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Quasiparticle band structure

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1. Introduction

Electrons in solids behave in most cases like independent particles, and that in spite of the strong interactions between them. The explanation of this apparent paradox relies on the concept of Landau quasiparticle: the multiple forces acting on one electron dress it up with an interaction cloud and these new dressed particles (quasiparticles) are effectively independent one from the other. A specific tool to investigate the very existence of quasiparticles is photoemission spectroscopy; the time evolution of the system with one removed particle is what is actually measured and when this state evolves as a coherent superposition of oscillations of approximately the same frequency it corresponds to the propagation of a quasiparticle with a reasonably well defined energy and a sufficiently long life-time. In this situation the low-energy excitations of the interacting electrons can be put into a one-to-one correspondence with those of non-interacting electrons with renormalized properties (energy and mass) and the measured spectra can be reduced to a quasiparticle band structure.

From a theoretical point of view, the simplest way to account for e–e interaction is to include it as a mean field where each electron moves independently under the influence of the average charge distribution of all the others. The independent-particle approximation is at very heart of the computational approaches of the band structure of solids. Among these computational approaches, schemes based on the density functional theory (DFT) [1] have proven to be very successful and are by far the most widely used approach for quantitative calculations of realistic systems. Materials for which this rudimentary mean-field description of e–e interaction is sufficient have broad energy bands associated with large values of the kinetic energy of the electrons: this implies that the electrons are highly itinerant and therefore it is reasonable to describe them using a picture in which interactions become smooth and can be averaged out. On the contrary when bands are narrower and the associated kinetic energy smaller, namely when electrons tend to localize around lattice ions, they see each other as individual point charges and the correlation between their motion becomes important. For these systems the single particle picture is inadequate and their electronic properties can be described only treating the multiple pair-wise e–e interaction as a true many-body term.

Strongly correlated electron systems have been one of the most important topics in theoretical solid state research. The major challenge is that the interesting features occur in the regime of intermediate coupling strength, where perturbation theory does not apply. The search for non perturbative approaches has been intense in the last decades, leading now to some widely accepted results, the first one being the choice of the Hubbard model as the general framework to describe strong e–e correlation.

The Hubbard model, where electrons feel their mutual repulsion only when localized on the same site, captures the essential physics of narrow band materials where the itinerant character of valence electrons coexists with strong local correlations responsible of spectroscopic features such as satellites, band-narrowing, and opening, in some cases, of a Mott-Hubbard gap. Traditionally, many-body theories have been formulated for very simple models that are believed to contain the relevant physics of a particular

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phenomenon but are very far from true materials; only recently the attention has been devoted to approaches that allow to combine the ideas and methods of many body theory with a realistic description of the system.

A variety of non-perturbative techniques have been proposed during the years to tackle this problem, ranging from dynamical mean field theory (DMFT) [2,3], Gutzwiller variational method on top of local density functional approximation (LDA+G) [4–6], 3-body scattering (3BS) theory [7–11]. In all these method the single particle multi-orbital Hamiltonian is supplemented by the local Coulomb interaction among electrons. LDA+G relies on an ansatz for the ground state wave function where the weight of the energetically unfavored configurations containing double occupancies is reduced. In DMFT the lattice problem of the Hubbard model is mapped onto a single-impurity model embedded in a fermionic bath whose structure has to be determined self-consistently. This mapping is an exact solution of the Hubbard Hamiltonian in the limit of infinite spatial dimensions. The LDA+DMFT scheme is presently implemented in many DFT-band structure packages and is one of the most widely used techniques to compute electronic structures of strongly correlated solids.

In the 3BS approach the interacting many-body state is expanded on the configurations obtained by adding single electron-hole (e-h) pairs to the ground state of the single-particle Hamiltonian. The response of the interacting system to the creation of one hole is then described in terms of interactions between configurations with one hole plus one e-h pair, giving rise to multiple h-h and h-e scattering. The advantage of 3BS with respect to the above mentioned approaches is to provide a rather intuitive interpretation of the effect of electron correlation on one electron removal energies in terms of Auger-like relaxations. In the following we will mainly concentrate on this approach, presenting in some detail the underlying theory. Interestingly the results of DMFT and 3BS in many cases are quantitatively very similar, as we will show.

