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Quasiparticle band structure of Ni and NiSi$_2$

C. Calandra

Dipartimento di Fisica, Università degli Studi di Modena, Via Campi 213/a, I-41100 Modena, Italy
and Laboratorio TASC-INFM, Area di Ricerca, Padriciano 99, Trieste, Italy

F. Manghi

Dipartimento di Fisica, Università degli Studi di Modena, Via Campi 213/a, I-41100 Modena, Italy

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Expressions for the hole self-energies of a metal with hybridized *sp* and *d* bands have been obtained using the low-density *t*-matrix approximation and a Hubbard Hamiltonian to treat correlation effects. The theory provides a significant improvement with respect to previous calculations based on the Hubbard Hamiltonian, since it takes into account the details of the single-particle band structure in the calculations of the two-hole propagator and uses a self-consistent approach for the evaluation of self-energy corrections. The theory is applied to the evaluation of the quasiparticle density of states and dispersion for Ni and NiSi$_2$. The results allow elucidation of the role of many-band and hybridization effects in determining the self-energy behavior.

I. INTRODUCTION

The role of Coulomb correlation in determining the shape of transition-metal quasiparticle spectra has been the subject of several theoretical investigations in the last few years.[1] Most of this work has been performed using a single-band Hubbard model[2] and working either in the weak-correlation[3–5] or in the strong-correlation[6,7] limit. The results obtained using the single-band model have often been applied to describe the photoemission spectra of realistic systems, both pure metals and compounds. In particular, this approach has been used to explain the spectral features of nickel,[8–10] a material which has been widely studied in the past, being a sort of canonical example of a metal whose band structure cannot be entirely explained within the single-particle approach. Only in a few cases[4,6] has a realistic description of the band structure been taken into account.

This situation is rather unsatisfactory: Indeed, if detailed statements concerning the electronic structure of a specific material are to be made, the single-band model is totally inadequate; the orbital degeneracy of the highly correlated *d* bands must be explicitly included, as well as the effects of the hybridization with the large dispersive *sp* bands. This may be even more important in those systems where transition-metal atoms are chemically bonded to ligands of some sort, as in oxides or silicides.

In this paper we address the problem of the multiband effects in the evaluation of the correlated quasiparticle hole states, studying the cases of Ni and NiSi$_2$ as examples. Rather than using a perturbative approach, which can be useful only under the condition of either a very large or a very small Hubbard U parameter compared to the total bandwidth, we adopt the *t*-matrix low-density approximation,[11,12] extending it to the multiband case. This allows us to get formal expressions that can be applied for any U value, provided that the particle density is low enough. In particular, we show that the self-energy, evaluated with full account of the *spd* hybridization and of the different energy distribution of the various *d* orbitals, depends both on the lattice wave vector $\mathbf{k}$ and on the band index n. Such a dependence, neglected in single-band models, is quite significant. Moreover, we show that the whole band structure, not only the pure *d* bands, can be modified by correlation. We expect the theory to be applicable to all situations in which both hybridization and correlation play very important roles, as in near-noble-metal or noble-metal compounds.[12–14]

In the case of nickel the limitations of the *t*-matrix theory in describing the quasiparticle spectra are well known. Referring to the hole-state distribution, as probed by valence-band photoemission, there are three main factors of disagreement between the observed spectra and band theory: (i) the exchange splitting is only half of the theoretical value, (ii) the measured *d*-band width is at least 30% smaller than the calculated one, (iii) a satellite occurs at about 6 eV binding energy with practically no dispersion.[1] All these effects are qualitatively accounted for by a *t*-matrix calculation, especially if three-body scattering is included in the theory,[12,15] but a quantitatively consistent picture of the situation cannot be achieved, since the U value that gives the correct satellite position, does not allow one to obtain the right reduction of exchange splitting and bandwidth.

We will see that, in spite of the significant differences present in the hole self-energy when the multiband effects are included, such a quantitative consistency cannot be achieved even by the present theory. We will show, however, that the consequences of the self-energy dependence upon the lattice wave vector and the band index are important and have to be included in any quantitative evaluation of the correlation effects in this metal.

This paper is organized as follows: in Sec. II we derive the formalism for calculating the self-energy starting from the results of an accurate band-structure calculation; in Sec. III we describe the results for paramagnetic nickel and for nickel disilicide; Sec. IV is devoted to a comparison with experiments and to the conclusions.

II. THE LOW-DENSITY APPROXIMATION FOR A MULTIBAND SYSTEM

A. Basic formulas

The central assumption defining the so-called low-density approximation, originally formulated by Kanomori[11] for the single-band case, is that the number of particles (either electrons or holes) experiencing the Coulomb repulsion is so small as to allow reduction of the many-body problem to a two-body one, describing the correlation effects as the scattering between two particles only. The Hamiltonian of the interacting system is

$$H=H_1+H_2+H_{12} , \tag{1}$$

where H_1 and H_2 depend only on the coordinates of particles 1 and 2, respectively, and H_{12} is the interaction term.

The solution of the single-particle Shrödinger equation

$$H_1\psi_{\mathbf{k}}^n=\varepsilon_{\mathbf{k}}^{0n}\psi_{\mathbf{k}}^n \tag{2}$$

defines the ordinary single-particle band structure $\varepsilon_{\mathbf{k}}^{0n}$, $\psi_{\mathbf{k}}^n$ being a Bloch state of wave vector $\mathbf{k}$ and band index n which can be expressed as a combination of localized orbitals

$$\psi_{\mathbf{k}}^n(\mathbf{r})=\sum_{\alpha} c_{\alpha}^n(\mathbf{k})\sum_{i} e^{i\mathbf{k}\cdot\mathbf{R}_l}\phi_{\alpha}(\mathbf{r}-\mathbf{R}_l) . \tag{3}$$

Here $\phi_{\alpha}(\mathbf{r}-\mathbf{R}_l)$ is the αth atomic orbital centered on lattice site $\mathbf{R}_l$ and $c_{\alpha}^n(\mathbf{k})$ are the expansion coefficients, α and n the orbital and band indexes, respectively.

