

We note that $\mathcal{E}_{a\vec{k}'}$ stands for the sum $\mathcal{E}_a^{(N)}(h) + \mathcal{E}_a^{(N+1)}(e)$ which appears in Eq. (16b). In the present formalism, such a separation is *not* possible. For simplicity, we will still call $\mathcal{E}_{a\vec{k}'}$ the electron self-energy. Similarly, for the valence and core bands, we get

$$\epsilon_{i\vec{k}} = \epsilon_{i\vec{k}}^0 + \mathcal{E}_{i\vec{k}} , \tag{42}$$

where

$$\mathcal{E}_{i\vec{k}} = \langle \bar{\Psi}_{i\vec{k}} \,|\, H^{(N-1)} \,|\, \bar{\Psi}_{i\vec{k}} \rangle - \langle \Psi_{i\vec{k}} \,|\, H^{(N-1)} \,|\, \Psi_{i\vec{k}} \rangle . \tag{43}$$

Again for convenience we call this the hole self-energy, even though it stands for the sum of the two terms in Eq. (16a).

We note that Eqs. (41) and (43), in principle, contain all correlation effects, as did the configuration-interaction formalism. In evaluating them, we can seek a limit in which only short-range effects are included. Then the corrections obtained from the polaron or plasmon models of the previous sections will be additive with the new corrections.

We do this for Eq. (43) by writing it using Eq. (34),

$$\begin{aligned}\mathcal{E}_{i\vec{k}} = {} & \frac{1}{\sqrt{N_A}} \sum_{\lambda=1}^{N_A} \sum_{\lambda'=1}^{N_A} e^{i\vec{k}\cdot(\vec{R}_\lambda - \vec{R}_{\lambda'})} \\ & \times \left( \langle \bar{\Phi}_\lambda^+ \,|\, H^{(N-1)} \,|\, \bar{\Phi}_{\lambda'}^+ \rangle - \langle \Phi_\lambda^+ \,|\, H^{(N-1)} \,|\, \Phi_{\lambda'}^+ \rangle \right)\end{aligned} \tag{44}$$

and note that the limit of interest occurs when overlaps are negligible. This is thus particularly suited for core states. Thus, neglecting all overlaps, in which case $H^{(N-1)}$ becomes a collection of noninteracting atomic/ionic Hamiltonians, we get

$$\mathcal{E}_{i\vec{k}} = \frac{1}{\sqrt{N_A}} \sum_{\lambda=1}^{N_A} \left( \langle \bar{\phi}_\lambda^+ \,|\, H_\lambda^+ \,|\, \bar{\phi}_\lambda^+ \rangle - \langle \phi_\lambda^+ \,|\, H_\lambda^+ \,|\, \phi_\lambda^+ \rangle \right) , \tag{45}$$

where $H_\lambda^+$ is the Hamiltonian of a positive ion at the $\lambda$th site. Defining

$$E_{\text{tot}}^+ = \langle \phi_\lambda^+ \,|\, H_\lambda^+ \,|\, \phi_\lambda^+ \rangle , \tag{46}$$

$$\bar{E}_{\text{tot}}^+ = \langle \bar{\phi}_\lambda^+ \,|\, H_\lambda^+ \,|\, \bar{\phi}_\lambda^+ \rangle , \tag{47}$$

we see that

$$\mathcal{E}_{i\vec{k}} = \bar{E}_{\text{tot}}^+ - E_{\text{tot}}^+ , \tag{48}$$

which is simply the difference in total energy between the unrelaxed and the relaxed ion. It is thus an inherently *positive* quantity, it raises the occupied-band energies, and thus reduces absorption thresholds even further. It can best be calculated by writing Eq. (48) as

$$\mathcal{E}_{i\vec{k}} = (E_{\text{tot}}^0 - E_{\text{tot}}^+) - (E_{\text{tot}}^0 - \bar{E}_{\text{tot}}^+) . \tag{49}$$