Among the non-perturbative methods that are used to augment band structure with on-site correlations, schemes based on cluster formalisms are worth mentioning. These so-called quantum cluster (QC) theories [12] share the basic idea to solve the problem of many interacting electrons in an extended lattice by a *divide-et-impera* strategy, namely solving first the many body problem in a subsystem of finite size and then embedding it within the infinite medium. The embedding procedure can be variationally optimized as in the dynamical cluster approach [13] and cellular dynamical mean field theory (CDMFT) [14,15]. Even neglecting self-consistency in the embedding procedure the method, that in this case has been called cluster perturbation theory (CPT)[16,17], gives access to non trivial many body effects, reproducing exactly both the limit $U/t=0$ (non-interacting band limit) and $U/t=\infty$ (atomic limit); for intermediate values of U/t CPT opens a gap in metallic systems at half occupation [17,18]. QC approaches account for the momentum dependence of many-body corrections (self-energies) more appropriately than DMFT or 3BS and for this reason they should provide a more accurate description of quasiparticle dispersion. However QC approaches have been mostly applied to model systems and only few quasiparticle calculations for realistic systems have been reported up to now [19,20].

We will restrict to the simplest examples of materials where e–e correlation plays a crucial role, namely transition metals and transition metals mono-oxides. The article is organized as follows: in Section 2 we will introduce the essential many body concepts and the details of 3BS theory. This will allow us to clearly identify the dependence of correlation effects on band occupation and on spin-polarization. The results for transition metals and transition metal oxides will be presented in Section 3. Section 4 is devoted to open problems and outlook.

2. Beyond the one-electron picture

2.1. Basic many-body concepts

The starting point is the generalized Hubbard Model described by the Hamiltonian where electrons are itinerant – they hop from site to site and are characterized by a band structure dispersion – but at the same time experience mutual repulsion when localized on the same site

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

with $\hat{n}_{i\alpha\sigma} = \hat{c}^{\dagger}_{i\alpha\sigma} \hat{c}_{i\alpha\sigma}$ and $\hat{c}_{i\alpha\sigma}, \hat{c}^{\dagger}_{i\alpha\sigma}$ 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. Notice that for a single orbital $U=J$ and Hamiltonian (1) reduces to the standard Hubbard model where only electrons of opposite spin experience an on-site repulsion.

We are interested in the excitation energies of the system when an electron is either removed (like in a photoemission experiment) or added (like in inverse photoemission). These excitation energies correspond to differences between energies of the extended system with a variable number of particles, namely $E_0^N - E_n^{N-1}$ and $E_n^{N+1} - E_0^N$ respectively, where E_0^N is the ground state energy of N interacting electrons and $E_n^{N\pm1}$ is any excited state of the same system with one particle added/removed.

In the absence of e–e interaction, these total energies are a sum of single particle eigenvalues and the excitation energies trivially correspond to individual single particle eigenvalues. This is no more true for interacting systems. In this case the excitation energies are obtained, according to many-body theory, as the poles of the one-particle Green's function describing the propagation of an added/removed electron

$$G(k,\omega) = \frac{1}{\omega - \epsilon_k^n - \Sigma(k,\omega)} \quad (2)$$

Here ϵ_k^n are the single-particle band energies and $\Sigma(k,\omega)$ is the self-energy correction to them. It embodies all many-body interactions and is the quantity to be calculated.

The poles of $G(k,\omega)$ occur at $\omega = \epsilon_k^n + \Sigma(k,\omega)$. Since self-energy turns out to be a complex function its effect is twofold: its real part shifts the energy position of the quasiparticle excitations (the band eigenvalues that are in this sense "renormalized" by the interaction) and its imaginary part gives a finite life-time to them. Only long-lived excitations correspond effectively to quasiparticle excitations and appear as sharp maxima of the spectral function

$$A(k,\omega) \equiv \frac{1}{\pi} ImG(k,\omega) \quad (3)$$

On the contrary when the poles occur far from the real axis, the life-time of the excitation is short, the spectral weight is spread out on a large energy window and no quasiparticle – no long lived-excitation – exists any more. These two opposite situations, corresponding to *quasiparticle renormalization* and *quasiparticle quenching*, are illustrated in Fig. 1.

The calculation of self-energy requires inevitably approximations. In order to define them it is useful to consider other exact representations of the one-particle Green's function. The Lehman