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Three-particle approximation for transition-metal oxides

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Quasiparticle spectra are calculated for NiO and CuO on the basis of band structures obtained within the *ab initio* self-interaction-corrected local-spin density (SIC-LSD) and LSD+U approximations. On-site Coulomb correlations are described by a multiband Hubbard model, which is treated within Igarashi's three-particle approximation. The transition-metal d-state spectral weight is split into a main $d^n\underline{L}$ peak and a d^{n-1} satellite. We show that mean-field band structures in this way can lead to a good description of the experimental photoemission spectra of these compounds. The validity of the three-particle approach is investigated, and it is concluded that the method is best suited for a system which is well orbitally polarized on the mean-field level. [S0163-1829(97)11507-7]

I. INTRODUCTION

During the last three decades band-structure calculations based on the local (spin) density approximation (L(S)DA) to the density-functional theory have been extremely successful in predicting not only ground-state properties (like total energies and magnetic moments), but also excitation spectra of solids.[1] It has long been known, however, that several classes of materials are poorly described by the LDA theory. Prominent examples of LDA failure are band-gap calculations in semiconductors,[2] bandwidths of metals, excited states and magnetic structures of transition-metal oxides,[3] and quasiparticle spectra, as well as total energies and magnetic structures of various systems with partially filled f shells.[4] Since the density-functional theory is formally a ground-state theory, the problems with ground-state properties are, of course, the more disturbing ones. On the other hand, it is an empirical fact that the LDA usually gives good spectral predictions, and it is natural to ask what makes the above-mentioned cases different.

The band-gap problem in semiconductors has to a large extent been resolved by the application of the GW approximation[5] (essentially a perturbative approach). This method has also had some success when applied to transition-metal oxides,[6] but not nearly as impressive as in the semiconductor case. Indeed, the systems are quite different. The oxides are characterized by the presence of incompletely filled d shells, giving rise to a set of narrow bands around the Fermi energy in LDA calculations. It is commonly accepted that the failure of the LDA theory has to do with incomplete screening effects for these d electrons, making the on-site Coulomb repulsion an important parameter.[7,8] This repulsion suppresses the hybridization, since the electrons tend to avoid each other by localizing, and this will in turn make the LDA less adequate, based as it is on correlation effects in a uniform electron gas.

A suitable scheme for studying these systems might thus be based on the Hubbard or Anderson models,[9,10] where on-site Coulomb repulsions are explicitly included in a model Hamiltonian. The parameters of the models would be understood to be renormalized quantities, and their calculation is in principle not trivial. However, it has been shown that good results are obtained from LDA calculations with constrained occupancies.[11] For spectral predictions, many-body calculations on the Anderson impurity model have been used, and good agreement with photoemission data has been obtained.[12,13] On the other hand, ground-state properties, in particular the magnetic structures, have been calculated with success in mean-field schemes like the self-interaction-corrected local-spin-density (SIC-LSD) formalism[14–17] or the LDA+U methods.[8] In both methods one essentially tries to obtain a more correct first-order treatment of the Coulomb repulsion, and they both reproduce the metal-insulator transition as a result of strong orbital polarization. In addition, more or less reasonable values for the band gaps are obtained. However, the comparison with actual photoemission—or inverse-photoemission spectra[18]—is not so good. This is to be expected from mean-field theories since the experimental spectra include various aspects of strong electron-electron correlation effects, such as band narrowing, and well-defined satellite structures clearly separated from the main peaks. In order to test whether the SIC-LSD and LDA+U models of the ground state are compatible with the experimental spectra, it is thus of interest to calculate the many-body corrections to their band structures. This is the primary goal of the present study.

Many-body calculations based on realistic band structures are extremely complicated, and one has to rely on approximations for the self-energy operator. In the present work we will focus attention on an approach particularly suited to the problem at hand, namely the three-particle approximation originally formulated by Igarashi.[19,20] In the three-particle approximation, an initial photoinduced hole may generate a single electron-hole pair, from which it subsequently scatters. Multiple scatterings are allowed, but not the generation of more than one electron-hole pair. The three-particle approximation is inherently nonperturbative, i.e., the theory can be formulated without appealing to a (possibly divergent) series expansion in the interaction strength. Furthermore, it has an exact strong-coupling limit, as shown by Igarashi.[19] We will discuss the range of validity of this approach, and use it to calculate photoemission spectra for NiO and CuO on the basis of SIC-LSD and LSD+U band structures. It will be shown that the mean-field picture of the *ground states* of these materials to a large extent can be reconciled with photoemission data, when many-body effects in the *excited states* are taken into account. Essential for the three-particle approximation to be appropriate is that the Hartree-Fock ground state of the model system is a good approximation of the true ground state. This will only be the case if there is strong orbital polarization, since the available phase space for electron-electron scattering in this way is reduced. In the abovementioned methods such a strong orbital polarization is produced. Eight or nine (for NiO and CuO respectively) metal $3d$ states turn out to be fully occupied, while the remaining are partially filled and strongly hybridized with the O $2p$ states.[15–17,8]

The rest of this paper is organized as follows: In Sec. II the derivation of the multiband three-particle theory is briefly reviewed. For a more thorough discussion we refer to the Appendix, and to the papers of Igarashi[19,20] and of Calandra and co-workers.[21,22] In Sec. III we discuss the range of validity of the method, while in Sec. IV we present our numerical results for the spectra of NiO and CuO. Section V summarizes our conclusions.

II. FORMAL THEORY

In this work we will assume that the quasiparticle spectra of transition-metal oxides are well described by a multiband Hubbard model[9] of the form

$$\hat{H}=\hat{H}_0+\hat{V}, \tag{1}$$

with

$$\hat{H}_0=\sum_{n\mathbf{k}} \varepsilon_{n\mathbf{k}}\hat{c}^{\dagger}_{n\mathbf{k}}\hat{c}_{n\mathbf{k}} \tag{2}$$

and

$$\hat{V}=\tfrac{1}{2}\sum_{\mathbf{R},\alpha\neq\beta} U^{\alpha\beta}(\hat{n}^{\alpha}_{\mathbf{R}}-n^{\alpha}_{\mathbf{R}})(\hat{n}^{\beta}_{\mathbf{R}}-n^{\beta}_{\mathbf{R}}). \tag{3}$$

Here the $\varepsilon_{n\mathbf{k}}$'s are single-particle (band) energies, while the $U^{\alpha\beta}$'s represent the Coulomb repulsion of two particles occupying orbitals α and β on the same site. $\mathbf{R}$ specifies lattice translations, while n and $\mathbf{k}$ label the band index and point in the first Brillouin zone, respectively. α and β are combined orbital and spin indices. $n^{\alpha}_{\mathbf{R}}$ denotes the mean value of the operator $\hat{n}^{\alpha}_{\mathbf{R}}$ in the ground state. We assume that the Hartree-Fock (HF) Coulomb energy is included in the single-particle energies, which is why it is explicitly subtracted in the second term. As mentioned in Sec. I, one should keep in mind that the single-particle energies as well as the interaction parameters (the U's) are renormalized quantities. In particular, we are going to assume that the U parameters are negligible (presumably due to screening effects) except for some limited subset of orbitals, which in the transition-metal oxides will be taken to be the metal $3d$ states.