The first term is simply the true ionization energy for the atom, whereas the second term corresponds to the eigenvalue approximation for the ionization energy. This is the form of the correction used in Ref. 17. We see that the correction is important in crystals made up of atoms for which Koopmans's theorem is appreciably unsuitable. Such atoms are the first-row elements for which the number of electrons is small. This explains why the correction was necessary for LiF. In fact, the same correction (about 3.4 eV) must be present for the valence bands of all fluorides. For chlorides, on the other hand, the correction is smaller, of order 1.5 eV. In Table I we list estimates of the valence-band hole self-energy corrections obtained from Eq. (49) and published HF calculations for atoms and ions[29,30] for a number of elements. We conclude that these corrections are important in nitrides, oxides, and fluorides.

We emphasize that these are upper-bound estimates.[31] The valence atomic orbitals are actually smeared out in the crystals, and don't polarize the core orbitals as much. A similar approach can be worked out for conduction-band states. For these cases, however, overlaps are very large, the electrons are largely excluded from the core regions, and their presence does not polarize the core electrons appreciably. For first-row elements, about 1 eV would be an upper bound for such a correction, and for larger elements it should be negligible.

Finally, for core states, the approximation of neglecting overlaps works best, and estimates in terms of Eq. (49) are expected to be quite accurate.[31] In Fig. 4 we plot the size of these corrections for a number of atoms, and we observe that they increase in magnitude with increasing atomic number $Z$. These estimates have already been used in the case of MgO (Ref. 7) to correct the HF x-ray transition energies. With the additional corrections arising from the long-range correlation effects discussed in Sec. IV, the final theoretical values were found to agree exceedingly well with experimental values. In Table II we reproduce the results of that calculation as an illustrative example.

TABLE I. Estimates of short-range-correlation corrections to valence-band-hole self-energies.

| Material | Self-energy correction (eV) |
|---|---|
| Fluorides | 3.4 |
| Oxides | 4.9 |
| Nitrides | 4.7 |
| Clorides | 1.5 |
| Sulfides | 1.9 |
| Phosphides | 2.6 |
| Neon | 2.2 |
| Argon | 1.3 |
| Diamond | 1.0 |
| Silicon | 0.4 |

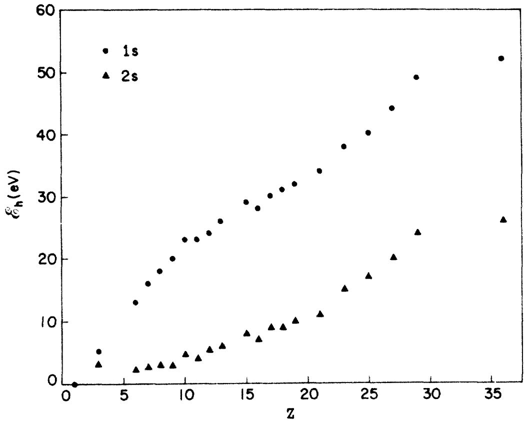

FIG. 4. Estimates of short-range correlation effects due to core-band polarizations. $Z$ is the atomic number of the atom from which a band of interest originates.

## VII. WAVE FUNCTIONS AND OSCILLATOR STRENGTHS

We have thus far concentrated on the effect of correlation on the band-to-band excitation energies. Experimentally, however, one obtains both the transition energies and the strength of various transitions by measuring absorption coefficients or the intensity of emitted photons as a function of energy. Theoretically, these quantities are proportional to the imaginary part of the dielectric function $\epsilon_2(\omega)$. This is given by

$$\epsilon_2(\omega)=\frac{e^2\hbar^2}{m}\sum_{ij}\int\frac{d^3k}{(2\pi)^3}\,\frac{f_{ij}(\vec{k})}{\epsilon_j(\vec{k})-\epsilon_i(\vec{k})}\times\delta(\epsilon_i-\epsilon_j-\hbar\omega), \tag{50}$$

where

$$f_{ij}(\vec{k})=\frac{2}{3m}\,\frac{|\langle\psi_{j\vec{k}}|\vec{p}|\psi_{i\vec{k}}\rangle|^2}{\epsilon_j(\vec{k})-\epsilon_i(\vec{k})}\;. \tag{51}$$