We are interested in two-particles states; according to the Hubbard model, the interaction H_{12} involves only states of antiparallel spin so that we will consider the wave function of the interacting system as a single state; moreover, since we are now interested in the paramagnetic phase, we will ignore the spin dependence of the wave function. We start by considering the case of electrons. We can easily write the wave function of the *noninteracting* two-particle system $\Psi_{\mathbf{kk}'}^{0nm}$ as a symmetrized product of the single-particle Bloch state of different $\mathbf{k}$ vectors and band indices and the two-particle wave function *in the presence of* the interaction as a scattering state,

$$\Psi_{\mathbf{kk}'}^{nm}=\Psi_{\mathbf{kk}'}^{0nm}+\sum_{\mathbf{k}''}\sum_{\mathbf{k}'''}\sum_{r}\sum_{s}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{k}''-\mathbf{k}''')\times A_{\mathbf{k}''\mathbf{k}''',\mathbf{kk}'}^{rs,nm}\Psi_{\mathbf{k}''\mathbf{k}'''}^{0rs} . \tag{4}$$

Here the summation is over unoccupied states; $A_{\mathbf{k}'',\mathbf{k}''',\mathbf{kk}'}^{rs,nm}$ are scattering coefficients, and $\delta(\mathbf{k}+\mathbf{k}'-k''-\mathbf{k}''')$ guarantees the $\mathbf{k}$ conservation. The Schrödinger equation for the interacting system is

$$H\Psi_{\mathbf{kk}'}^{nm}=E_{\mathbf{kk}'}^{nm}=\Psi_{\mathbf{kk}'}^{nm} . \tag{5}$$

Let us assume, in agreement with the Hubbard model, that the interaction H_{12} is to be effective only on the same site and define

$$U_{\alpha\gamma\beta\delta}=\int d\mathbf{r}_1\int d\mathbf{r}_2\phi_{\alpha}^*(\mathbf{r}_1)\phi_{\gamma}^*(\mathbf{r}_2)H_{12}\phi_{\beta}(\mathbf{r}_1)\phi_{\delta}(\mathbf{r}_2) . \tag{6}$$

It has been shown[4] that for $3d$ states the $U_{\alpha\gamma\beta\delta}$ are significantly differently from zero only if $\alpha=\beta$ and $\gamma=\delta$; moreover, the $U_{\alpha\gamma\alpha\gamma}$ for the five $3d$ orbitals are practically identical. For this reason we will put

$$U_{\alpha\gamma\beta\delta}=U\delta_{\alpha\beta}\delta_{\gamma\delta}$$

and neglect the integrals involving s or p atomic orbitals. With these assumptions and definitions it is a matter of tedious but straightforward calculations to obtain the following formulas:

$$E_{\mathbf{kk}'}^{nm}=\varepsilon_{\mathbf{k}_1}^{0n}+\varepsilon_{\mathbf{k}_2}^{0m}+\Delta E_{\mathbf{kk}'}^{nm} , \tag{7}$$

where

$$\Delta E_{\mathbf{kk}'}^{nm}=U\sum_{\alpha\beta}\left[|c_{\alpha}^n(\mathbf{k})|^2\,|c_{\beta}^m(\mathbf{k}')|^2+\sum_{r,s}\sum_{\mathbf{k}'',\mathbf{k}'''}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{k}''-\mathbf{k}''')A_{\mathbf{k}''\mathbf{k}''',\mathbf{kk}'}^{rs,nm}c_{\alpha}^{n*}(\mathbf{k})c_{\beta}^{m*}(\mathbf{k}')c_{\alpha}^r(\mathbf{k}'')c_{\beta}^s(\mathbf{k}''')\right] . \tag{8}$$

The scattering coefficients $A_{\mathbf{k}''\mathbf{k}''',\mathbf{kk}'}^{rs,nm}$ turn out to be related to the two-particle Green function according to the following expression:

$$\sum_{r,s}\sum_{\mathbf{k}'',\mathbf{k}'''}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{k}''-\mathbf{k}''')A_{\mathbf{k}''\mathbf{k}''',\mathbf{kk}'}^{rs,nm}c_{\alpha}^r(\mathbf{k}'')c_{\beta}^s(\mathbf{k}''')=-U\frac{G_{\alpha\beta}(\mathbf{k}+\mathbf{k}',E_{\mathbf{kk}'}^{nm})c_{\alpha}^n(\mathbf{k})c_{\beta}^m(\mathbf{k}')}{1+UG_{\alpha\beta}(\mathbf{k}+\mathbf{k}',E_{\mathbf{kk}'}^{nm})} , \tag{9}$$

where

$$G_{\alpha\beta}(\mathbf{k}+\mathbf{k}',E_{\mathbf{kk}'}^{nm})=\sum_{r,s}\sum_{\mathbf{k}'',\mathbf{k}'''}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{k}''-\mathbf{k}''')\frac{|c_{\alpha}^r(\mathbf{k}'')|^2\,|c_{\beta}^s(\mathbf{k}''')|^2}{\varepsilon_{\mathbf{k}''}^{0r}+\varepsilon_{\mathbf{k}'''}^{0s}-E_{\mathbf{kk}'}^{nm}} . \tag{10}$$

By substituting (9) and (10) into expression (8), one gets

$$\Delta E_{\mathbf{kk}'}^{nm}=U\sum_{\alpha,\beta}\frac{|c_{\alpha}^n(\mathbf{k})|^2\,|c_{\beta}^m(\mathbf{k}')|^2}{1+UG_{\alpha\beta}(\mathbf{k}+\mathbf{k}',E_{\mathbf{kk}'}^{nm})} . \tag{11}$$