If the Hubbard model is to be a reasonable approximation to the real solid, it is necessary that the orbitals α and β are well localized on the individual sites, which means that we cannot take them to be just the Wannier orbitals of the bands indexed by n. Instead one must use some kind of atomic orbitals, for instance spherical or cubic harmonics times a radial function not extending beyond nearest-neighbor distance. The Bloch sums of these orbitals will in general not be eigenfunctions of the single-particle Hamiltonian, and this gives the model some additional complications compared with the simple case of a single orbital, which has been widely studied in model calculations. Throughout this paper we shall denote band indices by Roman letters, and atomic orbital indices by Greek letters.

In order to calculate photoemission spectra we must consider the N-electron ground state (N being the number of electrons in the neutral crystal), as well as the spectrum of $N-1$ particle states. In the three-particle approximation to the single-band Hubbard model[19–21] the N-particle ground state is taken to be the mean-field (HF) solution, while the $N-1$ particle states are expanded in the set of states with two holes and one electron added to the ground state. In the multiband case we shall also describe the ground state in this way, and expand the $N-1$ particle states in the set of single hole states $|s\rangle$,

$$|s\rangle=\hat{c}_{n\mathbf{k}_0}|0\rangle, \quad \varepsilon_{n\mathbf{k}_0}\leqslant E_F \tag{4}$$

and states with two holes and one electron, $|t\rangle$,

$$\begin{gathered}|t\rangle=\hat{c}^{\dagger}_{n_1\mathbf{k}_1}\hat{c}_{n_2\mathbf{k}_2}\hat{c}_{n_3\mathbf{k}_3}|0\rangle,\\ \varepsilon_{n_1\mathbf{k}_1}\geqslant E_F, \quad \varepsilon_{n_2\mathbf{k}_2},\varepsilon_{n_3\mathbf{k}_3}\leqslant E_F, \qquad (5)\\ \mathbf{k}_3+\mathbf{k}_2-\mathbf{k}_1=\mathbf{k}_0.\end{gathered}$$

The N-particle HF ground state is denoted by $|0\rangle$. In this way the many-particle problem is effectively reduced to a three-particle one, which may be described by the Faddeev theory.[23] We use the labels s and t as combined indices for single- and three-particle states, respectively. The basic processes that can occur in our subspace are electron-hole scattering and hole-hole scattering. Accordingly, the interaction in Eq. (3) is partitioned as follows:

$$\hat{V}=\hat{V}_e+\hat{V}_h+\hat{V}_{13}. \tag{6}$$

Here $\hat{V}_e$ and $\hat{V}_h$ are the electron-hole and hole-hole scattering terms, respectively. $\hat{V}_{13}$ is the term coupling the single one-particle state to the set of three-particle states.

The central quantity to evaluate is the hole Green's function

$$G^{h}_{n\mathbf{k}_0}(\omega)=\left\langle s\left|\frac{-1}{\overline{\omega}-\hat{H}}\right|s\right\rangle. \tag{7}$$

Here $\overline{\omega}=-\omega+E_0+i\delta$, where E_0 is the N-particle ground-state energy, in the three-particle approximation taken to be the Hartree-Fock energy. From this, the spectral function for angle-resolved photoemission may be obtained as

$$D^{h}_{\mathbf{k}_0}(\omega)=\frac{1}{\pi}\sum_{n} \operatorname{Im}G^{h}_{n\mathbf{k}_0}(\omega). \tag{8}$$

We will primarily concern ourselves with the angle-integrated spectral function given by

$$D^h(\omega)=\sum_{\mathbf{k}} D^h_{\mathbf{k}}(\omega), \tag{9}$$

which gives the total photoemission density of states (DOS). With the definitions

$$R_{tt'}=\left\langle t\left|\frac{1}{\overline{\omega}-(\hat{H}-\hat{V}_{13})}\right|t'\right\rangle \tag{10}$$

and

$$V_{st}=\langle s|\hat{V}_{13}|t\rangle, \tag{11}$$

one may show that, within the three-particle approximation,[21]

$$G^h_{n\mathbf{k}_0}(\omega)=\frac{1}{\omega-\varepsilon_{n\mathbf{k}_0}+\Sigma_{tt'}V_{st}R_{tt'}V_{t's}}. \tag{12}$$

Therefore, the hole self-energy in the band representation is

$$\Sigma^h_{n\mathbf{k}_0}(\omega)=-\sum_{tt'} V_{st}R_{tt'}V_{t's}. \tag{13}$$

These formulas are derived assuming that the self-energy operator (and therefore the hole Green's function) is diagonal in the band representation. This is consistent with an assumption made later on in this section, that the hybridization between different d orbitals can be neglected in the self-energy calculations. A similar formalism may of course be set up for calculating electron Green's functions (relating to inverse photoemission data). Since this is completely analogous to the hole case, only the latter will be treated explicitly here.

The Faddeev analysis of these equations is carried through in the Appendix. Here we only want to summarize the results relevant for our discussion. The resolvent operator $\hat{R}$, introduced in Eq. (10), can be expressed as:

$$\hat{R}\equiv\frac{1}{\overline{\omega}-(\hat{H}-\hat{V}_{13})}=(1+\hat{D}\hat{T}_h)(\hat{D}+\hat{A}). \tag{14}$$

The $\hat{D}$ and $\hat{T}$ operators are defined by

$$\hat{D}=\frac{1}{\overline{\omega}-\hat{H}_0}, \tag{15}$$

$$\hat{T}_e=\hat{V}_e+\hat{V}_e\hat{D}\hat{T}_e=\frac{1}{1-\hat{V}_e\hat{D}}\hat{V}_e, \tag{16}$$

$$\hat{T}_h=\hat{V}_h+\hat{V}_h\hat{D}\hat{T}_h=\frac{1}{1-\hat{V}_h\hat{D}}\hat{V}_h. \tag{17}$$

The operator $\hat{A}$ is to be determined from the operator identity

$$\hat{A}=\hat{D}\hat{T}_e\hat{D}(1+\hat{T}_h(\hat{D}+\hat{A})), \tag{18}$$

In the single-band case the above equations constitute an integral equation for $\hat{A}$ in three-dimensional momentum space, which is in itself a difficult computational task. In the multiband case a complicated matrix structure is added to the operators due to the presence of several orbitals, and the fact that $\hat{D}$ is not diagonal in the atomic orbital representation, while the scattering matrices $\hat{T}_e$ and $\hat{T}_h$ are not diagonal in the band representation. In order to get around this problem, and obtain simple equations for the scattering matrices and $\hat{A}$, we shall need several approximations, which will be stated below. We will discuss their validity in Sec. III.

