

3-Body Scattering (3BS) theory of on-site correlation in narrow band materials

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Abstract

We present the results of a recently developed approach where the interplay between the itinerant and localized character of electrons in narrow band materials is described by adding on-site correlation effects to a first principle band calculation: the single particle band states are treated as mean field solutions of a multi-orbital Hubbard Hamiltonian and the many-body term associated to localized e-e interaction is described in a configuration-interaction scheme. The method allows to calculate hole and electron spectral functions which can be directly compared with spectroscopical results.

8.1 Introduction

The Hubbard model, dominated by the competition between inter-site hopping and on-site electron-electron repulsion, is believed to describe the physics of narrow band materials such as transition metals, transition metal oxides, cuprates, etc. [1]. In these systems the itinerant character of valence electrons - clearly shown by the \mathbf{k} -dispersion observed in photoemission - coexists with strong local correlations responsible of other spectroscopical features - satellites, band-narrowing, and opening, in some cases, of a Mott-Hubbard gap.

In spite of the enormous amount of theoretical and experimental work which has been done on cuprates since the discovery of high T_c superconductors, an unified theoretical description of the whole valence spectrum, from the high binding energy region characterized by satellites, up to the valence band top, including both unperturbed single particle like and strongly correlated Cu derived structures, is still missing; this is due to the difficulty to combine an accurate treatment of many body terms with a realistic description of the band structure.

Most of the work on this subject has been based on a drastic simplification of either the band structure or the e-e interaction; if the complex structure of these systems is reduced to a model description involving only CuO planes, the e-e interaction can be treated accurately, for instance by exact diagonalization techniques of finite (and small) CuO clusters [1], by refined mean-field solutions of a two dimensional t - J Hamiltonian [2] etc. . However, in this search for the simplest model containing the relevant physics of superconductors one may miss some important effects, related for instance to the coupling between adjacent CuO planes [3], and the possibility of a quantitative comparison with spectroscopical results.

Photoemission data of highly correlated materials have been also interpreted using theoretical approaches based on impurity and cluster configuration-interaction models which assume a strong wave function localization and adopt a rather simplified description of the band structure, with a considerable number of adjusting parameters. They have been widely used to describe the main structures and satellite peaks observed in the angle-integrated photoemission spectra of CuO [4] and of cuprate superconductors [5]. Other approaches have been proposed based on the density functional approximation (self-interaction corrected [6] and LDA+U [7] functionals) which fully include the itinerant character of electron states but describe the electron-electron interaction as a mean-field effective single-particle potential.

A theoretical approach is then needed which includes both the hybridization between Cu and the ligands (or between sp and d states in the case of transition metals) accounted for by first principle band theory, and a treatment of e-e interaction which must be non-perturbative - to deal with systems which are in the high correlation regime - and beyond mean field - to include finite life-time excitations.

The 3BS method [8, 9, 10, 11] can be seen as an extension to the solid state of the configuration-interaction scheme used for finite systems: the Hubbard Hamiltonian is projected on a set of states obtained by adding a finite number of e-h pairs to the ground state of the single-particle Hamiltonian and this expansion is truncated to include one e-h pair. The effect of electron correlation on one electron removal energies from a partially filled band is then described as hole-hole and hole-electron interaction. The 3BS theory corresponds to the solution of a 3-body scattering problem involving two holes and one electron and has been originally formulated by Igarashi [8]. Self-energy corrections, spectral functions and quasi-particle band structure can be calculated for systems in different correlation regimes, getting a complete picture of the whole valence spectrum, including both long-lived coherent quasiparticle structures and incoherent short-lived ones.

8.2 Hamiltonians

Since we want to augment band theory with the inclusion of on-site correlation it is essential to define the relationship between band and Hubbard Hamiltonian in order to avoid double counting of e-e interaction. The exact many body Hamiltonian in second quantization is

$$\hat{H} = \sum_{i\alpha\sigma} \epsilon_{i\alpha} \hat{n}_{i\alpha\sigma} + \sum_{\alpha\beta\sigma} \sum'_{ij} t_{i\alpha,j\beta} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma}$$

$$\begin{aligned}
& + \frac{1}{2} \sum_{\alpha\beta} \left[\sum_i (U_{\alpha\beta} - J_{\alpha\beta}) \sum_{\sigma} \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta\sigma} + \sum_i U_{\alpha\beta} \sum_{\sigma} \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta-\sigma} \right] \\
& + \dots(\text{multi-center terms}), \tag{1}
\end{aligned}$$

with $\hat{n}_{i\alpha\sigma} = \hat{c}_{i\alpha\sigma}^{\dagger} \hat{c}_{i\alpha\sigma}$ and $\hat{c}_{i\alpha\sigma}, \hat{c}_{i\alpha\sigma}^{\dagger}$ destruction and creation operators.