Quasiparticle eigenvalues $\varepsilon_{\mathbf{k}}^n$ can be defined from these eigenvalues of the two-particle interacting system as

$$\varepsilon_{\mathbf{k}}^n=\varepsilon_{\mathbf{k}}^{0n}+\Sigma_{\mathbf{k}}^n , \tag{12}$$

where $\Sigma_{\mathbf{k}}^{n}$ are the self-energy corrections to the single-particle eigenvalues

$$\Sigma_{\mathbf{k}}^{n}=\sum_{\mathbf{k}'}\sum_{m}\Delta E_{\mathbf{k}\mathbf{k}'}^{nm}\ ,\tag{13}$$

the sum being over occupied states. It is seen from Eq. (13) that the self-energy is written as a sum of complex binary interactions; this form is typical of the low-density approximation. The above expressions cannot be used directly to calculate $\Delta E_{\mathbf{k}\mathbf{k}'}^{nm}$ and self-energy corrections since just these quantities enter the definition of the two-particle Green function. What is generally done to bypass this difficulty is to calculate the two-particle Green function at any energy ξ

$$G_{\alpha\beta}(\mathbf{k}+\mathbf{k}',\xi)=\sum_{r,s}\sum_{\mathbf{k}'',\mathbf{k}'''}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{k}''-\mathbf{k}''')\times\frac{|c_{\alpha}^{r}(\mathbf{k}'')|^{2}\,|c_{\beta}^{s}(\mathbf{k}''')|^{2}}{\varepsilon_{\mathbf{k}''}^{0r}+\varepsilon_{\mathbf{k}'''}^{0s}-\xi}\ .\tag{14}$$

Let us consider now the case of hole states; we want, in fact, to reproduce the photoemission spectrum where an extra hole is created and interacts with the holes already present in the partially filled d band of the material. To move from electrons to holes one has to change the sign of energies and to interchange the summation over filled and empty states. Having done this, one gets the expression for the two-hole Green function as follows (notice the change in the energies sign and the integration over filled states):

$$G_{\alpha,\beta}(\xi)=\int_{-\infty}^{E_F^0}d\varepsilon_1\int_{-\infty}^{E_F^0}d\varepsilon_2\,\frac{n_{\alpha}(\varepsilon_1)n_{\beta}(\varepsilon_2)}{-\varepsilon_1-\varepsilon_2+\xi}\ ,\tag{15}$$

where we have introduced the orbital density of states

$$n_{\alpha}(\varepsilon)=\sum_{n}\sum_{\mathbf{k}}|c_{\alpha}^{n}(\mathbf{k})|^{2}\delta(\varepsilon-\varepsilon_{\mathbf{k}}^{0n})\ ,$$

the sum being over filled states. In (15) we got rid of the momentum dependence by taking advantage of the result of Treglia, Ducastelle, and Spanjard, who have shown that a momentum average of this expression is the leading term (the "local" term in Ref. 3). We are now able to write the self-energy of Eq. (13) more conveniently as follows:

$$\Sigma_{\mathbf{k}}^{n}(\omega)=\sum_{\alpha}|c_{\alpha}^{n}(\mathbf{k})|^{2}\Sigma_{\alpha}(\omega)\ ,\tag{16}$$

where

$$\Sigma_{\alpha}(\omega)=-\sum_{\beta}\int_{E_F^0}^{\infty}n_{\beta}(\varepsilon)t_{\alpha,\beta}(\varepsilon+\omega)d\varepsilon\ ,\tag{17}$$

with the scattering matrix $t_{\alpha\beta}$ defined as

$$t_{\alpha,\beta}(\xi)=\frac{U}{1+UG_{\alpha,\beta}(\xi)}\ .\tag{18}$$

Notice that, since the Coulomb correlation is effective only on d states, in these last formulas the indices α,β refer to d orbitals only. This will be true in all the following.

Equations (15)–(18) describe the actual procedure for calculating self-energy corrections. They allow one to elucidate how the inclusion of many bands may affect the hole self-energy; if we consider a hole in the d atomic state ϕ_{α}, it can be scattered by the Coulomb interaction with another hole in the d orbital ϕ_{β} through the $t_{\alpha,\beta}$ scattering matrix. The self-energy Σ_{α} of this hole is obtained by summing over all the d atomic orbitals, included the ϕ_{α} orbital itself, weighing every scattering process with the partial density of hole states, i.e., with the contribution of every d orbital to the density of empty states [see Eq. (17)]. To get the self-energy for a specific wave vector and band index $\Sigma_{\mathbf{k}}^{n}$, one has to sum the d orbital self-energies, weighing each of them with the square modulus of the corresponding coefficients in the expansion of the single-particle Bloch wave function.

The multiband effects enter the theory in many ways. First, through the orbital density of filled states: the filled part of the orbital densities of states determines the energy dependence of the two-particle Green functions $G_{\alpha,\beta}$ and, therefore, of $t_{\alpha,\beta}$. The crucial characteristic of the filled orbital densities of states in this context are their widths and their center of gravity with respect to E_F^0—they determine the amplitude and the energy position of the structures in $G_{\alpha,\beta}$ and $t_{\alpha,\beta}$, respectively. This is also true in the single-band theories, even assuming simplified forms of the density of states; what is different here is the fact that differences are allowed in the orbital densities of states which may turn out in strong differences among the various orbital components of the two-particle Green's functions and scattering matrices.

The relation between these two last quantities and the orbital self-energies involves the empty part of the orbital densities of states. This is another point where the multiband effects are active, making Σ_{α} depend upon the orbital distribution of the hole states and not only upon the total hole number, as commonly assumed in single-band theories. As a result of these combined effects, we expect that in strongly anisotropic systems, where significant differences among the orbital components of the density of states exist, $G_{\alpha,\beta}$, $t_{\alpha,\beta}$, and Σ_{α} may vary considerably on passing from one orbital to another. In such a situation, we expect that the conditions for the occurrence of a two-hole bound state, corresponding to the vanishing of the denominator in Eq. (18), may be significantly different for the various orbitals and many satellites may be found in the quasiparticle spectra.[14] On the other hand, if the orbital densities of states do not vary appreciably with α, as in highly symmetric systems, the $t_{\alpha,\beta}=t_{\alpha,\alpha}$ for any α and a single-band model may be adequate.

Finally, band effects are explicitly present in Eq. (16): notice that the wave vector and band index dependence are a consequence of the presence of the square modulus of $c_{\alpha}^{n}(\mathbf{k})$ in this equation. This allows one to understand how the hybridization between the nearly free sp bands and the localized d bands affects the self-energy. Since no direct Coulomb repulsion exists in sp orbitals or as a consequence of the interaction between electrons in these states and electrons in d orbitals, the influence of the hybridization can only be indirect, i.e., connected with its effects on the density of d states and on the composition of a specific Bloch orbitals. In particular, if we consider a band arising from the coupling between a *d* orbital and free-electron states, the self-energy turns out to be reduced compared to the value determined from the partial *d* density of states by a factor $|c_{\alpha}^{n}(\mathbf{k})|^2$.