The full Coulomb potential in momentum space is given by

$$\sum_{\alpha\neq\beta} U^{\alpha\beta}\sum_{\mathbf{k}\mathbf{k}'\mathbf{p}} \hat{c}^{\dagger}_{\alpha\mathbf{k}+\mathbf{p}}\hat{c}_{\alpha\mathbf{k}}\hat{c}^{\dagger}_{\beta\mathbf{k}'-\mathbf{p}}\hat{c}_{\beta\mathbf{k}'}. \tag{19}$$

As mentioned earlier, it is understood that U's are only nonzero for a limited subset of orbitals. The $\hat{c}_{\alpha\mathbf{k}}$'s are Bloch sums of the atomic-orbital creation operators. Thus, if an injected hole is sitting in an orbital α, it may create an electron-hole pair in orbital β, by the Coulomb interaction, provided that orbitals α and β are part of the ''interacting'' subset. The complexity of the above equations comes partly from the fact that the $\hat{D}$ operator can scatter the particles to different orbitals, and partly from the ability of the Coulomb potential to annihilate the electron-hole pair and recreate it on another orbital.

In order to simplify the equations, we therefore assume that the $\hat{D}$ operator cannot take an electron (or a hole) from one of the Coulomb-interacting orbitals to another. Thus, in NiO we would neglect hybridization, in a particular band, between Ni $3d$ orbitals with different quantum numbers, while allowing for hybridization between Ni $3d$ and O $2p$ states. Furthermore, we shall neglect the above-mentioned terms in the Coulomb potential, that take an electron-hole pair from one orbital to another. With these approximations, expression (13) for the self-energy can be written

$$\Sigma^h_{n\mathbf{k}_0}(\omega)=-\sum_{\alpha}|a^{\alpha}_{n\mathbf{k}_0}|^2\sum_{\beta\neq\alpha}(U^{\alpha\beta})^2\sum_{tt'}R^{\alpha\beta}_{tt'}. \tag{20}$$

Our physical picture is now the following: When a hole is injected in band n, it will be on orbital α with probability $|a^{\alpha}_{n\mathbf{k}_0}|^2$ (this quantity being the projection of band n onto orbital α at $\mathbf{k}_0$). If an electron-hole pair is now created on orbital β, all subsequent Coulomb scattering processes must take place on these orbitals, within the approximations mentioned above. These multiple scatterings are summed up in the $\hat{R}^{\alpha\beta}$ operator. To obtain the total self-energy one must then sum over all interacting orbitals. The complicated many-orbital equation thus separates into a set of effective ''two-band problems'' which are much more tractable from an analytical as well as a numerical point of view. The $\hat{R}^{\alpha\beta}$ operator is determined from the equations

$$\hat{R}^{\alpha\beta}=(1+\hat{D}^{\alpha\beta}\hat{T}^{\alpha\beta}_h)(\hat{D}^{\alpha\beta}+\hat{A}^{\alpha\beta}), \tag{21}$$

$$\hat{A}^{\alpha\beta}=\hat{D}^{\alpha\beta}\hat{T}^{\alpha\beta}_e\hat{D}^{\alpha\beta}(1+\hat{T}^{\alpha\beta}_h(\hat{D}^{\alpha\beta}+\hat{A}^{\alpha\beta})). \tag{22}$$

Here $\hat{A}^{\alpha\beta}$, $\hat{T}^{\alpha\beta}_{e,h}$, and $\hat{D}^{\alpha\beta}$ denote the $\hat{A}$, $\hat{T}$, and $\hat{D}$ operators in the various $\alpha\beta$ subspaces.

Finally, we are going to assume, that the so-called local approximation[24] is valid. As discussed by Müller-

Hartmann,[25] this corresponds to the neglect of momentum conservation at the vertices of the Coulomb interaction. With this approximation the **k**-space convolutions entailed in the above equations can be replaced by integrals over the orbital projected density of states since no explicit **k** dependence remains in the operators. In this way one ends up with the formulas given in the Appendix, as originally derived by Manghi, Calandra, and Ossicini.[22]

III. RANGE OF VALIDITY

In Sec. II we approximated the many-body calculation of the $N-1$ particle state by a set of effective two-band problems, where the band structures were given by the orbital projections of the N-particle mean-field density of states. We will, of course, only obtain a nonvanishing contribution to the self-energy from a given pair of orbitals if at least one of them is partially filled, so that scattering processes can occur. Thus two distinct cases of interest emerge.

A. One partially filled band

When only one of the orbitals is partially filled, the only nontrivial process is electron or hole injection in the other orbital (depending on whether it is empty or full). In this case the method is correct in the low-U limit, since the only process that can occur, to second order in U, is the creation and subsequent annihilation of an electron-hole pair in the partially filled orbital. It is also correct in the strong-coupling limit, which may be defined as the limit were the bandwidths go to zero. In this limit it was shown by Igarashi[19] that the three-particle approximation to the Green's function for the two-band problem becomes

$$G^h(\omega)=\frac{1-n}{\omega}+\frac{n}{\omega-U}. \tag{23}$$

Here we consider hole injection in a filled band, and n denotes the occupation fraction of the partially filled one. This is also the result of an exact treatment of this limit, so that the three-particle method in the case of only one partially filled band has the highly desirable property of interpolating between two correct limits: The noninteracting limit, $U \ll W$, and the ''atomic'' limit, $U \gg W$, where W is a measure of the bandwidths.

B. Two partially filled bands

In this case the many-body problem is considerably more complicated, and both hole and electron Green's functions are nontrivial. The three-particle approximation is no longer correct in the low-U limit, since two electron-hole pairs (one in each band) may now be created and destroyed in a second-order process. Evaluating the strong-coupling limit with an occupation fraction of n in both orbitals, one finds

$$G^h(\omega)=\frac{1}{2\sqrt{(1-n)^2+\frac{1}{4}}}\left(\frac{x_+}{\omega-Unx_-}-\frac{x_-}{\omega-Unx_+}\right), \tag{24}$$

where the pole strengths are given by

$$x_\pm=\tfrac{1}{2}-n\pm\sqrt{(1-n)^2+\tfrac{1}{4}} \tag{25}$$

and

$$G^e(\omega)=\frac{1}{2\sqrt{n^2+\frac{1}{4}}}\left(\frac{y_+}{\omega-U(1-n)y_-}-\frac{y_-}{\omega-U(1-n)y_+}\right), \tag{26}$$

with pole strengths

$$y_\pm=\tfrac{1}{2}-n\pm\sqrt{n^2+\tfrac{1}{4}}. \tag{27}$$

Thus the three-particle approximation does not show the correct strong-coupling limit in the case of two partially filled bands. Actually, the above result is quite disturbing, since the absence of a well-defined Fermi level is evident: The high pole of G^h lies above the low pole of G^e. Consider, for instance, the case of $n=\frac{1}{2}$. In this case both the hole and electron Green's functions will have poles at $\pm(U/2\sqrt{2})$, and we cannot find a single value for the Fermi energy separating the hole and electron contributions to the spectral function. This problem is easily seen to be a consequence of the fact that we are not treating the N-particle state on the same footing as the $N\pm1$ particle states. Denoting the N-particle ground state energy E_N^0 and the energies of the excited states $E_{N\pm1}^m$ (m labeling the excited states of the $N\pm1$ system), a necessary condition for the existence of a Fermi level is[26]

$$E_{N+1}^m-E_N^0 \geqslant E_N^0-E_{N-1}^{m'} \tag{28}$$

for all values of m and m'. If the system is metallic in the mean-field approximation, the equality will hold for $m=m'=0$. In the three-body approach, the N-particle ground state energy is equal to the mean-field value, while the energies of the $N\pm1$ states are lowered due to correlations, and we see at once that the requirement (28) is violated, leading to an instability of the many-particle system. This is of course an unphysical result, and we conclude that the three-particle method is not suited for handling correlation effects between partially occupied bands (if there are gaps in the Hartree-Fock bands of a size comparable to, or larger than, the value of U, one might obtain a well-defined Fermi energy, and one might even, to some extent, justify the neglect of ground-state correlations compared to the ones in the $N\pm1$ states. However, this is a case of limited interest, since it could equally well be treated by ordinary perturbation theory).