Here $\epsilon_{i\alpha}$ and $t_{i\alpha,j\beta}$ are the intra- and inter-atomic matrix elements of the one-particle Hamiltonian and $U_{\alpha\beta}, J_{\alpha\beta}$ are on-site Coulomb and exchange terms:

$$U_{\alpha\beta} = V_{i\alpha\sigma,i\beta\sigma,i\beta\sigma,i\alpha\sigma} = V_{i\alpha\sigma,i\beta-\sigma,i\beta-\sigma,i\alpha\sigma},$$

$$J_{\alpha\beta} = V_{i\alpha\sigma,i\beta\sigma,i\alpha\sigma,i\beta\sigma},$$

with

$$V_{i\alpha\sigma,j\beta\sigma',l\gamma\sigma',m\delta\sigma} = \sum_{ss'} \int \phi_{i\alpha\sigma}^*(\mathbf{r}, s) \phi_{j\beta\sigma'}^*(\mathbf{r}', s') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_{l\gamma\sigma'}(\mathbf{r}', s') \phi_{m\delta\sigma}(\mathbf{r}, s) d\mathbf{r} d\mathbf{r}'.$$

Different approximations to the exact Hamiltonian (1) can be obtained using a mean field approach which amounts to neglect fluctuations in the electron occupation

$$\begin{aligned}
\hat{n}_{i\alpha\sigma} \hat{n}_{i\beta\sigma'} & = \hat{n}_{i\alpha\sigma} \langle \hat{n}_{i\beta\sigma'} \rangle + \hat{n}_{i\beta\sigma'} \langle \hat{n}_{i\alpha\sigma} \rangle - \langle \hat{n}_{i\alpha\sigma} \rangle \langle \hat{n}_{i\beta\sigma'} \rangle \\
& + (\hat{n}_{i\alpha\sigma} - \langle \hat{n}_{i\alpha\sigma} \rangle) (\hat{n}_{i\beta\sigma'} - \langle \hat{n}_{i\beta\sigma'} \rangle) \\
& \simeq \hat{n}_{i\alpha\sigma} \langle \hat{n}_{i\beta\sigma'} \rangle + \hat{n}_{i\beta\sigma'} \langle \hat{n}_{i\alpha\sigma} \rangle - \langle \hat{n}_{i\alpha\sigma} \rangle \langle \hat{n}_{i\beta\sigma'} \rangle.
\end{aligned}$$

The mean field approximation can be applied to all the many body terms of (1) transforming it into a single particle Hamiltonian

$$\hat{H}^{MF} = \sum_{i\alpha\sigma} \epsilon_{i\alpha\sigma}^{MF} \hat{n}_{i\alpha\sigma} + \sum_{\alpha\beta\sigma} \sum_{ij}' t_{i\alpha,j\beta} \hat{c}_{i\alpha\sigma}^{\dagger} \hat{c}_{j\beta\sigma}, \tag{2}$$

or selectively to the multi-center integrals, keeping the full many body character in the one-center terms; in this way one gets the generalized Hubbard model

$$\begin{aligned}
\hat{H}^H & = \sum_{i\alpha\sigma} \epsilon_{i\alpha\sigma}^H \hat{n}_{i\alpha\sigma} + \sum_{\alpha\beta\sigma} \sum_{ij}' t_{i\alpha,j\beta} \hat{c}_{i\alpha\sigma}^{\dagger} \hat{c}_{j\beta\sigma} \\
& + \frac{1}{2} \sum_{\alpha\beta} \left[\sum_i (U_{\alpha\beta} - J_{\alpha\beta}) \sum_{\sigma} \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta\sigma} + \sum_i U_{\alpha\beta} \sum_{\sigma} \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta-\sigma} \right]. \tag{3}
\end{aligned}$$

Since \hat{H}^{MF} and \hat{H}^H differ only for the treatment of the on-site correlation - included in \hat{H}^{MF} as a mean field and treated as a many body term in \hat{H}^H - it is easy to show that

$$\epsilon_{i\alpha\sigma}^{MF} = \epsilon_{i\alpha\sigma}^H + \sum_{\beta} [(U_{\alpha\beta} - J_{\alpha\beta}) \langle \hat{n}_{i\beta\sigma} \rangle + U_{\alpha\beta} \langle \hat{n}_{i\beta-\sigma} \rangle]. \tag{4}$$

Using a Bloch basis set the two approximate Hamiltonians become

$$\begin{aligned}
\hat{H}^H & = \sum_{\mathbf{k}n\sigma} \epsilon_{\mathbf{k}n\sigma}^H \hat{a}_{\mathbf{k}\sigma}^{n\dagger} \hat{a}_{\mathbf{k}\sigma}^n + \sum_{\alpha\beta} \sum_{\mathbf{k}\mathbf{k}'\mathbf{p}} \sum_{nn'} \sum_{mm'} \sum_{\sigma} \frac{1}{2N} \\
& \times \left[U_{\alpha\beta} C_{\alpha\sigma}^n(\mathbf{k})^* C_{\alpha\sigma}^{n'}(\mathbf{k} + \mathbf{p}) C_{\beta-\sigma}^m(\mathbf{k}')^* C_{\beta-\sigma}^{m'}(\mathbf{k}' - \mathbf{p}) \hat{a}_{\mathbf{k}\sigma}^{n\dagger} \hat{a}_{\mathbf{k}+\mathbf{p}\sigma}^{n'} \hat{a}_{\mathbf{k}'-\sigma}^{m\dagger} \hat{a}_{\mathbf{k}'-\mathbf{p}-\sigma}^{m'} \right. \\
& \left. + (U_{\alpha\beta} - J_{\alpha\beta}) C_{\alpha\sigma}^n(\mathbf{k})^* C_{\alpha\sigma}^{n'}(\mathbf{k} + \mathbf{p}) C_{\beta\sigma}^m(\mathbf{k}')^* C_{\beta\sigma}^{m'}(\mathbf{k}' - \mathbf{p}) \hat{a}_{\mathbf{k}\sigma}^{n\dagger} \hat{a}_{\mathbf{k}+\mathbf{p}\sigma}^{n'} \hat{a}_{\mathbf{k}'\sigma}^{m\dagger} \hat{a}_{\mathbf{k}'-\mathbf{p}\sigma}^{m'} \right], \tag{5}
\end{aligned}$$

