Two-particle excitations of the Hubbard Hamiltonian: alloy analogy solution

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Abstract. The spectra of the two-hole and the two-electron excitations are calculated for a single-band Hubbard Hamiltonian. Equations of motion for retarded two-particle double-time Green function are solved using a decoupling based on the alloy analogy. The solution is correct in exactly solvable limiting cases and has also correct behaviour in the regime of the strong electron–electron correlations.

1. Introduction

The spectrum of the two-particle excitations can be qualitatively different in systems of strongly correlated electrons from that in systems with only weak interaction. This is in particular the case for the density of two-hole or two-electron excitations which are related to Auger electron spectra (AES), or to appearance potential spectra (APS). The Auger spectra of transition metals are quite different from the spectra of normal metals [1–3].

The effect of the electron correlations on the core–valence–valence (CVV) Auger spectra has been studied in the framework of the Hubbard model. For systems with completely filled, or empty bands there is an exact solution which was used to explain the Auger spectra of transition metals on qualitative level [4–6]. However, for the partially filled bands that are typical for most transition metals the situation is more complex. In this case, various approximative treatments were used: (i) perturbative theory [7–9], (ii) cluster calculations [10–12], and decoupling procedures [13–15].

Validity of the perturbation theory is limited either to weak interactions or to small particle concentration. The cluster calculations are restricted to small systems and their results may be impaired by finite size effects. The problem with the decoupling technique is that it is not a systematic approach, but it is simple enough to be applied in the interesting regime of strong correlations (for any concentration of electrons), whereas the perturbation theories suffer from various problems or are very complicated.

Recently we have developed a Hartree–Fock-like solution for two-particle excitations [14]; it is correct in all exactly solvable limits including the atomic limit. However, it turns out that the way it approaches the atomic limit is incorrect. In the present work we improve this solution by developing the theory based on alloy analogy.

2. Preliminaries

The two-particle excitation spectrum of the single-band Hubbard Hamiltonian

$$H = \sum_{ij\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \qquad n_{i\sigma} = a_{i\sigma}^+ a_{i\sigma} \tag{1}$$

can be studied using the retarded two-particle double-time Green function (GF):

$$G_{ijkl}(z) = \langle\langle a_{i\uparrow} a_{j\downarrow} | a_{l\downarrow}^+ a_{k\uparrow}^+ \rangle\rangle_z. \tag{2}$$

We use the standard notation: i, j, k, l are site indices, $\sigma = \uparrow, \downarrow$ is the spin index; GF is written in energy representation for complex energy z. The AES and APS are given by the spectral density

$$A(E) = \frac{1}{\pi} |\mathrm{Im}\, G_o(E + io)| \tag{3}$$

where $G_o(z) = G_{0000}(z)$ is a superdiagonal element of the two-particle GF (2). The GF $G_{ijkl}(z)$ obeys the equation of motion

$$zG_{ijkl}(z) = \kappa_{ijkl} + \sum_n t_{in} G_{njkl}(z) + \sum_n t_{jn} G_{inkl}(z) + U\delta_{ij} G_{ijkl}(z)$$

$$+ U(1 - \delta_{ij})\Gamma_{ijkl}(z) \tag{4}$$

where

$$\kappa_{ijkl} = \delta_{ik}\delta_{jl} - \delta_{jl}\langle a_{k\uparrow}^+ a_{i\uparrow}\rangle - \delta_{ik}\langle a_{l\downarrow}^+ a_{j\downarrow}\rangle \tag{5}$$

and

$$\Gamma_{ijkl}(z) = \langle\langle (n_{i\downarrow} + n_{j\uparrow}) a_{i\uparrow} a_{j\downarrow} | a_{l\downarrow}^+ a_{k\uparrow}^+ \rangle\rangle_z. \tag{6}$$

3. Alloy analogy solution

To find the solution for GF G we need an approximative expression for the higher-order GF Γ. In a previous paper [14], we employed a simple local approximation

$$\Gamma_{ijkl}(z) \approx \langle n_{i\downarrow} + n_{j\uparrow}\rangle G_{ijkl}(z). \tag{7}$$

This leads to the solution applicable to any electron concentration $0 \leqslant n \leqslant 2$ and to any strength of the interaction U. This Hartree–Fock-like solution is correct in four exactly solvable limiting cases: (i) the limit of non-interacting electrons ($U \to 0$), (ii) the atomic limit (band width $W \to 0$), (iii) the limit of low concentration of electrons ($n \to 0$), and (iv) the limit of low concentration of holes ($n \to 2$). Moreover, it behaves correctly at the electron–hole transformation. However, it is not a genuine interpolating solution between the weak and strong interaction regimes because it is not correct in the neighbourhood of the atomic limit.