It is difficult to see how the approach may be resurrected from these limitations. One might formulate the problem with time-ordered Green's functions, which treat ground- and excited-state correlations on an equal footing, and write down the Feynman diagrams corresponding to the three-particle approximation. This approach is, however, numerically more cumbersome than the present formalism, and we have not been able to verify any correct strong-coupling limit of the equations. Indeed, being inherently perturbative in its character, such an approach is probably not suited for the high-U calculations that interest us.

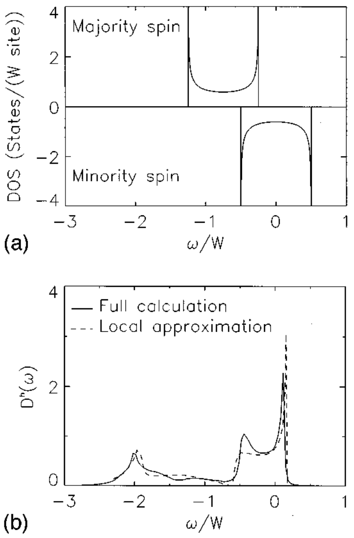

FIG. 1. Comparison of the **k**-independent spectral function [Eq. (9)] for a one-dimensional Hubbard model with $U/W=1.5$, calculated in the three-particle formalism with and without the local approximation. (a) shows the unperturbed ferromagnetic bands, while (b) shows the correlated spectral functions. The energies are measured relative to the Hartree-Fock Fermi level.

C. Validity of approximations

1. Local approximation

It is well known that the local approximation to the self-energy becomes exact in either the strong-coupling (narrow-band) limit, or the limit of infinite dimensionality.[24,25] Since we are going to treat three-dimensional crystals where at least some of the bandwidths may be a sizable fraction of U, it is not immediately clear how the approximation can be justified. Indeed, our primary reason for its inclusion is the great calculational simplifications it entails. A fairly simple test of its validity can be performed by investigating the single-band ferromagnetic Hubbard model in one dimension, where a calculation without the local approximation is more tractable than in three dimensions. Calculations of this kind were first reported by Igarashi.[20] In Fig. 1 we compare **k**-integrated spectral functions for hole injection in a filled band, calculated with and without the local approximation. The bandwidth is unity, U is 1.5, and the occupation fraction of the partially filled band is 0.5. It is seen that the two calculations agree almost perfectly on the energy positions of the various structures. On analyzing the **k**-resolved spectra, it is found that the primary effect of the local approximation is to suppress the band narrowing induced by the correlations, thus smoothing out the peak around $\omega=-0.4$. This calculation is by no means a rigorous proof of the validity of the local approximation in three-dimensional crystals with complex band structures. However, it is somewhat reassuring to see that the approximation has little effect on the integrated spectra for a moderate U value, even in the lowest possible spatial dimension.

2. Orbital decoupling

The natural generalization of the local approximation to a multiband case would be to assume that the self-energy operator was diagonal in the atomic orbital representation. The approximation made in Sec. II is, however, more stringent than this, since hybridizations to other orbitals with nonzero U are neglected throughout the self-energy calculation. At the same time hybridizations to other orbitals (e.g., the O $2p$ states in NiO and CuO) are included. Thus we must examine the band structures we are going to use as input in the calculation in order to determine whether the approximation is justified.

From the discussion in Sec. III B it followed that the three-particle method is not suited to treat correlation effects between partially filled orbitals. This means that the outputs of conventional LSD calculations on, e.g., transition-metal oxides, would be an inadequate starting point for us, since in these band structures the $3d$ orbitals usually end up being all partially filled. Furthermore, one may argue that whatever treatment the LSD approximation gives of a Hubbard-like correlation term, it certainly is not the Hartree-Fock treatment implied in our single-particle energies in Eq. (2). In this respect a more natural approach would be to start out from the results of SIC-LSD or LDA+U calculations, since in these schemes one attempts more or less explicitly to include a correct first-order treatment of the on-site Coulomb interactions. For the transition-metal oxides these models give band structures which are quite different from the LSD results, with sizable band gaps caused mainly by a splitting of the $3d$ density of states. This splitting is in turn caused by strong orbital polarization effects, so that some $3d$ orbitals are fully occupied, while others remain empty. At the same time hybridization between $3d$ orbitals is suppressed. This is particularly evident in SIC calculations, where a set of localized $3d$ states, which are essentially Bloch sums of the atomic orbitals (with a small O $2p$ hybridization), appear at high binding energies. First-principles Hartree-Fock band structures[27] provide the same picture of the electronic structure, though with very large gaps. Thus the three-particle scheme is seen to be fairly well justified in these compounds, when the first-order Coulomb effects are properly treated. This is quite fortunate, since our main interest is precisely the many-body corrections to the various mean-field models of the on-site interaction effects.

The last approximation made in Sec. II was the neglect of Coulomb scatterings, taking the excited electron-hole pair from one partially occupied orbital to another. If only one orbital is partially occupied (this will be the case in CuO), the approximation is exact. If two or more orbitals are partially occupied (as in NiO), such processes can occur, but even if we had a way (perhaps approximate) of including them, it would probably be dangerous to do so. The reason is, that we would thereby include correlation effects between two partially filled orbitals in the $N+1$ and $N-1$ particle states, without treating similar effects in the N-particle ground state, where they might equally well be present. We shall therefore continue to neglect these processes in all of the following calculations. It should, however, be noted that this approximation is not exact in the atomic limit. Consider, for simplicity, a density of states with one filled band and two degenerate bands with filling fraction n, all of zero bandwidth. Our approximation will account for the presence of two partially filled bands by simply multiplying the self-