$$\hat{H}^{MF} = \sum_{\mathbf{k}n\sigma} \epsilon_{\mathbf{k}n\sigma}^{MF} \hat{a}_{\mathbf{k}\sigma}^{n\dagger} \hat{a}_{\mathbf{k}\sigma}^n; \quad (6)$$

here $\hat{a}_{\mathbf{k}\sigma}^n, \hat{a}_{\mathbf{k}\sigma}^{n\dagger}$ are destruction/creation operators of electrons with wave vector \mathbf{k} , spin σ , band index n and $C_{\alpha}^n(\mathbf{k}\sigma)$ are the expansion coefficients of Bloch states in terms of localized orbitals.

The relationship between single particle eigenvalues $\epsilon_{\mathbf{k}n\sigma}^{MF}$ and $\epsilon_{\mathbf{k}n\sigma}^H$ appearing in the two Hamiltonians is now

$$\epsilon_{\mathbf{k}n\sigma}^{MF} = \epsilon_{\mathbf{k}n\sigma}^H + Q_{\mathbf{k}\sigma}^n, \quad (7)$$

$$Q_{\mathbf{k}\sigma}^n = \sum_{\alpha\beta} |C_{\alpha\sigma}^n(\mathbf{k})|^2 \left[U_{\alpha\beta} \frac{1}{N} \sum_{\mathbf{k}'n'}^{occ} |C_{\beta-\sigma}^{n'}(\mathbf{k}')|^2 + (U_{\alpha\beta} - J_{\alpha\beta}) \frac{1}{N} \sum_{\mathbf{k}'n'}^{occ} |C_{\beta\sigma}^{n'}(\mathbf{k}')|^2 \right], \quad (8)$$

which is the analogue of eq. (4) for Bloch states. Any band structure calculation corresponds to the solution of some \hat{H}^{MF} describing the interacting system as an effective single particle problem and equations (7,8) contain the correct recipe to include Hubbard correlation starting from band structure eigenvalues, avoiding e-e interaction double counting.

8.3 Hole spectral function, self-energy and the Faddeev method

We are interested in the hole spectral function

$$D_{\mathbf{k}\sigma}^-(\omega) = \frac{1}{\pi} \sum_n \text{Im} \mathcal{G}^-(\mathbf{k}n\sigma, \omega), \quad (9)$$

which describes the removal of one electron of wave-vector \mathbf{k} , band index n and spin σ and is related to the hole-propagator

$$\mathcal{G}^-(\mathbf{k}n\sigma, \omega) = - \langle \Psi_0 | \hat{a}_{\mathbf{k}\sigma}^{n\dagger} \hat{G}(z) \hat{a}_{\mathbf{k}\sigma}^n | \Psi_0 \rangle, \quad z = -\omega + E_0(N_e) + i\delta; \quad (10)$$

$E_0(N_e)$ and $|\Psi_0\rangle$ define the ground state of the N_e particle system and

$$\hat{G}(z) = \frac{1}{z - \hat{H}^H} \quad (11)$$

is the resolvent operator. By projecting the Hamiltonian (5) over a complete set appropriate for the $N_e - 1$ particle system one gets an expression for \hat{H}^H appropriate to describe one electron removal. The key approximation is to choose a subset of all the excited states of the *non-interacting* system and assume it to be complete. Any N particle non-interacting state can be obtained by repeated applications of creation/destruction operators to the ground state Slater determinant $|\Phi_0\rangle$ i.e. by adding e-h pairs to it; according to 3BS the *interacting* state with one removed electron of momentum \mathbf{k} and spin σ is expanded in terms of the basis set including 1-hole and 3-particle configurations

$$|s\rangle \equiv \hat{a}_{\mathbf{k}n\sigma} |\Phi_0\rangle, \quad |t\rangle \equiv \hat{a}_{\mathbf{q}_3 n_3 \sigma_3}^\dagger \hat{a}_{\mathbf{q}_2 n_2 \sigma_2} \hat{a}_{\mathbf{q}_1 n_1 \sigma_1} |\Phi_0\rangle, \quad (12)$$

with

$$\mathbf{q}_1 + \mathbf{q}_2 - \mathbf{q}_3 = \mathbf{k}, \quad \sigma_1 + \sigma_2 - \sigma_3 = \sigma.$$