The fact that the self-energy may depend upon $\mathbf{k}$ and the band index has been previously pointed out.[12] The contribution of the present work is that we calculate the two-hole propagator without introducing any averaging over the orbital indices. As a consequence, the *t*-matrix is not diagonal in the orbital indices as was previously assumed.

The present approach also allows one to overcome one of the difficulties found in the application of the Hubbard model within a single-band theory, i.e., the choice of the actual width of the *d* band to be considered in the calculation. A common approximation[3] is to start from a single-particle density of states obtained, neglecting any hybridization effect, and to consider pure *d* bands only, this leads to an unrealistic description of the electronic distribution. Our approach does not rely on this or similar assumptions; rather, it treats consistently both the *sp* and the *d* bands.

The effects of the correlation on the filled part of the single-particle spectrum can be described in terms of the hole spectral function

$$A_{\mathbf{k}}^{n}(\omega)=\frac{1}{\pi}\mathrm{Im}\frac{1}{\omega-\varepsilon_{\mathbf{k}}^{0n}-\Sigma_{\mathbf{k}}^{n}(\omega)} , \tag{19}$$

which defines the total density of quasiparticle states

$$N(\omega)=\sum_{\mathbf{k}} N_{\mathbf{k}}(\omega) \tag{20}$$

with

$$N_{\mathbf{k}}(\omega)=\sum_{n} A_{\mathbf{k}}^{n} , \tag{21}$$

and the local density of quasiparticle states

$$N_{\alpha}(\omega)=\sum_{\mathbf{k}}\sum_{n}|c_{\alpha}(\mathbf{k},n)|^2 A_{\mathbf{k}}^{n}(\omega) . \tag{22}$$

B. Self-consistency

The theory we have considered up to now does not include any self-consistent procedure. This point has been explicitly addressed in recent studies.[5,16–18] With reference to the satellite structure, it is generally agreed that its intensity turns out to be considerably smaller in a self-consistent calculation than in a non-self-consistent one. The problem of self-consistency has to do with the definition of the Fermi level after the inclusion of self-energy corrections. The single-particle Fermi level E_F^0, in the same way as the single-particle eigenvalues, should in fact be self-energy corrected to give rise to the Fermi level for the interacting system

$$E_F=E_F^0+\mathrm{Re}[\Sigma_{\mathbf{k}}^{n}(E_F)] . \tag{23}$$

A difficulty is implicit in this expression, that is the violation of the important requirement that the imaginary part of $\Sigma_{\mathbf{k}}^{n}(\omega)$ would vanish for $\omega=E_F$: the self-energy is, in fact, equal to zero by construction at the one-electron Fermi level E_F^0 causing quasiparticles at the true E_F to have finite lifetimes. This requirement can be artificially restored[4,19] by adjusting the origin of energy in the self-energy

$$\tilde{\Sigma}_{\mathbf{k}}^{n}(\omega)=\Sigma_{\mathbf{k}}^{n}(\omega-\Delta) \tag{24}$$

with

$$\Delta=E_F-E_F^0 \tag{25}$$

and substituting $\Sigma_{\mathbf{k}}^{n}(\omega)$ with $\tilde{\Sigma}_{\mathbf{k}}^{n}(\omega)$ in all the preceding formulas and, in particular, in expression (19) of the spectra function and in the calculation of the related quantities (20)–(22).

This method is, however, empirical and does not tackle the problem of a consistent determination of the Fermi energy *and* of the occupancy of the *d* band; the normalization of the quasi-particle density of states is, in fact, another important requirement and its fulfillment can define a self-consistent loop which ends up with the correct determination of E_F.[17] Calculations for a single band with model rectangular or semielliptical density of states have shown unambiguously that self-consistency reduces the intensity of the satellite structures considerably compared with the results of a non-self-consistent theory, the effect being larger when a perturbative expansion is used[18] than for a *t*-matrix approach.[17] The requirement of self-consistency is, therefore, important in order to achieve realistic results.

Unfortunately, this self-consistent procedure, while easy in the case of simplified models (single-band and simplified density of states), is not practical in our multiband theory. We have, therefore, adopted an alternative approach which amounts to adjusting the origin of the energy scale in $\Sigma_{\mathbf{k}}^{n}(\omega)$ as in (24) defining the quantity Δ in such a way that

$$\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{E_F^0+\Delta}\frac{1}{\omega-\varepsilon_{\mathbf{k}}^{n0}-\Sigma_{\mathbf{k}}^{n}(\omega-\Delta)}=N , \tag{26}$$

N being the number of occupied states. In the following, we will show that this shift in the energy scale turns out to be not too different from the one defined in Eq. (25); in this way it is possible to fulfill both requirements at the same time.

In applying the previous theory to specific cases, one is faced with the difficulty that the single-particle energies $\varepsilon_{\mathbf{k}}^{0n}$ are usually obtained from a density-functional calculation of the band structure, where correlation effects are already treated in a statistical approach through a local self-consistent potential. While this has the advantage that the effects of all the interactions not covered by our model Hamiltonian are taken into account, it also implies that the interactions present in H_{12} have been partially accounted for in the band-structure calculation. To avoid a double counting of these interactions, one should derive a renormalized spectrum, i.e., a distribution of single-particle energies where the effects due to H_{12} have been subtracted.