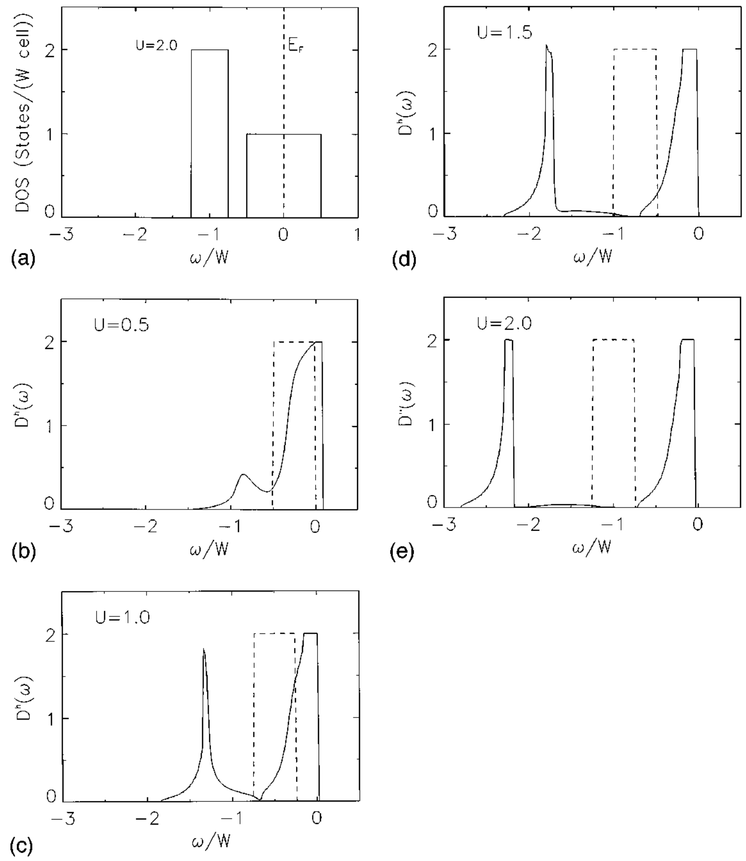

FIG. 2. Three-particle calculations for a simple two-band model. (a) shows the Hartree-Fock bands for $U=2.0$. (b)–(e) show the majority spin spectral function resulting from the three-particle calculation, for different U values. The positions and widths of the upper band are the same in all calculations. The lower unperturbed band is shown with a dashed line. It is always centered around $-U/2$. Energies are measured relative to the Hartree-Fock Fermi level.

energy by a factor of 2 [there being two orbitals β to sum over in Eq. (20)]; that is,

$$G^h(\omega)=\frac{1}{\omega+U(1-n)-2\Sigma(\omega)}, \tag{29}$$

with

$$\frac{1}{\omega+U(1-n)-\Sigma(\omega)}=\frac{n}{\omega-U}+\frac{1-n}{\omega}, \tag{30}$$

measuring the energy relative to the HF Fermi level. One can readily show that this leads to the following form of the hole Green's function:

$$G^h(\omega)=\frac{W_-}{\omega-\omega_-}+\frac{W_+}{\omega-\omega_+}, \tag{31}$$

where

$$W_\pm=\frac{1}{2}\pm\frac{n-\frac{1}{2}}{\sqrt{1+4n(1-n)}}, \tag{32}$$

and

$$\omega_\pm=\frac{U}{2}\pm U\sqrt{\tfrac{1}{4}+n(1-n)}. \tag{33}$$

If we take $n=\frac{1}{4}$ as an example, we find from the above formulas, that the hole Green's function will have two poles with weights $\frac{1}{2}\mp(1/2\sqrt{7})$ in $\omega=(U/2)\pm U(\sqrt{7}/4)$. Thus the quasiparticle DOS is correctly centered around $U/2$, but the splitting in energy of the two peaks is overestimated by a factor of $\sqrt{7}/2\sim1.3$, i.e., about 30%, due to our neglect of correlations between the ''metallic'' electrons. It should be emphasized that this is not a failure of the three-particle approximation as such, but of our orbital decoupling scheme.

IV. NUMERICAL RESULTS AND DISCUSSION

A. Model calculations

We shall begin by illustrating the basic physics of our method considering some simple model calculations with flat bands. Our generic picture of the mean-field $3d$ density of states in NiO and CuO will be that of a set of low-lying narrow d bands, all fully occupied, and a set of broader bands around the Fermi level, predominantly of O p character, with some metal d character mixed in. This is the band picture emerging from a SIC-LSD calculation. To mimic this situation we shall consider a two-band model where holes are injected in a fully occupied band, Coulomb interacting with electrons in a partially filled one (corresponding to partially filled d orbitals in the oxides). We shall take the partially filled band to be metallic and half-filled, and set its width to unity. The filled band is taken to be of width 0.5 and is centered around $-U/2$. The bands are pictured in Fig. 2(a). In Figs. 2(b)–2(e) the quasiparticle spectra resulting from the three-particle calculations for different U values are displayed. We see that the filled band splits into two main structures with a splitting in energy given by U. The high-lying structure essentially corresponds to final states where the injected hole is bound to an electron (or, in the atomic picture, the hole is introduced on a doubly occupied site). The lower peak corresponds to hole-hole binding (the hole is introduced at a singly occupied site). We note that the center of gravity of the total quasiparticle density of states is shifted downwards relative to the unperturbed case, because of the kinetic-energy cost of creating the bound states. The shift is approximately equal to the energy difference between the centers of gravity of the filled and empty parts of the metallic band. It is characteristic that the energy splitting between the two structures is close to U even in the intermediate case of $U=1.0$. The main effect of increasing U (apart from changing the energy scale of the splitting) is thus to change the distribution of spectral weight between the two peaks, and eliminate the intermediate structures in the energy region of the unperturbed band. For the intermediate-U values the peaks represent states of finite lifetime, signified by a nonvanishing imaginary part of the self-energy. As the U value is increased, the imaginary term tends to zero in accordance with the limiting form (23).

If the initial position of the fully occupied band is shifted, the entire quasiparticle structure is shifted rigidly by the same amount. This follows at once from the equations in the Appendix. If a gap is introduced in the partially filled band (as is seen in the transition-metal oxides), the spectrum is shifted further down in energy, since the cost of creating an electron-hole pair is increased. Finally, changing the width of the fully occupied band results mainly in a change in the widths of the corresponding quasiparticle structures. The atomic limit is essentially realized beyond $U=2$.

From these simple model calculations, we see that the three-particle approximation is capable of bringing the mean-field picture of the transition-metal oxides into better agreement with photoemission experiments by introducing exactly the splitting between main band and satellite structures seen in these measurements.[18] It is interesting to note that the present model entails no modifications of the N-particle ground state of the materials. This may to some extent explain the success of the SIC-LSD and LDA+U models in predicting ground-state properties like, for instance, the magnetic structures. To test the mean-field picture in more detail it is, however, necessary to go beyond the simple model calculations and insert realistic band structures in the equations. This will be the subject of the following subsections.

B. CuO

In this subsection we shall discuss the quasiparticle spectrum of CuO on the basis of the formalism described above. Our first starting point will be a self-consistent SIC-LSD calculation with linear muffin-tin orbitals as described in Ref. 28. In order to simplify the calculations we have replaced the complicated crystal structure of CuO with a simple NaCl structure. The SIC ground state in this structure is antiferromagnetic, with a moment of 0.65μ.