The effective Hamiltonian for the $N-1$ particle system is then

$$\hat{H}_{N_e-1}^H \simeq \hat{H}_1 + \hat{H}_3 + \hat{V}, \quad (13)$$

where \hat{H}_1 is associated to one-hole configurations

$$\hat{H}_1 = \langle s | \hat{H}^H | s \rangle | s \rangle \langle s |,$$

\hat{H}_3 describes the contribution of 3-particle configurations

$$\hat{H}_3 = \sum_{tt'} \langle t | \hat{H}^H | t' \rangle | t \rangle \langle t' |,$$

and \hat{V} is the coupling between 1- and 3-particle states

$$\hat{V} = \sum_t \langle s | \hat{H}^H | t \rangle | s \rangle \langle t | + h.c. \quad .$$

We can now calculate the resolvent (11). We define the 3-particle resolvent, that is the resolvent associated to the 3-particle interaction

$$\hat{F}_3(z) = \frac{1}{z - \hat{H}_3},$$

and the Dyson equation which relates $\hat{G}(z)$ to it

$$\hat{G}(z) = \hat{F}_3(z) + \hat{F}_3(z) [\hat{H}_1 + \hat{V}] \hat{G}(z). \quad (14)$$

The Faddeev scattering theory allows to determine $\hat{F}_3(z)$ by separating the 3-body Hamiltonian in diagonal and non-diagonal parts

$$\hat{H}_3^D = \sum_t \langle t | \hat{H}^H | t \rangle | t \rangle \langle t |,$$

$$\hat{H}_3^{ND} = \sum_{tt'}' \langle t | \hat{H}^H | t' \rangle | t \rangle \langle t' |,$$

defining the *diagonal* 3-body resolvent

$$\hat{F}_3^D(z) = \frac{1}{z - \hat{H}_3^D},$$

and the scattering operator

$$\hat{S} = \hat{H}_3^{ND} + \hat{H}_3^{ND} \hat{F}_3^D \hat{S}.$$

The *full* 3-body resolvent can be written in terms of the diagonal one and of the scattering operator as

$$\hat{F}_3 = \hat{F}_3^D + \hat{F}_3^D \hat{S} \hat{F}_3^D. \quad (15)$$

As shown in references [9, 10] the non-diagonal 3-body interaction is the sum of two potentials

$$\hat{H}_3^{ND} = \hat{V}_{h-h} + \hat{V}_{h-e},$$

which describe h-h and h-e multiple scattering. We define partial scattering operators $\hat{S}_{h-h}, \hat{S}_{h-e}$ such that $\hat{S} = \hat{S}_{h-h} + \hat{S}_{h-e}$, i.e.

$$\begin{aligned} \hat{S}_{h-h} &= \hat{V}_{h-h} + \hat{V}_{h-h} \hat{F}_3^D \hat{S}, \\ \hat{S}_{h-e} &= \hat{V}_{h-e} + \hat{V}_{h-e} \hat{F}_3^D \hat{S}, \end{aligned}$$

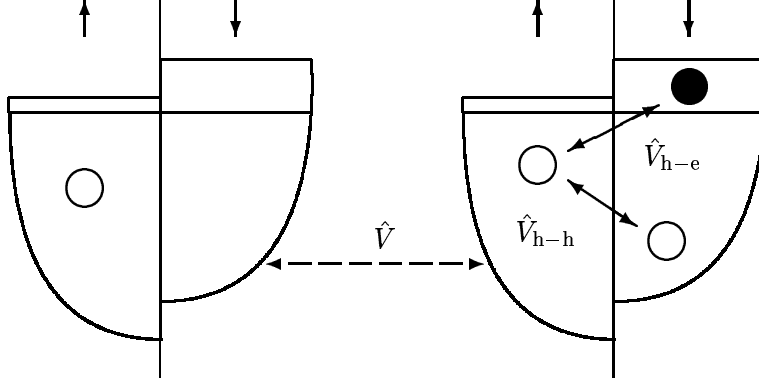


Figure 1: Pictorial representation of non-diagonal terms in the effective hole Hamiltonian: \hat{V} couples one- and three-particle configurations while \hat{V}_{h-h} and \hat{V}_{h-e} describe scattering between three-particle states, namely hole-hole and hole-electron scattering respectively.

which are related to the scattering T-matrices

$$\hat{T}_{h-h} = \hat{V}_{h-h} + \hat{V}_{h-h} \hat{F}_3^D \hat{T}_{h-h}, \quad (16)$$

$$\hat{T}_{h-e} = \hat{V}_{h-e} + \hat{V}_{h-e} \hat{F}_3^D \hat{T}_{h-e}, \quad (17)$$

through the Faddeev equations [12]

$$\begin{aligned} \hat{S}_{h-h} &= \hat{T}_{h-h} + \hat{T}_{h-h} \hat{F}_3^D \hat{S}_{h-e}, \\ \hat{S}_{h-e} &= \hat{T}_{h-e} + \hat{T}_{h-e} \hat{F}_3^D \hat{S}_{h-h}. \end{aligned} \quad (18)$$

Inserting (18) into (15) one gets the expression for the 3-particle resolvent in terms of scattering operators S_{h-e} and T_{h-h}

$$\hat{F}_3 = \hat{F}_3^D + \hat{F}_3^D \left(\hat{T}_{h-h} + \hat{T}_{h-h} \hat{F}_3^D \hat{S}_{h-e} + S_{h-e} \right) \hat{F}_3^D. \quad (19)$$

In this expression \hat{F}_3^D and \hat{T} -operators -or rather their matrix elements between three-particle states- have an analytical expression, while the inclusion of scattering operator \hat{S}_{h-e} will require the solution of an integral equation.