The quantity $f_{ij}(\vec{k})$ is the oscillator strength for the transition between bands $i$ and $j$. If $f_{ij}(\vec{k})/[\epsilon_j(\vec{k})-\epsilon_i(\vec{k})]$ is assumed constant, then $\epsilon_2(\omega)$ becomes proportional to the joint density of states of bands $i$ and $j$. As is well known, the position of peaks and valleys in $\epsilon_2(\omega)$ is almost entirely determined

TABLE II. Transition energies (in eV) from the top of the valence band to the core levels of Mg and O in MgO.

| Core level[a] | $\Delta E_{HF}$ | $\Delta\mathscr{E}$ | $\Delta E_{HF}+\Delta\mathscr{E}$ | Experiment[b] | % error |
|---|---|---|---|---|---|
| O $L_1$ | 30.6 | 2.5 | 28.1 | 22–23 | 22–27% |
| O $K$ | 557.7 | 16.6 | 541.1 | 528.5 | 2% |
| Mg $L_{2,3}$ | 49.1 | 1.9 | 47.2 | 46.2 | 2% |
| Mg $L_1$ | 89.9 | 1.9 | 88.0 | 85.0 | 3% |
| Mg $K$ | 1322.6 | 20.5 | 1302.1 | 1299.8 | ... |

[a] Spectroscopic notation is used for the core bands.
[b] Reference 32.

by the joint density of states. Subsequent inclusion of $f_{ij}(\vec{k})$ generally alters the height of peaks and the depth of valleys, but does not shift their positions appreciably.

Thus, having computed a Hartree-Fock band structure for a crystal, and having corrected the bands for correlation effects, a joint density of states ought to predict the positions of peaks and valleys in $\epsilon_2(\omega)$ quite accurately. In order to compute a theoretical $\epsilon_2(\omega)$, one needs the oscillator strengths [Eq. (51)]. Use of one-electron Bloch functions for such a calculation cannot, however, be expected to yield good agreement with experiment. This can be seen as follows: as we have seen in Secs. III–V, a large part of the correlation correction to the Hartree-Fock bands is obtained by a polaron-type model. The correction is obtained by *second*-order perturbation theory (the first-order correction vanishes) from Eqs. (19) or (25) and (26). To the *same* order in perturbation theory, the wave function is given by

$$\Psi_{\vec{k}} = \psi^0_{\vec{k}}(\vec{r}) + \sum_{\vec{K}} \frac{V_{\vec{K}}}{\epsilon^0_{\vec{k}} \pm \hbar\omega_{\text{ex}} - \epsilon^0_{\vec{k}-\vec{K}}} \psi^0_{\vec{k}-\vec{K}}(\vec{r})\, X_{\vec{K}}\,, \qquad (52)$$

where $X_{\vec{K}}$ is the wave function of the exciton (or plasmon) of wave vector $\vec{K}$, which is a many-electron function. Thus $\Psi_{\vec{k}}$ is also a many-electron function which describes the quasiparticle (the electronic polaron). Equation (52) makes clear the fact that it is the quasiparticle that has a definite wavevector $\vec{k}$, while the bare particle, electron or hole, describes by $\psi_{\vec{k}}(\vec{r})$, constantly shares part of its momentum with virtual excitons. Thus, since the corrections [Eqs. (25) and (26)] to the Hartree-Fock energies are important, the correction to $\psi_{\vec{k}}(\vec{r})$ given in Eq. (52) may be expected to be equally important in the evaluation of oscillator strengths.[33] In the cases where short-range correlation effects are also important in correcting the Hartree-Fock energies, one would expect that Hartree-Fock oscillator strengths would be even worse.