The procedure that has been commonly used in previous studies, based on a perturbation expansion to second order in U, consists of introducing an additional parameter Δ^0 into the self-energy, i.e., defining a self-energy for the renormalized band structure as

$$\Sigma_{\text{ren}}(\omega)=U^2\Delta^0+\Sigma(\omega)\ .$$

Since the real and imaginary parts of the self-energy are related by a Hilbert transformation, Δ^0 has to be energy independent. Its value is determined empirically by fitting the theoretical one-hole spectra with the experimental energy distribution curves.[8,10]

One easily recognizes that this empirical correction cannot be applied to the results of a self-consistent calculation since it may lead to a substantial deviation from the self-consistency requirement [Eq. (26)]. A better prescription to derive renormalized bands can be achieved within a tight-biding description of single-particle states. If one regards the intra-atomic parameters as mean-field values resulting from the approximate treatment of correlation provided by band theory, then it would be appropriate to calculate the hole self-energy with the bare intra-atomic parameters obtained by subtracting Coulomb effects from the one-particle Hamiltonian. Expressions for these corrections are given elsewhere.[20,21] Inserting our hole values for Ni and NiSi$_2$ into such expressions lead to small displacements of the intra-atomic parameters. However, the self-energy calculated in a self-consistent way from this renormalized band structure is not significantly different from the one obtained, starting from the original band structure. This suggests that in our cases the need for a renormalized band structure may be overcome by the self-consistency of the calculation.

III. RESULTS FOR NICKEL AND NICKEL DISILICIDE

The calculation of self-energy corrections requires as a first step the determination of the single-particle eigenvalues and eigenfunctions. We have performed a tight-binding parametrization of the band structure of paramagnetic Ni and of NiSi$_2$ obtained from first principles in the linear-muffin-tin-orbital (LMTO) scheme.[22] The tight-binding parameters obtained for the two systems via least-squares fitting are shown in Tables I and II.

Since our purpose is not to achieve an accurate description of the Ni band structure, which would be impossible within the low-density approximation,[15,20] but, rather, to discuss the effects of a realistic band description, particularly of the hybridization, on the self-energy corrections, we have limited our interest to the paramagnetic phase of nickel. For this reason, we have extended our study to NiSi$_2$, where the effects of hybridization are even stronger, involving both Ni and Si sp states.[13]

The total densities of states $n(\varepsilon)$ of Ni and NiSi$_2$ and the Ni d-orbital contributions $n_\alpha(\varepsilon)$ to them are shown in Figs. 1 and 2. Notice that the two systems exhibit a different degree of anisotropy, the width and center of gravity of the orbital components of the d density of states being almost identical for Ni and significantly different in the case of the disilicide. The total Ni d-orbital occupancies turn out to be very similar in the two systems, 8.86 and 8.88 electrons for Ni and NiSi$_2$, respectively, but they arise from different distributions: the orbital occupancies, in fact, are 1.71 (1.88) and 1.67 (1.94) electrons per orbital for t_{2g} (e_g) symmetry of Ni and NiSi$_2$, respectively. In order to calculate the self-energy $\tilde{\Sigma}^n_{\mathbf{k}}(\omega)$ it is necessary (a) to fix a value for the parameter U describing the correlation between d electrons, and (b) to determine the shift in the self-energy scale defined by expression (26). In agreement with what is given in the literature[4,9] we have chosen a value $U=2.5$ for both Ni and NiSi$_2$. This shift Δ has been determined to be -0.804 and -0.275 for Ni and NiSi$_2$, respectively; these numbers turn out to be practically coincident with the values of the self-energy near the unperturbed Fermi level in the two cases, also satisfying, in this way [see definition (25)], the requirement of a vanishing quasiparticle lifetime at E_F.

TABLE I. Tight-binding parameters in eV of nickel.

	E_s	2.536	
	E_p	15.860	
	E_d	−3.008	
	First neighbor	Second neighbor	Third neighbor
($ss\sigma$)	−1.563	0.176	0.184
($pp\sigma$)	4.359	0.099	−0.142
($pp\pi$)	0.143	0.220	−0.143
($dd\sigma$)	−0.501	−0.098	
($dd\pi$)	0.332	0.033	
($dd\delta$)	−0.062	0.002	
($sp\sigma$)	1.665	−0.594	−0.251
($sd\sigma$)	0.618	0.245	0.023
($pd\sigma$)	0.824	0.230	0.098
($pd\pi$)	−0.086	0.052	0.098

In Figs. 3 and 4 we show the orbital components of the self-energy $\Sigma_\alpha(\omega)$. It appears that significant differences can occur in the shape of the self-energy curves for different symmetries. This is particularly evident in NiSi$_2$, where the structures in the curve for the e_g symmetry are less pronounced than for t_{2g} and occur at

TABLE II. Tight-binding parameters in eV of NiSi$_2$.

		Ni	Si	
	E_s	11.722	−6.756	
	E_p	44.119	3.344	
	E_d	−2.860	12.115	
	Ni-Ni	Si-Si	Si-Ni	Ni-Si
($ss\sigma$)	−0.213	−1.180	−0.306	−0.306
($pp\sigma$)	9.159	3.506	4.064	4.064
($pp\pi$)	1.240	−1.008	1.204	1.204
($dd\sigma$)	−0.148	−0.119	−0.526	−0.526
($dd\pi$)	−0.079	2.317	0.733	0.733
($dd\delta$)	0.033	−0.179	−0.233	−0.233
($sp\sigma$)	0.006	1.552	−1.098	0.855
($sd\sigma$)	−0.873	0.570	−1.260	−1.441
($pd\sigma$)	−0.545	2.224	−2.021	−4.961
($pd\pi$)	0.243	1.319	−0.323	−0.174

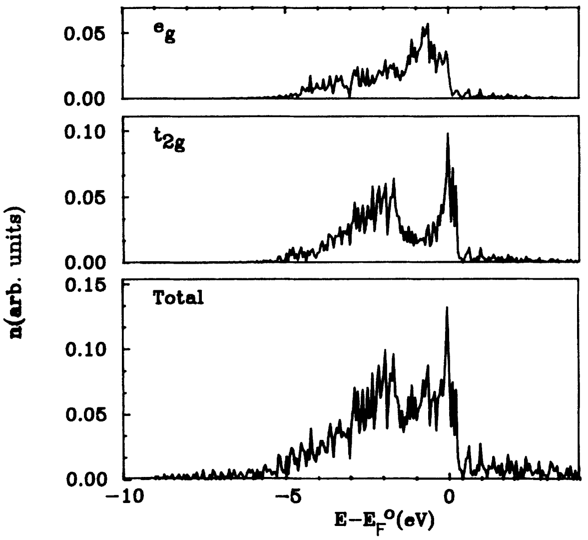

FIG. 1. Density of single-particle states of Ni. The lower panel shows the total density of states, while the upper ones the contributions from xy,yz,zx (t_{2g}) and $x^2-y^2,3z^2-r^2$ (e_g). Energies are in eV and are referred to as E_F^0.

different energies. This is a consequence of the anisotropy in the orbital densities of states for $NiSi_2$, as discussed above. Notice, moreover, that the mixing between different orbital occupancies involved by the definition of Σ_α [see Eq. (17)] is responsible for comparable Σ_α values, in spite of the large differences between the orbital occupancies.[23]

The differences between the two orbital symmetries in $NiSi_2$ and between $NiSi_2$ and Ni can be understood when considering how the characteristics of the partial densities of states affect the definition of the orbital self-energy.