After some algebra the hole propagator becomes

$$\mathcal{G}^-(\mathbf{k}n\sigma, \omega) = -G_{ss}(z) = \frac{1}{\omega - E_0(N_e) + H_{ss}^H + \sum_{tt'} F_{3tt'} V_{t's} V_{st}}; \quad (20)$$

with the notation $G_{ss} \equiv \langle s | \hat{G} | s \rangle$, $F_{3tt'} \equiv \langle t | \hat{F}_3 | t' \rangle$ etc.. Since the difference between the ground state energy of the N_e -particle system $E_0(N_e)$ and the average of \hat{H}^H over $|s\rangle$ states turns out to be

$$E_0(N_e) - H_{ss}^H = \epsilon_{\mathbf{k}n\sigma}^H + Q_{\mathbf{k}\sigma}^n = \epsilon_{\mathbf{k}n\sigma}^{MF},$$

the mean field band eigenvalues appear naturally in the denominator of the hole propagator. Comparing eq. (20) with the usual expression

$$\mathcal{G}^-(\mathbf{k}n\sigma, \omega) = \frac{1}{\omega - \epsilon_{\mathbf{k}n\sigma}^{MF} - \Sigma_{\mathbf{k}n\sigma}^-(\omega)}, \quad (21)$$

we can identify the self-energy correction to band eigenvalues as

$$\Sigma^-(\mathbf{k}n\sigma, \omega) = - \sum_{tt'} F_{3tt'} V_{t's} V_{st}. \quad (22)$$

The procedure we have outlined ends up with a result which has a simple physical interpretation: the creation of one hole in an unfilled valence band is followed by multiple h-h and h-e scattering which is responsible of a renormalization - through self-energy corrections - of the energy states. The efficiency of the scattering processes depends a) on the strength of the screened on-site e-e interaction and b) on the available empty states (i.e. on the number of *initial* valence holes). This explains the well known differences between various transition metals (Ni and Cu, for instance) and possibly those arising in cuprates as a consequence of hole doping.

The self-energy Σ^+ and spectral function D^+ for electron addition can be calculated in the same way as described above just exchanging empty states with filled ones and vice versa, as described in detail in ref. [9].

8.4 3BS at work

In order to calculate the self-energy $\Sigma^-(\mathbf{k}n\sigma, \omega)$ according to (22) one has to perform summations over the 3-particle states $|t\rangle$ involving \mathbf{k} -vector conservation; this is done within the so called *local* approximation [13]

$$\delta_{\mathbf{k}=\mathbf{k}'} = \frac{1}{N} \sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} \simeq \frac{1}{N}.$$

This approximation allows to transform the \mathbf{k} -vector summations into integrals involving the orbital density of states $n_{\alpha}(\epsilon)$ and to calculate T-matrices, scattering operators, resolvents, self-energy and finally spectral functions according to the computational strategy discussed in detail in ref. [9, 10] which can be summarized as follows:

- **Input:** band structure $(\epsilon_k^n, C_{\alpha\uparrow}^n(k), n_{\alpha\uparrow}(\epsilon))$ and U ;
- **free propagators**

$$g_{h-h}^{\alpha\beta}(\omega) = \int_{-\infty}^{E_f} d\epsilon' \int_{-\infty}^{E_f} d\epsilon \frac{n_{\alpha\downarrow}(\epsilon) n_{\beta\uparrow}(\epsilon')}{\omega - \epsilon' - \epsilon - i\delta},$$

$$g_{h-e}^{\alpha\beta}(\omega) = \int_{-\infty}^{E_f} d\epsilon' \int_{E_f}^{\infty} d\epsilon \frac{n_{\alpha\downarrow}(\epsilon) n_{\beta\uparrow}(\epsilon')}{\omega - \epsilon' + \epsilon - i\delta}, \quad g^{\beta}(\omega) = \int_{-\infty}^{E_f} d\epsilon' \frac{n_{\beta\uparrow}(\epsilon')}{\omega - \epsilon' - i\delta};$$

- **T-matrices**

$$T_{h-h}^{\alpha\beta}(\omega) = \frac{U}{1 + U g_{h-h}^{\alpha\beta}(\omega)}, \quad T_{h-e}^{\alpha\beta}(\omega) = \frac{-U}{1 - U g_{h-e}^{\alpha\beta}(\omega)};$$