It is not obvious how one should obtain a band structure within the SIC-LSD scheme. Pederson, Heaton, and Lin[29] suggested diagonalizing the matrix of Lagrange-multipliers (the ''λ matrix'') that ensure orthonormality of the SIC-LSD one-particle orbitals. This procedure leads to the SIC-LSD equivalent of the Kohn-Sham band structure, and a Koopman's theorem exists for the diagonalizing orbitals,[29] which in periodic systems become Bloch states. In Fig. 3(a) we show the density of states of CuO obtained by this procedure. The self-interaction corrected orbitals give rise to nine narrow bands lying ~11 eV below the valence-band maximum. These bands are almost entirely made up of Cu $3d$ orbitals, with only a small O $2p$ hybridization. The highest occupied bands are mainly composed of O $2p$ states hybridized with the last Cu orbital, which is of $e_g(x^2-y^2)$ spatial symmetry, and has an occupation fraction of 0.35. The band gap is 1.4 eV. A first-principles estimate for the Cu $3d$ U parameter may, within the SIC-LSD approximation, be obtained as the difference between the highest occupied and lowest unoccupied SIC orbital, before diagonalization of the λ matrix.[30] This yields a value for U of 10.2 eV, and is largely given as the average expectation value of the SIC potential. Other estimates of this parameter are somewhat smaller, e.g., 8 eV in Ref. 13 or 7.5 eV in Ref. 8.

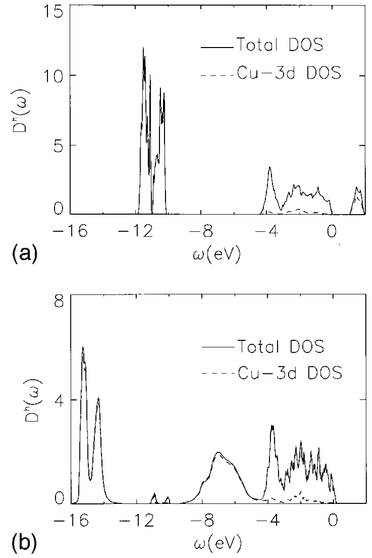

FIG. 3. (a) SIC-LSD density of states for CuO in the NaCl structure, obtained by diagonalizing the λ matrix. The Fermi level is at zero energy. (b) Quasiparticle density of hole states in CuO calculated from the unperturbed DOS in (a) within the three-particle approximation. U was taken to be 10.2 eV. Units are states/formula unit and eV.

With only one partially occupied orbital, CuO is an ideal case for study with the three-particle approximation. As already indicated, we shall assume that the Hubbard U is only significant on the Cu $3d$ orbitals. With an antiferromagnetic structure we should in principle consider 20 such orbitals, but since orbitals on different sites do not interact in the Hubbard model, and are pairwise equivalent, we only have to consider ten orbitals within our approximations. In Fig. 3(b) we show the quasiparticle spectrum obtained by a three-particle calculation with a U value of 10.2 eV. Similar to the model studies of Sec. IV A, the low-lying Cu $3d$ bands are split into a high-lying ($d^9\underline{L}$) peak, around 7 eV below the valence-band edge, and a low-lying (d^8) satellite structure. The splitting is slightly smaller than the U value, due to the small O $2p$ component of the SIC orbitals. The experimental CuO photoemission spectra of Gunnarson, Jepsen, and Shen[13] show the $d^9\underline{L}$ structure around −5 to −1 eV below the valence-band edge, and the d^8 peak at −11 eV, i.e., the calculated energy positions of the Cu $3d$-derived peaks are

$\sim$4 eV too low compared to experiment. Taking a lower value for U (for instance, 8 eV) does not improve the situation very much.

The trouble is that the SIC-LSD band structure is somewhat at variance with our expectations for a multiband Hubbard model. In a first-order treatment of the Hubbard model, we would expect an energy splitting (apart from hybridization effects) of $U(1-n)$ between a fully occupied orbital and one with occupation fraction n. In the SIC-LSD approximation the splitting is always $\sim U$, since the self-interaction-corrected orbitals are shifted down by approximately this quantity, while the partially filled d orbitals are left unchanged. The net result is, as can be seen from Fig. 3(a) that the λ bands reproduce the experimental position of the $d^8 \rightarrow d^9$ satellite directly, but make no particular contribution to the $d^9\underline{L}$ structure, which experimentally has the larger weight. This is in accord with the fact, observed previously,[14,29] that atomiclike excitations are well described by SIC-LSD eigenvalues, but also implies that these energies include some correlation effects, though clearly not all.

In light of the aforementioned problems, we now turn to the LSD+U approach as another candidate scheme for parametrizing the Hubbard model to first order. We assume the mean-field Hamiltonian $\hat{H}_0$ in Eq. (2) to be given by

$$\hat{H}_0=\hat{H}_{\mathrm{LSD}}+U\sum_{\mathbf{R}\alpha\neq\beta}(\langle\hat{n}^{\beta}_{\mathbf{R}}\rangle-n^0_{\sigma_\beta})\hat{n}^{\alpha}_{\mathbf{R}}, \qquad (34)$$

where $\hat{H}_{\mathrm{LSD}}$ is the usual LSD Hamiltonian, while the second term represents the mean-field contribution from the on-site Coulomb interaction. As in Sec. II, α and β are orbital indices, understood to be restricted to metal $3d$ states. $n^0_{\sigma_\beta}$ denotes the mean $3d$ occupation in the spin channel of orbital β. Using $\hat{H}_0$ in Eq. (34) as the mean-field Hamiltonian of our multiband Hubbard model assumes that the LSD approximation describes the effects of on-site Coulomb interactions correctly in the absence of orbital polarization. No J parameter is employed, i.e., it is assumed that the LSD approximation properly describes exchange effects. In Fig. 4(a) the DOS emerging from a diagonalization of Eq. (34) is shown. The metal $3d$ states are now broadened, higher in energy, and more hybridized with the O $2p$ states. The U value was here taken to be 7.5 eV, as given by Anisimov, Zaanen, and Andersen.[8] Performing again the self-energy calculations, now with a new value of U, we obtain the quasiparticle spectrum shown in Fig. 4(b). The peak positions are now closer to the experimental ones, the d^8 peak being about 9 eV below the top of the valence band, and the $d^9\underline{L}$ structure in the range from 2 to 5 eV below the highest-lying states. The fact that the experimental d^8 peak is somewhat lower than calculated here indicates that a slightly higher U value may be appropriate for CuO. The form of the spectrum also matches the photoemission results rather well. A valence-band edge of mixed O and Cu character is seen, the main Cu $3d$ peak coming up 1–2 eV below the Fermi energy. This constitutes a (somewhat crude) description of the so-called Zhang-Rice singlet.[31] Earlier calculations by Gunnarson, Jepsen, and Shen[13] based on the Anderson model tended to produce a split-off state at this point, but, as anticipated by these authors, the Hubbard-model treatment reproduces the experimental ''hump'' rather well. The weight of the lower peak seems somewhat too high compared to the experimental spectrum. This can partly be ascribed to matrix-element effects, and partly to the fact that the LSD+U calculation slightly overestimates the antiferromagnetic moment of the Cu ions ($0.74\mu_B$, as compared to $0.65\mu_B$ from experiment[8]).

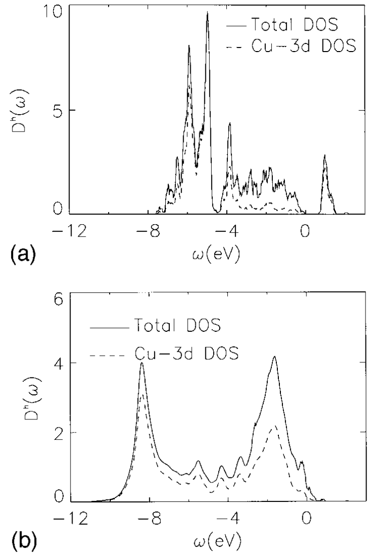

FIG. 4. (a) LSD+U DOS of CuO with a U value of 7.5 eV. The Fermi level is at zero energy. (b) Quasiparticle hole DOS calculated from the mean-field spectrum in (a).