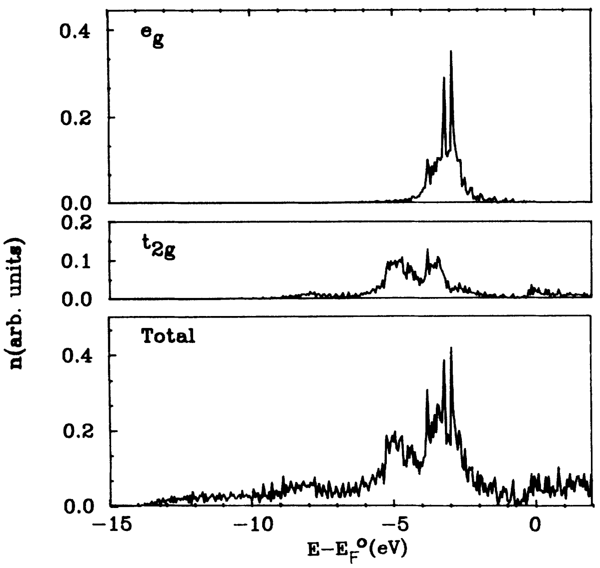

FIG. 2. Density of single-particle states of $NiSi_2$. Total (lower panel) and d-orbital (upper panels) contributions are shown. Energies are in eV and are referred to as E_F^0.

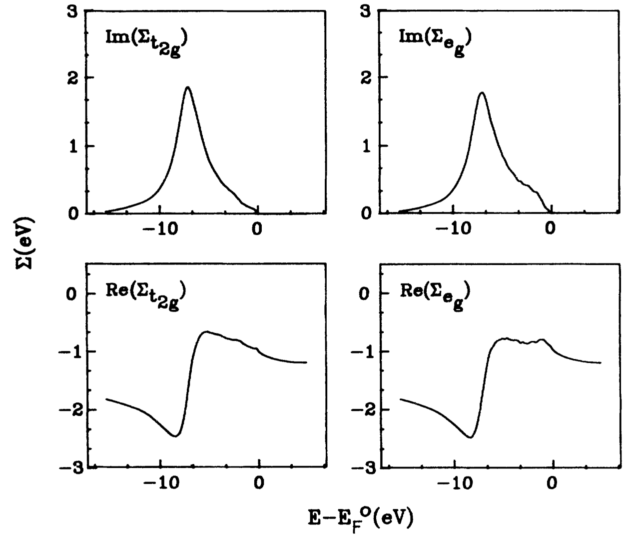

FIG. 3. Real and imaginary part of the calculated self-energy $\Sigma_\alpha(\omega)$ of Ni. Energies are in eV and are referred to as E_F^0.

As pointed out above, the energy positions of the structures in Σ_α and their absolute values are determined (i) by the filled part of the d orbital density of states entering the definition of $G_{\alpha,\beta}$ and $t_{\alpha,\beta}$, and (ii) by the empty parts of such densities of states (number of holes) which appear as a multiplying factor in expression (17). The strong hybridization with silicon sp orbitals present in the disilicide is responsible for the self-energy reduction in that case compared with Ni, since it causes a broadening of the energy range where the Ni d character is present. This is true of states of t_{2g} symmetry, which give the dominant contribution to Σ_α for $NiSi_2$, since only in this symmetry do empty d states exist.

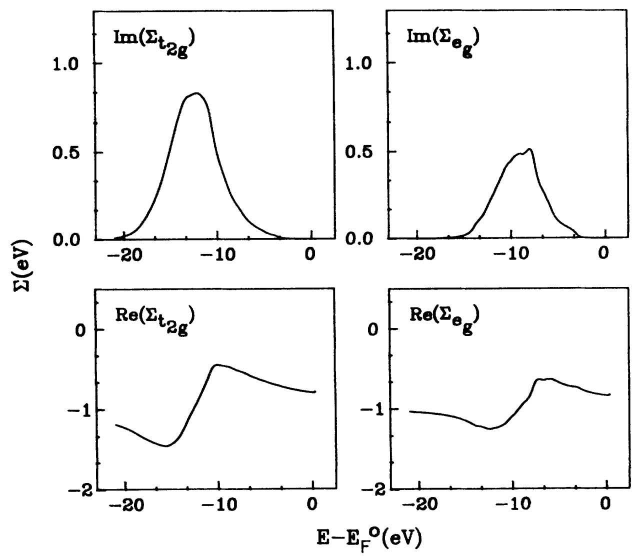

FIG. 4. Real and imaginary parts of the calculated self-energy $\Sigma_\alpha(\omega)$ of $NiSi_2$. Energies are in eV and are referred to as E_F^0.

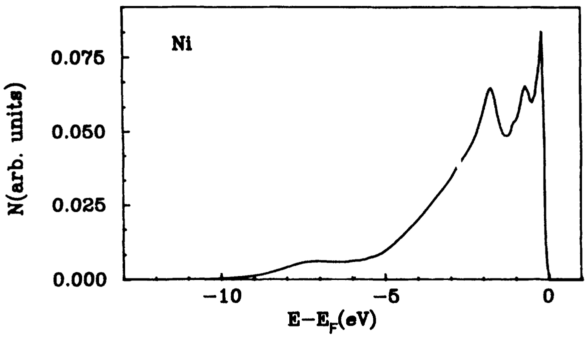

FIG. 5. d-orbital contribution to the density of quasiparticle states of Ni. Energies are in eV and are referred to as E_F.