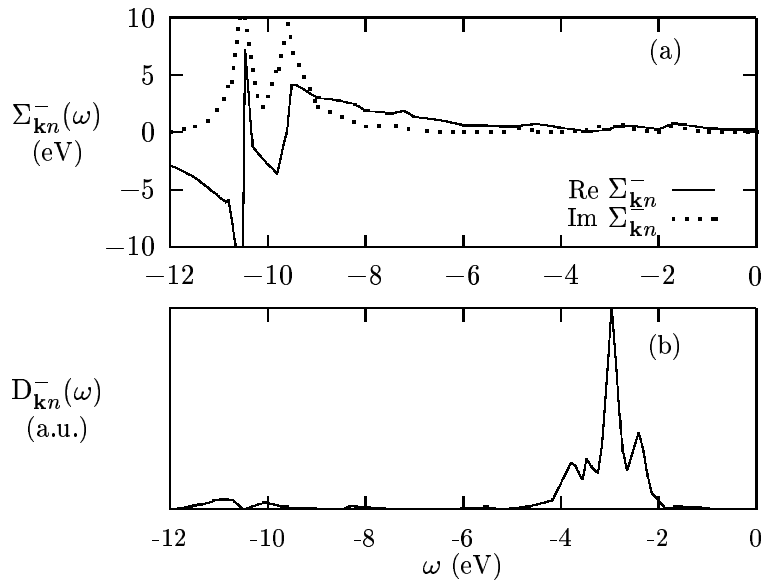


Figure 2: Real (solid line) and imaginary (dotted line) part of self-energy $\Sigma_{\mathbf{k}n}^-(\omega)$ (a) and spectral function (b) in paramagnetic CuGeO₃ for the creation of a hole at the Γ point corresponding to the single particle band energy $\epsilon_{\mathbf{k}}^n = -3.58$ eV. Energies are referred to E_f .

- kernel

$$K^{\alpha\beta}(\omega, \epsilon, \epsilon') = \int_{-\infty}^{E_f} d\epsilon'' n_{\alpha\downarrow}(\epsilon'') g^{\beta}(\omega + \epsilon'' - \epsilon) g^{\beta}(\omega + \epsilon'' - \epsilon') T_{h-e}^{\alpha\beta}(\omega + \epsilon'') T_{h-h}^{\alpha\beta}(\omega - \epsilon''),$$

and

$$B^{\alpha\beta}(\omega, \epsilon) = \int_{-\infty}^{E_f} d\epsilon' n_{\alpha\downarrow}(\epsilon') g^{\beta}(\omega + \epsilon' - \epsilon) T_{h-e}^{\alpha\beta}(\omega + \epsilon') \\ \times \left[g_{h-e}^{\alpha\beta}(\omega - \epsilon') + \int_{E_f}^{\infty} d\epsilon'' n_{\alpha\downarrow}(\epsilon'') g^{\beta}(\omega + \epsilon' - \epsilon'') g_{h-h}^{\alpha\beta}(\omega - \epsilon'') T_{h-h}^{\alpha\beta}(\omega - \epsilon'') \right];$$

- solve the integral equation

$$A^{\alpha\beta}(\omega, \epsilon) = B^{\alpha\beta}(\omega, \epsilon) + \int_{E_f}^{\infty} d\epsilon' n_{\alpha\downarrow}(\epsilon') K^{\alpha\beta}(\omega, \epsilon, \epsilon') A^{\alpha\beta}(\omega, \epsilon');$$

- orbital self-energy

$$\Sigma_{\beta\uparrow}^-(\omega) = \sum_{\alpha} \int_{E_f}^{\infty} d\epsilon n_{\alpha\downarrow}(\epsilon) T_{h-h}^{\alpha\beta}(\omega - \epsilon) \left[1 + U A^{\alpha\beta}(\omega\epsilon) \right];$$

- \mathbf{K} - and band-index dependent self-energy

$$\Sigma^-(kn \uparrow, \omega) = U \sum_{\beta} |C_{\beta\uparrow}^n(k)|^2 \left[\sum_{\alpha} \int_{-\infty}^{E_f} d\epsilon n_{\alpha\downarrow}(\epsilon) \Sigma_{\beta\uparrow}^-(\omega) \right];$$

- spectral function

$$D_{\uparrow}^{(-)}(\omega) = \frac{1}{\pi} \sum_{kn} \text{Im} \frac{1}{\omega - \epsilon_{\mathbf{k}}^n - \Sigma^-(kn \uparrow, \omega)}.$$