Since the spectrum of $N+1$ particle states is not altered by our model, we see that the small gap of the LSD+U calculation is closed by the correlation calculation, so the system becomes metallic. It is to be expected that a correlation calculation will narrow the gap compared to the mean-field result, so this problem should probably be cured by refining the mean-field scheme. Since we are mainly interested in the photoemission spectrum in this paper, we have not made any attempts in this direction.

C. NiO

With the above experiences in mind, we now turn to NiO. This is a somewhat more complicated problem since there are two partially filled Ni $3d$ orbitals. In principle we should, therefore, also calculate self-energy corrections for these orbitals. However, as explained in Sec. III this cannot be done within the framework of the three-particle formalism, so we will contend ourselves with correcting the filled orbitals, as before. The unperturbed DOS is shown in Fig. 5(a). We have, again, employed the LSD+U formalism, this time with a U value of 8.2 eV. The main part of the Ni $3d$ orbital weight lies between 5 and 8 eV below the valence-band edge, but there is now substantial hybridization to the higher-lying O states. These aspects of the valence-band structure are in agreement with first-principles Hartree-Fock calculations,[27] as well as SIC-LSD calculations including self-interaction on the O p states.[17]

The quasiparticle DOS obtained in the three-particle calculation is shown in Fig. 5(b). Similar to CuO, the correlated spectral density compares much better with the experimental photoemission data than the unperturbed LSD+U density of

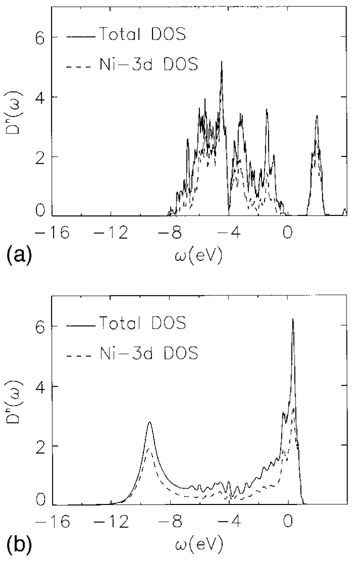

FIG. 5. (a) LSD+U DOS for NiO, with a U value of 8.2 eV. The Fermi level is at zero energy. (b) Quasiparticle density of hole states in NiO calculated within the three-particle approximation with the unperturbed DOS in (a).

states. Most significantly, for NiO the metal d states are pushed all the way up to the highest-lying valence states, and a steep valence-band edge develops. Below the main peak, a broad mixture of Ni and O states extend down to the d^7 satellite structure ~10.5 eV below the top of the valence band. The satellite is, as expected, primarily of Ni d character. The position of the satellite is ~1 eV lower than observed in experiment. This is probably due to our rather crude treatment of the multiorbital self-energy, as discussed in Sec. III C.

V. CONCLUSIONS AND OUTLOOK

We have shown that the three-particle approximation is well suited for evaluating many-body corrections to the spectra of filled orbitals, but is not appropriate for studying partially filled ones. We have performed *ab initio* calculations with this formalism on NiO and CuO, and have demonstrated that the method reproduces the splitting of d spectral weight into a $d^n\underline{L}$ main structure and a d^{n-1} satellite. Good quantitative agreement with experimental photoemission data is obtained using as input uncorrelated electronic levels the orbital polarized band structures derived from LSD+U *ab initio* calculations. It is of importance that these levels mimic a correct first-order treatment of the multiband Hubbard model, which means that SIC-LSD bands derived with the ''λ-matrix procedure'' are a less adequate starting point for our calculations, since the d levels come out too deep in energy.

An interesting application of the present formalism would be a comparison between spectra of CuO and high-T_c superconductors, in order to clarify to what extent variations in the DOS can be described within our rather unsophisticated many-body theory. Also earlier transition-metal compounds and some f-electron systems (like Yb) should be within reach of the method. On the other hand, a description of correlation effects in metallic systems (like transition metals, heavy fermion compounds, etc.) does not appear to be feasible with the present formalism.

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APPENDIX: DERIVATION OF FADDEEV EQUATIONS

In this appendix we shall give a more thorough review of the derivation of the three-particle formalism. We begin by deriving Eqs. (14) and (18) for the resolvent operator defined in Eq. (14). We first note the identities

$$1+\hat{V}_{e,h}\hat{R}=(\hat{D}^{-1}-\hat{V}_{h,e})\hat{R} \tag{A1}$$

and

$$\hat{D}\frac{1}{1-\hat{V}_{e,h}\hat{D}}=\frac{1}{\hat{D}^{-1}-\hat{V}_{e,h}}. \tag{A2}$$

Introducing the quantity

$$\hat{A}=\hat{D}\hat{V}_e\hat{R}, \tag{A3}$$

we see from the above identities that

$$\begin{aligned}\hat{R}&=\frac{1}{\hat{D}^{-1}-\hat{V}_h}(1+\hat{V}_e\hat{R})\\&=\hat{D}\frac{1}{1-\hat{V}_h\hat{D}}(\hat{D}^{-1}-\hat{V}_h+\hat{V}_h)\hat{D}(1+\hat{V}_e\hat{R})\\&=(1+\hat{D}\hat{T}_h)(\hat{D}+\hat{A}).\end{aligned} \tag{A4}$$

We can picture the operator $\hat{R}$ as the sum of all possible electron-hole and hole-hole scattering processes. $\hat{A}$ then corresponds to the partial sum in which the last process is an electron-hole scattering. The T matrices introduced in Eqs. (16) and (17) can similarly be pictured as partial sums of electron-hole and hole-hole processes, respectively. Our next task is to derive an integral equation for $\hat{A}$:

$$\hat{A}=\hat{D}\hat{V}_e\hat{R}=\frac{1}{1-\hat{D}\hat{V}_e}\hat{D}\hat{V}_e(1-\hat{D}\hat{V}_e)\hat{R}=\hat{D}\hat{T}_e\hat{D}(1+\hat{V}_h\hat{R}), \tag{A5}$$

which, after a few manipulations, yields

$$\hat{A}=\hat{D}\hat{T}_e\hat{D}(1+\hat{T}_h\hat{D}+\hat{T}_h\hat{A}). \tag{A6}$$

The first term represents the sums where only e-h scatterings occur, the next term the sums where a series of h-h scatterings is followed by a series of e-h scatterings, and the final term contains all the remaining contributions to the sum in the A operator.