More precisely, it is exact for $t_{ij} = 0$ and finite U but it does not have correct behaviour for finite, non-zero t_{ij} and $U/t \to \infty$. In this strong correlation regime one would expect that the peaks in the two-particle spectrum are separated by the distance of order U from each other independently of the filling n. To see this, let us consider a finite lattice, possibly with periodic boundary conditions. As a basis of the corresponding Fock space, we choose the many-particle states in site representation:

$$|\Psi(C)\rangle = \prod_{(i\sigma)\epsilon C} a^{+}_{i\sigma}|0\rangle. \tag{8}$$

Here C is the set of occupied spin orbitals. The Hamiltonian (1) is, in this space, represented by a matrix with diagonal elements Uk, where k is an integer. Off-diagonal elements of this matrix (which come from the hopping term) represent, in the large-U limit, a small perturbation proportional to a small parameter t. According to Gershgorin circle theorem (see e.g. [16]), the eigenvalues E of H fulfil the inequalities

$$|E - Uk| \leqslant \sideset{}{'}\sum_{C_2} |H_{C_1 C_2}| \leqslant tK \tag{9}$$

where K is some constant. It now follows from (9) and from the spectral representation of $G_o(z)$ that the two-particle excitation spectrum is concentrated around integer multiples of U. On the other hand, the Hartree–Fock-like solution has peaks with the distance Un.

In order to find an improved solution, one could employ equations of motion for GF Γ, and then look for a suitable factorization of the higher-order GFs that enter these equations. An attempt to follow the derivation of the so-called 'Hubbard III' solution [17], which is a higher-order solution for the one-particle GF with both correct band and atomic limits, has shown that in the two-particle case the structure of equations is different. It turned out that this approach can yield either a simple solution that does not have the desired properties, or a rather complicated set of matrix equations that cannot be solved analytically. Therefore, we have decided to employ a more sophisticated decoupling for the GF Γ based on the alloy analogy idea.

Before describing our approximation let us recall the alloy analogy approximation used for the one-particle GF. In this case, the higher order GF $\langle\langle n_{i-\sigma} a_{i\sigma}|a^{+}_{j\sigma}\rangle\rangle$ is approximated as follows

$$\langle\langle n_{i-\sigma} a_{i\sigma}|a^{+}_{j\sigma}\rangle\rangle \approx \eta^{\sigma}_i \langle\langle a_{i\sigma}|a^{+}_{j\sigma}\rangle\rangle \tag{10}$$

where η^{σ}_i is a random variable taking two values 0 and 1 with the probabilities $\langle 1 - n_{i-\sigma}\rangle$ and $\langle n_{i-\sigma}\rangle$. In this way, the electron correlation problem (for the one-particle GF) is replaced by the effective binary alloy problem. The one-particle GF for this alloy problem can be calculated using the so-called coherent potential approximation (CPA) [18], and it has been shown [18] that the solution of the correlation problem obtained in this way is identical to the 'Hubbard III' solution [17].

In our case we approximate Γ_{ijkl} for $i \neq j$ as follows:

$$\Gamma_{ijkl} \approx (\eta^{\downarrow}_i + \eta^{\uparrow}_j) G_{ijkl} \tag{11}$$

where η^{σ}_i, as in the one-particle case, is a random variable taking two values: 0 or 1. For simplicity, we will neglect the internal correlations between the random variables

$\eta_i^{\downarrow}$ and $\eta_j^{\uparrow}$. Treating them as independent variables, we arrive at the approximation (valid for $i \neq j$)

$$\Gamma_{ijkl} \approx \epsilon_{ij} G_{ijkl} \tag{12}$$

where ϵ_{ij} is a random variable taking three values ϵ_m, $m = 1, 2, 3$, $\epsilon_1 = 0$, $\epsilon_2 = 1$, and $\epsilon_3 = 2$. The three values of ϵ can be interpreted as renormalized energies (note that factor U is not included in the definition of Γ) corresponding to the situations in which none, one or two electrons occupy the states at sites i and j. The probabilities of these situations are given by the correlation functions $\langle(1-n_{i\downarrow})(1-n_{j\uparrow})\rangle$, $\langle n_{i\downarrow}(1-n_{j\uparrow}) + (1 - n_{i\downarrow})n_{j\uparrow}\rangle$, and $\langle n_{i\downarrow}n_{j\uparrow}\rangle$. They determine the concentrations c_m of three components of the effective alloy with the site energies ϵ_m. In this way we have replaced the electron-correlation problem (for the two-particle GF) by the problem of the disordered ternary alloy in the space ($|i \downarrow j \uparrow\rangle$). Note that in equation (4) only terms with $i \neq j$ have to be approximated.