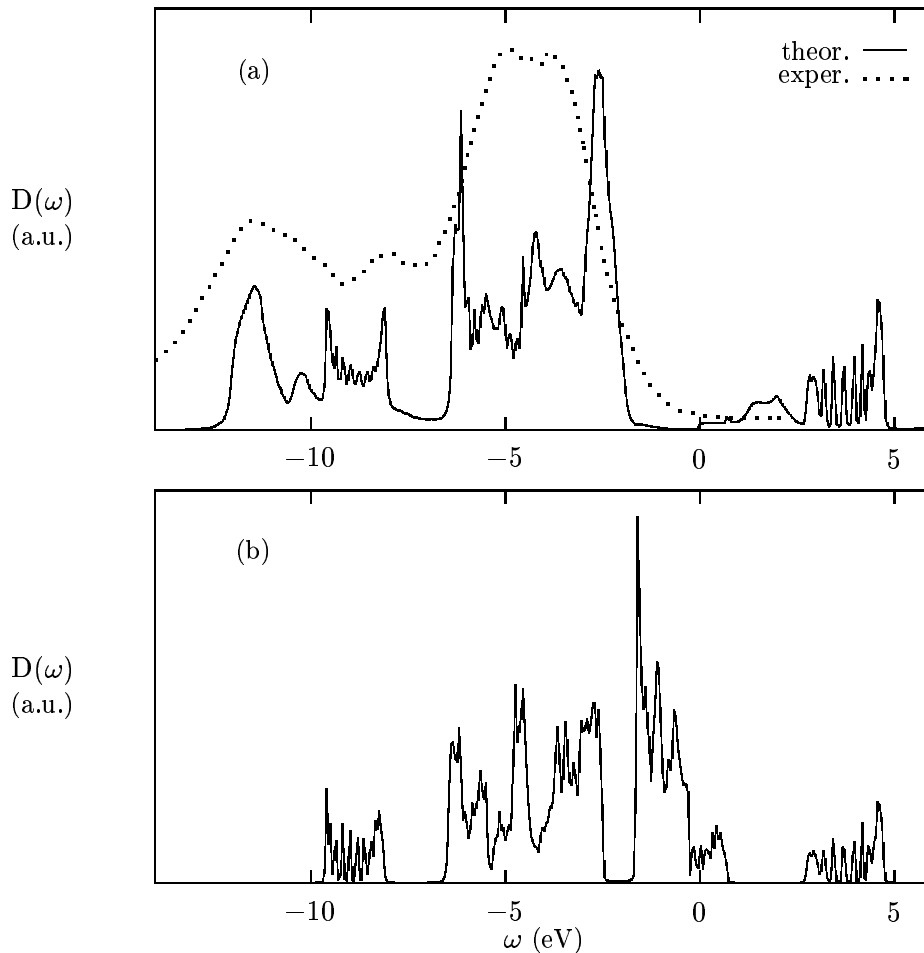


Figure 3: Total spectral function $D(\omega) = D^-(\omega) + D^+(\omega)$ for CuGeO_3 calculated by (a) 3BS theory with $U=8$ eV; (b) single particle density of states ref. [14]. E_f corresponds to $\omega = 0$ eV.

We report the results for a transition metal (nickel) and a cuprate (CuGeO_3) obtained by considering the interaction between opposite spin electrons localized on the transition metal sites as the dominant contribution, i.e.

$$U_{\alpha\beta} = \begin{cases} U_{dd} & \text{for } \alpha, \beta = d \text{ orbitals} \\ 0 & \text{elsewhere;} \end{cases}$$

$$U_{\alpha\beta} - J_{\alpha\beta} \simeq 0.$$

To apply this method to CuGeO_3 we have used the eigenstates/eigenvalues of ref. [14] and assumed $U_{dd} = 8$ eV. Fig. 2 shows the hole spectral function and self-energy for a particular eigenstate ($\epsilon_{\mathbf{k}}^n = -3.58$ eV at the Γ point). The peaks in the spectral function can be classified either as quasiparticle excitations or as satellites, according to the value of the imaginary part of the self-energy in the region of the peak: quasi-particle excitations correspond to small imaginary part, and give rise to the coherent part of the spectral function. Satellites occur where the imaginary part of self-energy is large and correspond to short-lived excitations with a large intrinsic line-width; we refer to them as to the incoherent part of the spectral function.