This difficulty with oscillator strengths is quite unfortunate; if one could calculate accurate *correlated* oscillator strengths, the result would be an accurate theoretical band-to-band spectrum. By comparing such a spectrum with an experimental spectrum, one could then identify all electron-hole-interaction effects, such as excitons, resonances and antiresonances, which are neglected in the band picture. The *ab initio* computation of these effects is, of course, even harder, and we do not discuss it at all in this paper.

## VIII. CONCLUSIONS

In this paper we have studied the effect of correlation on Hartree-Fock energy bands in the limit in which electron-hole interactions are not included. In this limit the concept of rigid bands, in terms of which excitation energies may be computed remains valid. We have seen that the "correlation corrections" may be formulated in a general way, from which a lot of information may be obtained for the special cases of insulators and metals, without appealing to explicit model calculations. The models that have appeared in the literature were seen to be special cases, and their ranges of validity were studied. We also formulated the problem of short-range correlations, which are not included in the polaron-type models, and gave estimates of their magnitudes.

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## APPENDIX: CASE OF FREE ATOMS

In the main text of this paper, we studied the effect of correlation corrections to Hartree-Fock bands in solids. For free atoms, instead of bands, one has discrete *term values*, namely the eigenvalues of the Fock operator. These eigenvalues are, of course, not true ionization energies. Two corrections must now be applied: (i) corrections which are within Hartree-Fock because Koopmans's theorem is not valid in small systems, and (ii) correlation corrections which go beyond Hartree-Fock. Thus the electron ionization energy may be written as

$$\epsilon_i = \epsilon^0_i + \Delta E_K + \mathcal{E}^{(N-1)}_i(h) + \mathcal{E}^{(N)}_i(e) \qquad (\text{A1})$$

by analogy to Eq. (16a). $\epsilon^0_i$ is again the Hartree-Fock eigenvalue. The quantity $\Delta E_K$ is the correction due to the failure of Koopmans's theorem in a small system. One usually calculates $\epsilon^0_i + \Delta E_K$ by doing a new Hartree-Fock calculation for the ion, and subtracting total energies[29]

$$\epsilon^0_i + \Delta E_K = E^{(N)}_{\text{HF}} - E^{(N-1)}_{\text{HF}}\,. \qquad (\text{A2})$$

The correlation corrections are not conventionally written as in Eq. (A1), but the expression allows us to unify the present study for an arbitrary $N$-electron system. We recall that in the case of insulators we found $\mathcal{E}^{(N-1)}_i(h)$ to be the dominant contribution [$\mathcal{E}^{(N)}_i(e)$ could be dropped], whereas in the case of metals we found both $\mathcal{E}^{(N-1)}_i(h)$ and $\mathcal{E}^{(N)}_i(e)$ to be comparable. In the case of atoms, it is found that, in general, the other extreme holds, namely, $\mathcal{E}^{(N)}_i(e)$ is dominant. In physical terms this is understood if we think of the correlation energy as a sum of "bonds" between pairs of electrons, as we did in Sec. III. The removal of one electron does two things: breaks all the correlation bonds of the one electron [this is

$\mathcal{E}_i^{(N)}(e)$] *and* alters the unbroken bonds [this is $\mathcal{E}_i^{(N-1)}(h)$]. In atoms "breaking of bonds" is more crucial, and empirical studies led to a set of rules for correlation corrections.[34] Note that this always leads to correlation corrections that make the ionization energy larger, since $\mathcal{E}_i^{(N)}(e)$ is always negative. Exceptions to these rules were found[35] and termed "anomalous". The interesting observation here, excluding these anomalies, is that atoms and insulators are the two extreme limits of Eq. (A1) where one or the other self-energy is dominant. Metals are, in some sense, a transition case, since for them both self-energies are comparable.

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