The equation (4) for the GF G can now be written in a matrix form

$$[z - W - UP - (1 - P)U\mathcal{E}]G = C \tag{13}$$

where $P = \sum_i |i \downarrow i \uparrow\rangle\langle i \downarrow i \uparrow|$ is a projector onto the single-site states and $\mathcal{E} = \sum_{ij}' |i \downarrow j \uparrow\rangle\epsilon_{ij}\langle i \downarrow j \uparrow|$ is a random operator. Here, W is the two-particle hopping term

$$W = \sum_{k_1}\sum_{k_2} |k_1 \downarrow k_2 \uparrow\rangle[E(k_1) + E(k_2)]\langle k_1 \downarrow k_2 \uparrow| \tag{14}$$

where

$$E(k) = \sum_j e^{ik(R_i - R_j)}t_{ij} \qquad |k_1 \downarrow k_2 \uparrow\rangle = \frac{1}{N}\sum_{ij} e^{i(k_1 R_i + k_2 R_j)}|i \downarrow j \uparrow\rangle \tag{15}$$

N is the number of sites, and C is a matrix constructed from the quantities κ_{ijlm}, (5)

$$C = \sum_{ijlm} |i \downarrow j \uparrow\rangle\kappa_{ijlm}\langle l \downarrow m \uparrow|. \tag{16}$$

The equation (13) is valid for one configuration of the effective alloy. A physically important quantity is the GF $\overline{G}$ averaged over all alloy configurations. Now there are in principle two possibilities: (i) consider the quantity C to be dependent on the configurations of the effective alloy too (this complicates the averaging procedure) or (ii) take the one-particle correlation functions entering C from an independent approximative solution for the one-particle excitations. For the sake of simplicity we choose the second possibility. One has to be, however, careful in selecting the approximate solution for the one-particle correlation functions because it may turn out to be inconsistent with the alloy analogy approximation for the two-particle GF. The different possibilities are discussed below. In order to calculate GF $\overline{G}$ we define the resolvent

$$R(z) = [z - W - UP - (1 - P)U\mathcal{E}]^{-1} \tag{17}$$

and its configurational average

$$\overline{R}(z) = [z - W - \Sigma(z)]^{-1} \tag{18}$$

with the self-energy $\Sigma(z)$. Then the averaged GF $\overline{G}$ is

$$\overline{G} = \overline{R}(z)C = [z - W - \Sigma(z)]^{-1}C. \tag{19}$$

To calculate the GF $\overline{G}$ we use a CPA-like approximation [18]. The self-energy in our case has the form $\Sigma = \sum_i U|i\downarrow i\uparrow\rangle\langle i\downarrow i\uparrow| + \sum_{ij}' |i\downarrow j\uparrow\rangle\Sigma_{ij}\langle i\downarrow j\uparrow|$, where the off-diagonal elements Σ_{ij} $(i \neq j)$ are given by the Soven equations

$$\sum_m \frac{c_m(U\epsilon_m - \Sigma_{ij})}{1 - (U\epsilon_m - \Sigma_{ij})F_{ij}} = 0 \qquad F_{ij} = \langle i\downarrow j\uparrow|\overline{R}|i\downarrow j\uparrow\rangle. \tag{20}$$

4. Approximate solution

Our effective alloy is inhomogeneous in the sense that the quantities Σ_{ij} and F_{ij} depend on the distance $|R_i - R_j|$ between the sites i and j. In general, one can look for a spatially inhomogeneous solution of (20), however, for the sake of simplicity, we shall calculate a homogeneous solution setting $\Sigma_{ij} = \Sigma$ and using a homogenized F:

$$F = \frac{1}{N(N-1)} \sum_{ij}{}' F_{ij} \tag{21}$$

instead of F_{ij}.

After this additional approximation the expression (19) for the GF can be written explicitly in the same way as in the case of the Hartree–Fock-like solution [14]. The superdiagonal element is then

$$G_o(z) = \frac{1}{N^2} \sum_{kq} \frac{1}{1 - \tilde{V}\Psi_o(k+q,\tilde{\xi})} \frac{1 - n_{k\uparrow} - n_{q\downarrow}}{\tilde{\xi} - E(k) - E(q)} \tag{22}$$

where

$$\Psi_o(k,\tilde{\xi}) = \frac{1}{N} \sum_q \frac{1}{\tilde{\xi} - E(k-q) - E(q)} \tag{23}$$

$n_{k\sigma} = \langle a_{k\sigma}^+ a_{k\sigma}\rangle$ is the average occupation number of the one-electron Bloch state $(k\sigma)$.

