FAST TRACK COMMUNICATION

Theory of optically forbidden d–d transitions in strongly correlated crystals

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Abstract

A general multiband formulation of the linear and nonlinear optical response functions for realistic models of correlated crystals is presented. Dipole-forbidden d–d optical transitions originate from vertex functions, which we consider assuming the locality of an irreducible four-leg vertex. The unified formulation for second- and third-order response functions in terms of the three-leg vertex is suitable for practical calculations in solids. We illustrate the general approach by consideration of intra-atomic spin-flip contributions, with an energy of 2\(J\), where \(J\) is a Hund exchange, in the simplest two-orbital model.

(Some figures in this article are in colour only in the electronic version)

From the physical point of view most of the natural mineral dyes are Mott or charge transfer insulators and their colors are determined essentially by correlation effects [1]. If a material has no energy gap or its value is smaller than the energy of visual light, it will be non-transparent, black or with a metallic sheen. In the case of broad-gap materials the absorption of visual light is determined by impurities (ruby, that is, Al2O3 doped with Cr3+ ions is a prototype example [1]) or by optically (dipole) forbidden d–d transitions between different terms and multiplets belonging to the same \(d^n\)-configurations of transition metal ions for a pure system. The latter processes are responsible for the green color of NiO [2] and the blue color of most of the divalent copper insulating compounds [3]. These systems are usually colored and transparent and the transparency itself is a manifestation of the dipole-forbidden character of the relevant optical transitions.

Up to now the optical properties of Mott or charge transfer insulators have been considered within the framework of cluster approaches [4, 5]. The present paper develops a general translationally invariant formalism to treat the d–d transitions in strongly correlated crystals. It is commonly accepted now that the standard LDA(GGA) approach is insufficient to describe the electronic structure of the Mott insulators [6]. To have a more adequate picture of the single-electron spectra, various approaches have been applied to the problem such as LDA + U [7], self-interaction corrections [8] and the GW-scheme [9]. However, all these approaches do not provide the correct atomic limit and in particular do not take into account the term and multiplet structures, which are crucial for optics. This problem can be solved within the LDA + DMFT (dynamical mean-field theory) [10, 11] and the Hubbard-I approximation [11, 12]. There were several attempts to calculate the optical properties within the LDA + DMFT using the Kubo formula for optical conductivity [13–15]. However, in all these calculations the vertex contributions were not taken into account and the two-particle Green functions were calculated as a convolution of two single-particle Green functions (for a review of the LDA + DMFT see [16]). The latter contains only transitions related to the promotion of d-electrons to the p-band with the change of transition metal configurations from \(d^n\) to \(d^{n\pm1}\) and thus this approach is not sufficient to explain why NiO is green.

In the DMFT approach the self-energy is local which leads to a cancelation of the vertex corrections in the single-band Hubbard model [17]. However, this is not the case for a generic multiband situation, similar to a treatment of the optical properties of disordered alloys in the coherent-potential approximation (CPA) [18]. Here we present the corresponding formulation for linear and nonlinear optical response functions.
We start with the general expression for linear optical conductivity
\[ \sigma_{ab}(i\omega) = \frac{e^2}{\omega} T^2 \sum_{v'v} \sum_{s} (4\langle v_{a} | 1 \rangle \langle 2 | v_{b} \rangle | 3 \rangle | v_{a} \rangle | v_{b} \rangle \chi_{1234}(iv, iv', i\omega) \]
(1)
where \( \chi_{1234} \) is a generalized susceptibility in a quasiatomic basis set [1] = \( iL\sigma \), where \( i, L, \sigma \) label sites, orbital quantum numbers and spin projections, respectively, \( v_{a} \) is the electron velocity operator (\( a = x, y, z \)), and we use the Matsubara Green functions; at the end of the calculations the analytical continuation \( i\omega \rightarrow \omega + i0 \) should be performed [19].