The resulting $\Sigma_{\mathbf{k}}^{n}(\omega)$ for each $\mathbf{k}$ and band index are a linear combination of the different $\Sigma_\alpha(\omega)$ weighted by the d-orbital composition of that particular eigenstate [see (16)]. This gives rise to the $\mathbf{k}$ dependence of the self-energy. In our cases this dependence is almost entirely due to the hybridization. To illustrate this point we consider the self-energy of the Δ_1 bands of Ni, which are strongly affected by the hybridization. With reference to the calculated band structure along the Δ direction (see Fig. 7), we notice that at the Brillouin zone center the Γ_1 state is pure s, while $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ are degenerate at Γ_{12}. On moving from Γ_{12} towards X the $d_{x^2-y^2}$ orbitals give rise to the Δ_2 band, while the $d_{3z^2-r^2}$ orbitals get mixed with s and p_z states along the Δ_1 band. This band shows an increasing sp character and, starting from the midpoint of the Δ direction, it has the concave upwards dispersion characteristic of a free-electron band. On the basis of these considerations one would expect the self-energy appropriate to Δ_1 bands to be strongly dependent upon $\mathbf{k}$, in particular, it should be reduced on moving away from Γ_{12} in the upper band and on going from X_1 toward Γ in the lower one. This behavior can be reproduced only by a multiband theory like the present one.

Such a pronounced $\mathbf{k}$ dependence is not found for the other bands in nickel. This is a consequence of the high symmetry of the Ni structure, which does not allow for significant variations in the shape of Σ_α curves for different d orbitals.

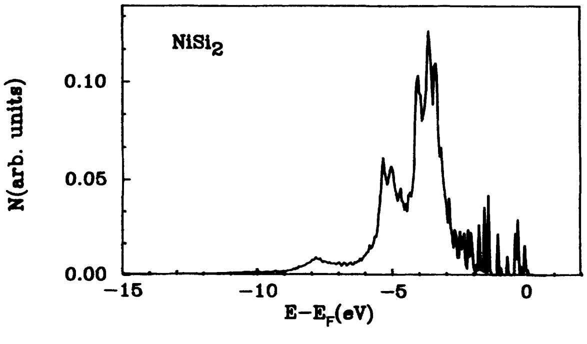

FIG. 6. d-orbital contribution to the density of quasiparticle states of NiSi$_2$. Energies are in eV and are referred to as E_F.

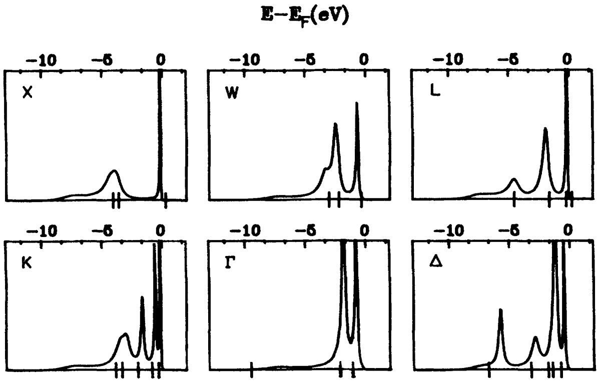

FIG. 7. $\mathbf{k}$-resolved quasiparticle density of states at high-symmetry points of the Brillouin zone of Ni. Vertical bars indicate single-particle eigenvalues, referred to as E_F^0.

Figs. 5 and 6 show the local d density of quasiparticle states $N_\alpha(\omega)$ for Ni and NiSi$_2$. Let us start by considering the case of Ni. It is well known that the density of quasiparticle states of Ni is dominated by a satellite structure which is experimentally found at about 6 eV below the Fermi level. In the t-matrix approach this structure is interpreted as the excitation of bound-hole pairs; its binding energy is overestimated by the present calculation by about 1 eV as in previous single-band theories; this fact has been attributed to the neglect of additional contributions to the self-energy due to electron-hole interactions.[19,24] The inclusion of both multiband effects and three-body interactions is, however, quite complicated and has not been considered here. The density of quasiparticle states of NiSi$_2$ does not present such satellite structure; this is a consequence of the smaller value of self-energy corrections in this case. By comparing the single-particle and the quasiparticle density of states of NiSi$_2$, the most relevant effect associated with the inclusion of correlation is the shift of the main peak around 4 eV toward higher binding energies.

As previously stated, the most important results of the present multiband theory is to include the wave-vector and band-index dependence in the self-energy; for this reason we have considered a $\mathbf{k}$-resolved density of quasi-

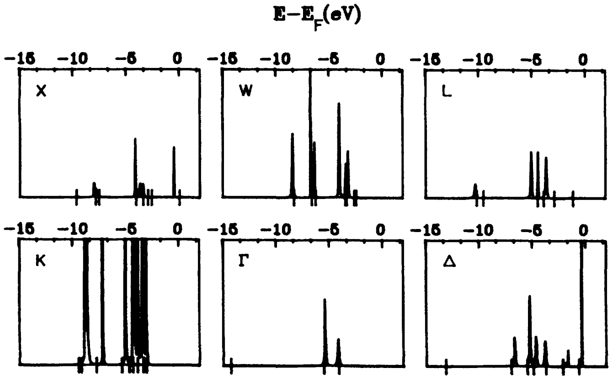

FIG. 8. $\mathbf{k}$-resolved quasiparticle density of states at high-symmetry points of the Brillouin zone of NiSi$_2$. Vertical bars indicate single-particle eigenvalues, referred to as E_F^0.

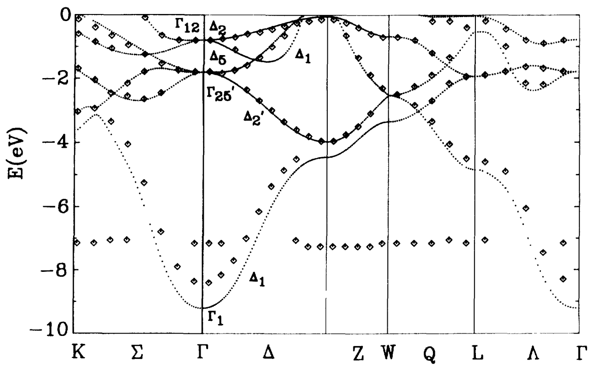

FIG. 9. Quasiparticle band structure of Ni (open diamonds), referred to as E_F, compared with single-particle states (dots), referred to as E_F^0. The symmetry labeling of bands at Γ and along the Δ direction is reported.

particle state defined in (21). Assuming negligible matrix element effects these quantities can be directly compared with the outcomes of angular dependent photoemission experiments. Figures 7 and 8 show the **k**-resolved density of quasiparticle states at the high-symmetry points of the Brillouin Zone of Ni and $NiSi_2$. In these figures the effects of both the real and imaginary part of $\Sigma_{\mathbf{k}}^{n}(\omega)$ are present, determining a shift of the single-particle eigenvalues and their broadening. Both these effects are smaller in the case of $NiSi_2$ due to the smaller absolute value of the self-energy.