The GF $G_o(z)$ has a similar form to the Hartree–Fock-like solution [14], but the renormalized energy $\tilde{\xi} = z - \Sigma(z)$ and the effective interaction $\tilde{V} = U - \Sigma(z)$ are now complex quantities depending on the self-energy Σ given by the Soven equation

$$\sum_m \frac{c_m(U\epsilon_m - \Sigma(z))}{1 - (U\epsilon_m - \Sigma(z))F(z)} = 0 \qquad F(z) = \phi(\tilde{\xi}) = \frac{1}{N^2} \sum_{pq} \frac{1}{\tilde{\xi} - E(p) - E(q)}. \tag{24}$$
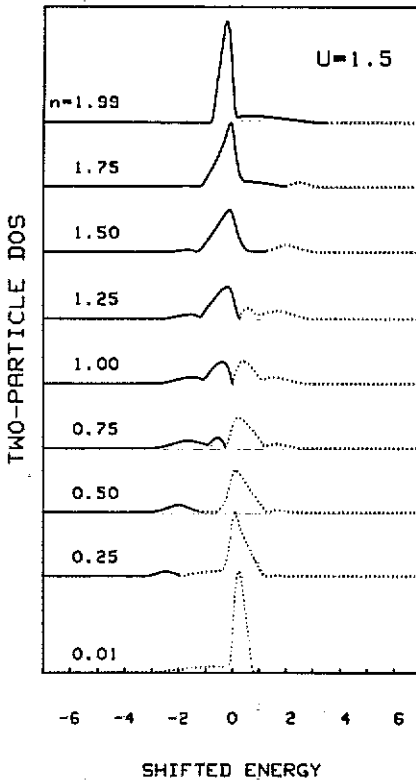
Figure 1. Density of the two-hole excitations (full curve) corresponding to the Auger spectrum and the two-electron excitations (dotted curve) corresponding to the appearance potential spectrum calculated within the simplified model for $U = 1.5$ and varying electron concentration n.

The equations (22)–(24) form a set of self-consistent equations for a new solution which is correct in all above-mentioned exactly solvable limits. The regime of the strong correlations $U \to \infty$ corresponds to the split-band limit in the alloy problem in which energy bands are separated by an energy of order U in agreement with the expected behaviour. The Hartree–Fock-like solution corresponds to the virtual crystal approximation in the alloy problem [18], i.e. $\Sigma = \sum_m c_m U \epsilon_m = U n$.

To solve the set of equations (22)–(24) we need to know the correlation functions $n_{k\sigma}$ and $\langle n_{i\downarrow} n_{j\uparrow} \rangle$. These functions are, of course, not known exactly for interacting systems and have to be calculated using some approximation scheme. The simplest method of approximation of the one-particle occupation numbers $n_{k\sigma}$ is to use their Hartree–Fock values, and we shall employ this in the following numerical illustration. Another possibility is to use the Gutzwiller approximation or the alloy analogy approximation for the one-particle GF. The former, however, leads to anomalous effect for large U as can be seen by direct calculation using a simplified model discussed in the next section. For example, for $n = 1$ and $U > U_c = 16\bar{\epsilon}$ ($\bar{\epsilon}$ is the average unperturbed kinetic energy) the two-particle spectra vanish. This case ($n = 1$) corresponds to the Mott metal-to-insulator transition [19]. We think that this effect is probably an artifact of incompatible approximations. The same defect also appears in the case of the Hartree–Fock-like solution. The latter possibility (employing the alloy analogy approximation for the one-particle GF) is probably more convenient and can
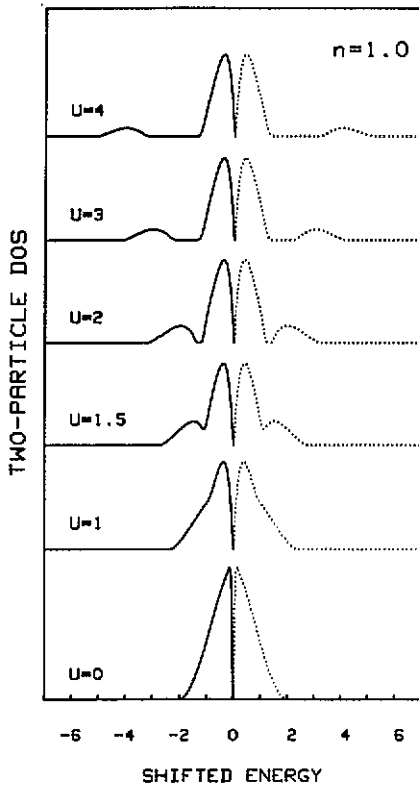
Figure 2. Similar to figure 1, but for $n = 1$ and varying U.