The two-particle Green function \( \hat{\chi} \) is expressed in terms of the single-particle Green function \( \hat{G} \) and the irreducible vertex function \( \hat{\Gamma} \) as [17, 20]:
\[ \chi_{1234}(iv, iv', i\omega) = -G_{12}(iv')G_{34}(iv)\delta_{v,v' + \omega} \]
(2)
\[ -T \sum_{v} \sum_{5678} G_{15}(iv')G_{26}(iv)\Gamma_{5678}(iv, iv', i\omega) \]
\[ \times \chi_{6237}(iv', iv', i\omega) \]
(3)
which can be written in the matrix form in the Fermionic Matsubara frequencies \( (iv, iv') \) and the pairs of electron quantum numbers (14, 23) as
\[ \hat{\chi} = \hat{\chi}_{0} + \hat{\chi}_{0}^{\dagger} \hat{\Gamma} \hat{\chi} \]
(4)
where \( \hat{\chi}_{0} = -\hat{G} \ast \hat{G} \). Within the DMFT approximation the self-energy \( \hat{\Sigma}(i\omega) \) is local, that is, diagonal in the site indices and \( K \)-independent in the momentum representation [17]. In addition we will assume a locality of the irreducible vertex function \( \hat{\Gamma} \); this is the only approximation we add. Then, it can be obtained from the local version of equation (4):
\[ \hat{\Gamma} = \hat{\chi}_{0}^{\dagger} - \hat{\chi}_{0}^{\dagger} \hat{\chi}_{0} \]
(5)
where \( \hat{\chi}_{0} \) and \( \hat{\chi}_{0}^{\dagger} \) are matrices in the Matsubara frequencies and pairs of orbital and spin indices; all cite indices are supposed to be the same [17]. Both single-particle and two-particle on-site Green functions can be found numerically using such a diagonalization scheme [21] or the continuous-time quantum Monte Carlo method [22].

Thus, the optical conductivity (1) can be expressed in the following form:
\[ \sigma_{ab}(i\omega) = -\frac{e^2}{\omega} T \sum_{v} \sum_{k} \sum_{v'} (4\langle k | v_{a}^{\text{eff}}(iv, i\omega) \rangle | 1k \rangle G_{12}(k, iv') \times \langle 2k | v_{b} \rangle | 3k \rangle G_{34}(k, iv + i\omega) \]
(6)
\[ \times \langle 4k | v_{a} \rangle \chi_{1234}(k, iv, iv', i\omega) \]
where \( (1234) \) are orbital and spin indices only and the effective matrix element (three-leg vertex) satisfies the equation
\[ \langle 4k | v_{a}^{\text{eff}}(iv, i\omega) \rangle | 1k \rangle = \langle 4k | v_{a} \rangle | 1k \rangle \]
\[ -T \sum_{k} \sum_{k'} \sum_{\Gamma_{5678}} (3k' | v_{a}^{\text{eff}}(iv', i\omega) \rangle | 2k' \rangle \]
\[ \times G_{25}(k', iv' + i\omega)G_{63}(k', iv')\Gamma_{5163}(iv, iv', i\omega) \]
(7)
Diagrammatically equation (6) is shown in figure 1.

The effective matrix element \( \langle 4k | v_{a}^{\text{eff}}(iv, i\omega) | 2k \rangle \) is convenient since its use allows us to present the linear and nonlinear response functions in a unified form. For example, the nonlinear optical susceptibility describing a second harmonic generation can be exactly represented as a sum of the diagrams shown in figures 2(a) and (b).

The corresponding analytical expression for figure 2(a) reads
\[ \chi_{abc}(i\omega, i\omega, 2i\omega) \]
\[ = \frac{e^2}{\omega} T \sum_{v} \sum_{k} \sum_{1234} (6k \langle v_{a}^{\text{eff}}(iv, i\omega) \rangle | 1k \rangle G_{12}(k, iv') \times (2k | v_{b} \rangle | 3k \rangle G_{34}(k, iv + i\omega) \times (4k | v_{c} \rangle | 5k \rangle G_{56}(k, iv - i\omega) \]
(8)

The calculations of the magnetic susceptibility in the one-band Hubbard model [23] show that the contributions of the six-leg vertex are small; one can hope that this is also the case for the second harmonic generations and then equation (8) will be sufficient for real calculations.

We proceed with the multiband Hubbard model with the Hamiltonian
\[ H = \sum_{im\sigma} \epsilon_{i} c_{i m \sigma}^{\dagger} c_{i m \sigma} + \sum_{imn \sigma' \sigma} t_{imn}^{l} c_{i m \sigma}^{\dagger} c_{j n \sigma'} \]
(9)
\[ + \frac{1}{\gamma} \sum_{im1234} U_{im1234} c_{i m \sigma}^{\dagger} c_{m1 \sigma'} c_{m2 \sigma'} c_{m3 \sigma'} c_{m4 \sigma} . \]