As in angle-resolved photoemission experiments, we can proceed to the determination of the quasiparticle eigenstates and satellite energy dispersion by looking for the energy position of maxima in $N_{\mathbf{k}}(\omega)$. The result of this procedure is the quasiparticle band structure shown in Figs. 9 and 10 for Ni and $NiSi_2$, respectively. The energy position of the relevant structures in $N_{\mathbf{k}}(\omega)$ are here referred to as E_F while the single-particle eigenstates drawn for comparison are referred to as E_F^0. Therefore, the differences between quasiparticle and single-particle results take into account both the self-energy corrections and the Fermi-level redefinition.

In the case of Ni the most evident structure is the one at about 7 eV associated with the above-mentioned satellite. Its disappearance at some **k** vectors is due to an increased broadening of the corresponding structure in $N_{\mathbf{k}}(\omega)$. The large shift of the bottom of the valence band with respect to the single-particle result is entirely due to the Fermi-level redefinition since, for a pure *sp* state, self-energy corrections are zero. The net correction to the single-particle eigenvalues does not amount, in general, to a rigid shift; in particular the dispersion of the hybridized *d* bands is significantly modified with respect to the original band structure.

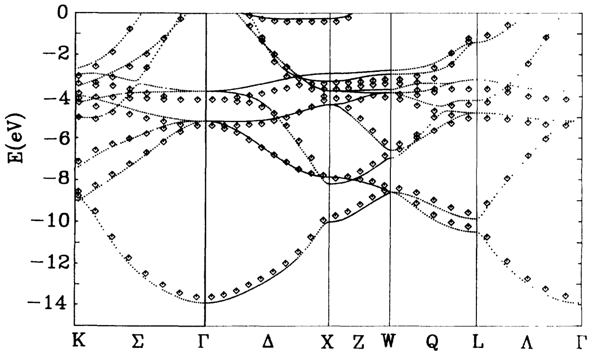

FIG. 10. Quasiparticle band structure of $NiSi_2$ (open diamonds) compared with single-particle states (dots). The reference level for quasiparticle (single-particle) states is E_F (E_F^0).

For $NiSi_2$ the quasiparticle band structure is quite similar to the single-particle one, the only relevant effect being the shift of the quasi-particle band around 4 eV, associated with *d* states, toward higher binding energies. This again reflects the small value of self-energy for this material. Notice again that the net shift from single-particle to quasiparticle states is negative for *d* states and positive for the *sp* states at the bottom of the valence band. This is a consequence of both self-energy corrections and the redefinition of the reference Fermi level.

IV. CONCLUDING REMARKS

The present work differs from other theoretical studies in the inclusion of the full hybridized band structure of Ni and $NiSi_2$ in the calculation of quasiparticle eigenstates. As has been extensively described, the most important consequence of the inclusion of these multiband effects is the restored orbital-index dependence of the two-particle propagator and of the *t* matrix. In strongly anisotropic systems, the differences between the orbital components of the density of states can lead to significant differences in the various components of $G_{\alpha\beta}$ and $t_{\alpha\beta}$; in particular, the energy position of the *t*-matrix divergence may be quite different for different orbital components. This fact has been proven to be responsible, in the case of high-T_c superconductors, for the occurrence of various satellite structures at different energies.[14] In the present instances of Ni and $NiSi_2$, these effects are less pronounced in the case of nickel, the cubic symmetry makes the orbital components of the densities of states rather similar; in the case of $NiSi_2$, where the anisotropy in the orbital densities of states gives rise to differences in the energy position of the structures in $G_{\alpha\beta}$, $t_{\alpha\beta}$, and Σ_α, the small number of holes in one of the symmetries reduces the absolute value of the self-energy corrections and the net effects are small. We have derived self-energy corrections which are **k**- and band-index dependent; this characteristic is particularly important when one is interested in **k**-resolved quantities, such as the dispersion of the quasiparticle eigenstates. The resulting quasiparticle band dispersion presents self-energy corrections which vary on going from pure *d* to pure *sp* states, introducing a shift with respect to single-particle states, which is far from being rigid.

We can draw the following conclusions from our analysis of the results for Ni and $NiSi_2$ concerning the role of the hybridization.

(i) Holes in *d* orbitals that are strongly hybridized are less effective in determining the self-energy corrections. This is partly a consequence of the lower density of states of the hybridized bands compared to the pure *d* ones (smaller Σ_α), and partly comes from the reduced *d* orbital composition of a particular hybridized band (smaller $\Sigma_{\mathbf{k}}^n$).

(ii) The hybridization can affect significantly the self-energy corrections, giving rise to a band dispersion different from the one obtained by single-particle calculations.

ACKNOWLEDGMENTS

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[23] Notice the negative sign of the self-energy corrections. As it appears from the definitions (15)–(18) the *t*-matrix approach gives rise to either positive or negtive self-energy corrections, depending on the value of the *U* parameter. This is in contrast with what was found by perturbation theory,[3] which gives positive self-energies for any *U* value. This contrast is reduced when the theory correctly includes the redefinition of the Fermi level as previously mentioned: by comparing quasiparticle eigenstates (referred to as the self-energy-corrected Fermi level) with the single-particle ones (referred to as the corresponding unperturbed E_F^0), it will appear that the overall shift is $\tilde{\Sigma}_{\mathbf{k}}^n(\varepsilon_{\mathbf{k}}^n)-\Delta$. This quantity turns out to be positive in most cases.

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