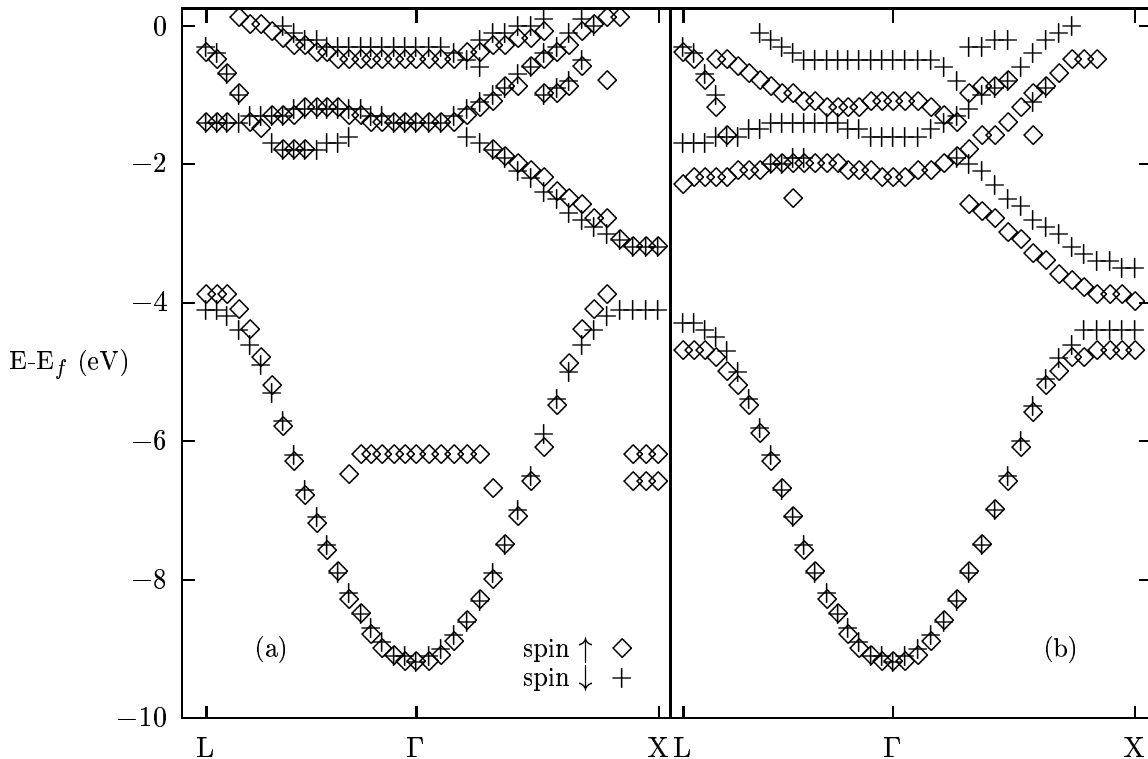


Figure 4: (a) Energy position of the peaks of nickel in the spectral function at \mathbf{k} -points along high symmetry lines of the Brillouin Zone. (b) Single particle band structure of ref. [10].

The hole and electron spectral functions are plotted in fig. 3 and compared with single particle results. The effect of electron correlation on single-particle states is dramatic: some bands are shifted to higher binding energies, spectral weight is removed from the upper part of the spectrum, and many new states (satellites) appear; only states around $-8 \div -9$ eV and $-5 \div -6$ eV are practically unaffected being mainly Ge and O derived. CuGeO_3 is an insulator but it is predicted to be a metal by single particle band calculation; the inclusion of electron correlation reproduces this insulating behavior and the energy gap, calculated as the energy separation between electron removal and electron addition spectra, reproduces the experimental one [15]. The same was proven to be true also in the case of NiO, where a 3BS description of Hubbard correlation was able to reproduce both the complex satellite structure and the measured value of the insulating gap [16].

The ability of 3BS approach to open up Hubbard gaps, i.e. to reproduce an insulating behaviour in a system which is metallic according to band theory, is related to its non-perturbative character; the method can be applied in any correlation regime and it has been shown [8, 16, 17] to reproduce for U much larger than the band width W ($\frac{U}{W} \rightarrow \infty$) the so called “Hubbard I” solution [18] of Hubbard Hamiltonian, i.e. the *atomic limit* where hole and electron states are separated by a Mott-Hubbard gap equal to U [19].

We describe now the results of the application of 3BS to nickel. In this case the on-site e-e repulsion is more effectively screened and the estimated value of U_{dd} is $\simeq 2$ eV [20]. Fig. 4, reporting the comparison between quasi-particle states and single particle ones, shows that e-e

correlation effects are still sizable and they are actually essential in order to reproduce the observed spectroscopical features, i.e. satellite structure at 6 eV binding energy, correct band width (overestimated in LDA), exchange splitting [21], and energy dispersion [10].

8.5 Summary and outlook

We have described a method to include on-site interactions in the description of hole and electrons states: ab-initio single-particle band states are used as input mean-field eigenstates for the calculation of self-energy corrections according to a 3-body scattering (3BS) solution of a multi-orbital Hubbard Hamiltonian. When applied to valence states of ferromagnetic nickel it allows to get a quasiparticle band structure which compares much more favorably with the experimental observation than conventional mean-field LDA, reproducing the observed band width, the energy dispersion, the satellite structure and the exchange splitting. Since the method does not rely on a perturbation expansion it has a wide range of application, including any correlation regime. In the case of a highly correlated system such as CuGeO_3 , 3BS is able to reproduce both the insulating behaviour and a correct overall picture of photoemission experiments.

Our present choice of empirically determining the parameter U of the Hubbard Hamiltonian - which has been fixed to reproduce the satellite binding energy - ensures that we obtain a good agreement with experiments; however the possibility of reproducing both the satellite structures and other spectroscopical features such as energy dispersion and spin dependence in nickel and the insulating gap in CuGeO_3 can be seen as a non trivial result and a success of the method itself: previous methods based on a simplified description of the scattering channels [22, 23] in fact have not been able to reproduce at the same time the satellite energy position and the valence band width which turned out to be systematically overestimated for values of the Coulomb integral fixed to reproduce the satellite binding energy. The problem of extracting Hubbard U from ab-initio calculation, either in the so called Constrained-Density Functional scheme [24] or as screened Coulomb interaction [20, 25], is an important issue which goes in the direction of a full match between model Hamiltonians and realistic systems and that we are presently considering as an implementation of our approach.

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