be used, too, for evaluation of the correlation functions $\langle n_{i\downarrow} n_{j\uparrow} \rangle$ via the conditionally averaged GF. It is, however, numerically more demanding and does not allow further simplifications as was possible in the two previous cases. For the sake of simplicity, we use here a crude approximation for the higher order correlation functions: $\langle n_{i\downarrow} n_{j\uparrow} \rangle \approx \langle n_{i\downarrow} \rangle \langle n_{j\uparrow} \rangle$ and we restrict ourselves to the paramagnetic solution.

5. Numerical illustration

After several approximations we arrived at the set of the equations (22)–(24). To obtain numerical results which will illustrate the properties of the new solution we use a simplified model introduced in [14] which contains further approximations. In this model the semi-elliptic unperturbed density of states is assumed (bandwidth $W = 2$) and the so-called scaling-factor approximation and a related interpolating approximation are employed (for details see [14]). The GF $\overline{G_o}$ is given by a one-dimensional integral which is evaluated numerically with the help of the analytical deconvolution technique.

The self-energy $\Sigma(z)$ needed to evaluate the GF $\overline{G_o}$ is obtained numerically by iterating the equation (24) with an approximative expression for

$$\phi(\xi) \approx -\tfrac{1}{6}\xi^3 + \xi + \tfrac{1}{6}(\xi^2 - 4)\sqrt{\xi^2 - 4}. \tag{25}$$

Examples of the two-particle densities calculated for this simplified model and some selected parameters n and U are presented in figures 1–3. The energy in these
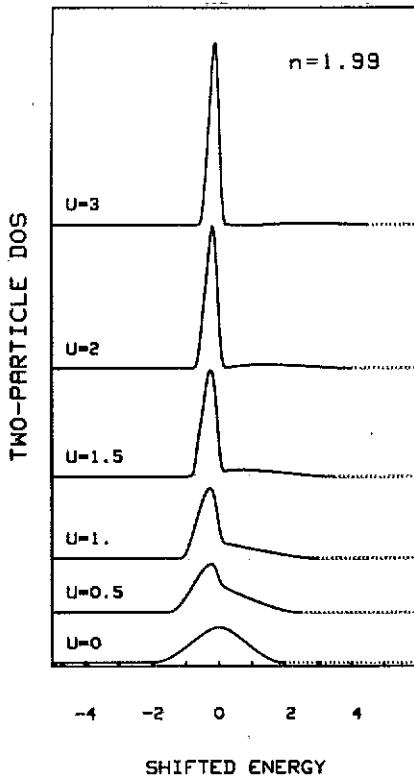
Figure 3. Similar to figure 1, but for $n = 1.99$ and varying U.

plots is shifted by U. Figure 1 shows spectra for medium interaction and different electron concentrations. The results are similar to the Hartree–Fock-like ones: with increasing electron concentration n the number of the two-hole excitations increases while the number of the two-electron excitations decreases and the spectra for the particle concentrations n and $2 - n$ are related by the hole–electron symmetry. The main difference is that new peaks with small weight appear. In particular, this is seen for the half-filled band. In this case the spectra calculated using the old solution were only shifted and their shapes did not change with U. Using the new solution they change and the satellites split off (figure 2). Figure 3 shows the situation for a nearly filled band. With increasing strength of pair interaction U the character of the spectra changes from band-like spectra to atomic-like ones; for large U an atomic-like peak with large weight splits off from the broad main band in agreement with previous theories [4–6].

6. Conclusions

Employing the alloy analogy in the space of the two-particle states we have developed a new approximate theory of the two-particle excitations for single-band Hubbard model. This is based on the alloy analogy decoupling for the two-particle double-time GF followed by several additional approximations some of which could be further improved. The theory can be applied to any electron concentration $0 \leqslant n \leqslant 2$ and to any strength of pair interaction U. It yields correct results in limiting cases for which

an exact solution is known. In addition it behaves correctly in the regime of strong interactions $U \rightarrow \infty$. The theory can be straightforwardly extended to the case of alloys and work on this problem is in progress.

Acknowledgment

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