To clarify a physical meaning of the vertex corrections to the response functions we discuss first the exactly solvable model of two sites with two orbitals \( (i = (1, 2), m = (1, 2)) \). The corresponding rotationally invariant interaction matrix is parametrized by the Hubbard energy \( U \) and the Hund exchange parameter \( J \) as [24]
\[ U_{m1m2m1m2} = U \]
\[ U_{m1m2m2m1} = U - 2J \]
(10)
\[ U_{m1m2m1m1} = J \]
Figure 3. Components of generalized susceptibility $\text{Im} \chi_{\text{in}, j\sigma' : \text{in}, j\sigma' \omega}$ summed up over $(\sigma, \sigma')$ for the two-site two-band model with $\epsilon_1 = \epsilon_2 = 0$, $U = 1$, $J = 0.2$, $t_{12} = t_{21} = 0.05$; (a): $t_{11} = t_{22} = 0.2$; (b) $t_{11} = t_{22} = 0.5$. The solid red curve corresponds to intrasite interband transitions $im = (11)$, $jm' = (12)$, the dashed blue curve to intersite intraband transitions $im = (11)$, $jm' = (21)$, and the dotted green curve to intersite interband $im = (11)$, $jm' = (22)$. We use the spectral representation where $\text{Im} \omega = 0.05$ and the temperature is $T = 0.05$. The energies are in units of $U$.

Figure 4. Density of the single-particle states for the same parameters as in figure 3. The energies are in units of $U$.

Figure 5. Intrasite, interband components of $\text{Im} \chi_{\text{in}, \omega} \propto \text{Re} \sigma(\omega)$ (solid red curve) and $\text{Im} \chi_{\text{in}, \omega} \propto \text{Re} \sigma_0(\omega)$ (dashed blue curve) for the square lattice in the nearest-neighbor approximation, with the same parameters as in figure 3(a). Energies are in units of $U$. 

$m_1 \neq m_2)$. The dimension of the Hilbert space is equal to $2^8$ so $\tilde{\chi}$ and $\tilde{G}$ can be easily found by exact diagonalization. The results for $\text{Im} \tilde{\chi} / \omega \propto \text{Re} \tilde{\sigma}(\omega)$ for real (not Matsubara) frequencies are shown in figures 3 and 4.

As one can see from the density of states the single-particle transitions which manifest themselves in $\tilde{\chi}_0$ start at the frequency $\omega \geq 1$ corresponding to the distance between the highest occupied and the lowest unoccupied orbitals. For small enough hopping (figure 3(a)) there are a lot of peaks at smaller energies which originate from the poles of the vertex functions and represent the optically forbidden transitions in our toy model. In particular, a transition with $\omega = 2J = 0.4$ is clearly visible for intraband intersite transitions $11 \rightarrow 21$. The transition corresponds to local intra-atomic spin-flip processes. It is visible in optical (summed up over spins) susceptibility, since the Coulomb interaction matrix couples spin-up and spin-down states. An interesting and unexpected result of the toy model is that for a moderate hopping (figure 3(b)) all these local term effects disappear.

Now we present the main part of our work related to the two-band lattice model with the use of local approximation for vertex $\tilde{\Gamma}$ as described above. The calculations have been done for the square lattice in the nearest-neighbor approximation. The local vertex function has been obtained from equation (5) by exact diagonalization calculations of $\tilde{\chi}$ and $\tilde{G}$. If the exact diagonalization was performed for the intra-atomic Coulomb interaction Hamiltonian only, this would correspond to the Hubbard-I approximation [11]. To go beyond this, in the spirit of the DMFT [17], we have added one more orbital to the bath.
Despite the simplicity of the model our calculations turned out to be rather time and memory consuming due to the inversion of the $\hat{\chi}$-matrices depending on two Matsubara frequencies $(i\nu, i\nu')$. To reach convergence, we had to use about one hundred frequencies and $20 \times 20$ $k$-points. The computational results are shown in figure 5. One can see that $\hat{\chi}_0$ has only one pronounced peak at $\omega = U$ corresponding to the transition from the lower to upper Hubbard bands. At the same time, $\hat{\chi}$ has an additional peak within the gap of the single-particle excitation spectrum, at its maximum around $\omega = 2J = 0.4$. This maximum originates from the spin-multiplet structure of the $d^5$ configuration.

To conclude, we present a general formalism which allows us to consider the term and multiplet effects on the linear and nonlinear optical properties of multiband strongly correlated systems. For a two-band model the computational results are quite reasonable and one can hope that the scheme can be applied to the first-principle investigations of realistic systems in the spirit of the LDA + DMFT. The approach can apply for other response functions such as magnetic susceptibilities and STM-spectroscopy where the transitions with energy $\omega = 2J$ have recently been observed for Mn-chains on a Pt surface [25].

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