In order to obtain a formula for the self-energy, we must evaluate the quantities

$$\sum_{tt'} R_{tt'}^{\alpha\beta} \tag{A7}$$

according to Eq. (20). The three-particle states in the sum are now restricted to the orbitals α and β and can thus be labeled by three $\mathbf{k}$ indices. As seen from Eq. (21), we only need to know the object

$$R_{e\mathbf{k}_1}^{\alpha\beta}=\sum_{\mathbf{k}_2\mathbf{k}_3\mathbf{k}_1'\mathbf{k}_2'\mathbf{k}_3'} \langle \alpha\mathbf{k}_3\beta\mathbf{k}_2\beta\mathbf{k}_1|\hat{A}^{\alpha\beta}|\beta\mathbf{k}_1'\beta\mathbf{k}_2'\alpha\mathbf{k}_3'\rangle, \tag{A8}$$

where momentum conservation is taken to be implicit in the $\mathbf{k}$ sums. Here $\mathbf{k}_1$ is the momentum of the excited electron. The result follows from the fact that the operator $\hat{T}_h^{\alpha\beta}$ is independent of the ingoing and outgoing hole coordinates (because the Hubbard potential is $\mathbf{k}$ independent), and thus only depends on the electron momentum (which is conserved in the h-h scattering processes). Accordingly, we only need to solve an integral equation in one variable. This is the main objective behind the above manipulations.

The $T^{\alpha\beta}$ matrices can be summed exactly:

$$\begin{aligned} T_{e\mathbf{k}_3}^{\alpha\beta}(\omega,)&\equiv\langle \alpha\mathbf{k}_3\beta\mathbf{k}_2\beta\mathbf{k}_1|\hat{T}_e^{\alpha\beta}|\beta\mathbf{k}_1'\beta\mathbf{k}_2'\alpha\mathbf{k}_3\rangle \\ &=\frac{-U^{\alpha\beta}}{1-U^{\alpha\beta}D_{e\mathbf{k}_3}^{\alpha\beta}(\omega)}, \end{aligned} \tag{A9}$$

$$\begin{aligned} T_{h\mathbf{k}_1}^{\alpha\beta}(\omega)&\equiv\langle \alpha\mathbf{k}_3\beta\mathbf{k}_2\beta\mathbf{k}_1|\hat{T}_h^{\alpha\beta}|\beta\mathbf{k}_1\beta\mathbf{k}_2'\alpha\mathbf{k}_3'\rangle \\ &=\frac{U^{\alpha\beta}}{1+U^{\alpha\beta}D_{h\mathbf{k}_1}^{\alpha\beta}(\omega)}, \end{aligned} \tag{A10}$$

with the definitions

$$D_{e\mathbf{k}_3}^{\alpha\beta}(\omega)\equiv\sum_{\mathbf{k}_1\mathbf{k}_2} \langle \alpha\mathbf{k}_3\beta\mathbf{k}_2\beta\mathbf{k}_1|\hat{D}^{\alpha\beta}|\beta\mathbf{k}_1\beta\mathbf{k}_2\alpha\mathbf{k}_3\rangle, \tag{A11}$$

$$D_{h\mathbf{k}_1}^{\alpha\beta}(\omega)\equiv\sum_{\mathbf{k}_2\mathbf{k}_3} \langle \alpha\mathbf{k}_3\beta\mathbf{k}_2\beta\mathbf{k}_1|\hat{D}^{\alpha\beta}|\beta\mathbf{k}_1\beta\mathbf{k}_2\alpha\mathbf{k}_3\rangle. \tag{A12}$$

We can now insert intermediate states in Eq. (A6), and sum up over the relevant $\mathbf{k}$ variables to obtain an integral equation for the quantity $R_e^{\alpha\beta}$. Using the local approximation, the momentum conservation implicit in the above summations is relaxed, and one can transform the sums into density-of-states integrals. In this way we end up with the following set of formulas, first given by Manghi, Calandra, and Ossicini:[22]

$$D_{\mathrm{eh}}^{\alpha}(\omega)=\int_{-\infty}^{E_f} d\varepsilon\frac{n^{\alpha}(\varepsilon)}{\omega-\varepsilon-i\delta}, \tag{A13}$$

$$D_e^{\alpha\beta}(\omega)=\int_{E_f}^{\infty} d\varepsilon n^{\beta}(\varepsilon)D_{\mathrm{eh}}^{\alpha}(\omega+\varepsilon), \tag{A14}$$

$$D_h^{\alpha\beta}(\omega)=\int_{-\infty}^{E_f} d\varepsilon n^{\beta}(\varepsilon)D_{\mathrm{eh}}^{\alpha}(\omega-\varepsilon), \tag{A15}$$

$$T_e^{\alpha\beta}(\omega)=\frac{-U^{\alpha\beta}}{1-U^{\alpha\beta}D_e^{\alpha\beta}(\omega)}, \tag{A16}$$

$$T_h^{\alpha\beta}(\omega)=\frac{U^{\alpha\beta}}{1+U^{\alpha\beta}D_h^{\alpha\beta}(\omega)}, \tag{A17}$$

$$\begin{aligned} R_e^{\alpha\beta}(\omega,\varepsilon)=R_{e0}^{\alpha\beta}(\omega,\varepsilon)+\int_{E_f}^{\infty} d\varepsilon' n^{\beta}(\varepsilon') \\ \times K^{\alpha\beta}(\omega,\varepsilon,\varepsilon')R_e^{\alpha\beta}(\omega,\varepsilon), \end{aligned} \tag{A18}$$

$$\begin{aligned} R_{e0}^{\alpha\beta}(\omega,\varepsilon)=\int_{-\infty}^{E_f} d\varepsilon' n^{\beta}(\varepsilon')D_{\mathrm{eh}}^{\alpha}(\omega-\varepsilon'+\varepsilon)T_e^{\alpha\beta}(\omega-\varepsilon') \\ \times\Bigg(D_e^{\alpha\beta}(\omega-\varepsilon')-\int_{E_f}^{\infty} d\varepsilon'' n^{\beta}(\varepsilon'') \\ \times D_{\mathrm{eh}}^{\alpha}(\omega-\varepsilon'+\varepsilon'')D_h^{\alpha\beta}(\omega+\varepsilon'')T_h^{\alpha\beta}(\omega+\varepsilon'')\Bigg), \end{aligned} \tag{A19}$$

$$\begin{aligned} K^{\alpha\beta}(\omega,\varepsilon,\varepsilon')=\int_{-\infty}^{E_f} d\varepsilon'' n^{\beta}(\varepsilon'')D_{\mathrm{eh}}^{\alpha}(\omega-\varepsilon''+\varepsilon)T_e^{\alpha\beta} \\ \times(\omega-\varepsilon'')D_{\mathrm{eh}}^{\alpha}(\omega-\varepsilon''+\varepsilon')T_h^{\alpha\beta}(\omega+\varepsilon'), \end{aligned} \tag{A20}$$

$$\begin{aligned} \sum_{tt'} R_{tt'}^{\alpha\beta}(\omega)=\frac{1}{U^{\alpha\beta}}\int_{E_f}^{\infty} d\varepsilon n^{\beta}(\varepsilon)T_h^{\alpha\beta}(\omega+\varepsilon)\big(R_e^{\alpha\beta}(\omega,\varepsilon) \\ -D_h^{\alpha\beta}(\omega+\varepsilon)\big). \end{aligned} \tag{A21}$$

The self-energy can hereafter be found by Eq. (20), and the quasiparticle spectrum may then be obtained as the imaginary part of the Green's function defined by Eq. (12).

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