Modeling of Co impurity in Cu host using DFT+ED

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Abstract. We investigate the electronic structure of a cobalt atom in a copper host using the density functional theory and the exact diagonalization of an Anderson impurity model. The spectral functions and spin moments at the impurity are calculated and are found to be close the ones calculated by DFT+QMC [1].

1. Introduction
The first-principles study of magnetic atoms embedded in non-magnetic metals is valuable for understanding quantum many-body systems, since it can provide a theoretical explanation for phenomena such as the Kondo effect in material-specific settings. One promising method for solving such a system is a combination of the density functional theory (DFT) and the exact diagonalization (ED) of the single impurity Anderson model (DFT+ED). Within the ED method, the hybridization between the correlated \(d\) orbitals and the host is approximated by discretized “bath” of the conduction electrons. Some of the advantages of using the ED over the quantum Monte Carlo (QMC) with the continuous bath are that it can work at very low temperatures, and can include the spin-orbit coupling (SOC) and the crystal field (CF) simultaneously.

We examine the electronic structure of CoCu\(_{15}\), a material approximating a single cobalt impurity in a copper bulk. The solution is performed in a system with no SOC and close to room temperature so that it can be directly compared to the results obtained with DFT+QMC [1]. This work follows an earlier study comparing the two methods, where the DFT+ED calculations were performed with a smaller discretized “bath”, at low temperature and with SOC [2].

2. Methods
The material under study is modeled as CoCu\(_{15}\), a \(2 \times 2 \times 2\) fcc supercell of Cu with a single atom substituted with a Co atom. The Co impurity atom has 10 electrons in its \(3d\) shell. The cubic symmetry of the crystal makes the \(3d\) shell diagonal in the basis of cubic harmonics: \(m \in \{ xy, xz, yz, x^2 - y^2, 3z^2 - r^2 \}\). The crystal field splits the orbitals into two blocks, the triply-degenerate \(t_{2g}\) (for \(xy, xz\) and \(yz\)) and the doubly-degenerate \(e_{g}\) (for \(x^2 - y^2\) and \(3z^2 - r^2\)), where the \(e_{g}\) block has a higher energy.

The dynamics of the Co \(3d\) electrons are described using the Anderson impurity model, in a basis where each spin-orbital \(d_{m\sigma}\) is coupled to bath states \(b_{m\kappa\sigma}\) [3]. The impurity Hamiltonian is

\[
H_{\text{imp}} = \sum_{m\sigma} (\epsilon_d + h_{\text{CF}}^{\text{MM}}) n_{m\sigma}^d + \sum_{m\kappa\sigma} \epsilon_{m\kappa} n_{m\kappa\sigma}^b + \sum_{m\kappa\sigma} \left( V_{m\kappa} d_{m\sigma}^\dagger b_{m\kappa\sigma} + \text{h.c.} \right) + U_{\text{Coul}},
\]
Table 1. Values of the “bath” parameters $\epsilon_{mk}$ and $V_{mk}$ obtained by fitting the hybridization function obtained from DFT, for models III (left) and IV (right).

| $m$ | $k$ | $\epsilon_{mk}$ (eV) | $V_{mk}$ (eV) |
|-----|-----|---------------------|----------------|
| 1   | t$_{2g}$ | 2 -2.062 | 1.150 |
|     | t$_{2g}$ | 2 0.316 | 0.407 |
|     | t$_{2g}$ | 3 3.655 | 1.508 |
|     | $e_g$   | 2 -1.237 | 1.077 |
|     | $e_g$   | 3 1.395 | 0.790 |

| $m$ | $k$ | $\epsilon_{mk}$ (eV) | $V_{mk}$ (eV) |
|-----|-----|---------------------|----------------|
| 1   | t$_{2g}$ | 2 -2.320 | 1.172 |
|     | t$_{2g}$ | 2 -0.053 | 0.136 |
|     | t$_{2g}$ | 4 3.955 | 1.511 |
|     | $e_g$   | 3 0.252 | 0.280 |
|     | $e_g$   | 4 2.306 | 0.830 |

where $n^d_{mk\sigma} = b^d_{mk\sigma} b_{mk\sigma}$, $n^d_{\sigma\sigma} = d_{\sigma\sigma}^\dagger d_{\sigma\sigma}$, and $U_{\text{Coul}} = \sum_{\alpha\beta\sigma\sigma'} d^\dagger_{\alpha\sigma} d_{\alpha\sigma'} d^\dagger_{\beta\sigma'} d_{\beta\sigma}/2$. The terms in eq. (1) represent, in order, the energy of the impurity orbitals (split into an average $d$-shell energy $\epsilon_d$ and a traceless crystal-field potential $h_{\text{CF}}^{m}$ that is diagonal in the basis of the cubic harmonics), the bath energy levels coupled to each spin-orbital in the impurity, the hybridization between the bath and the impurity electrons, and the spherically symmetric Coulomb interaction of the impurity electrons.

The continuous bath-impurity hybridization strength for an orbital $m$, $[V_{m}(\epsilon)]^2 = -\text{Im} [\Delta_{m}(\epsilon)]/\pi = -\text{Im} [G^{-1}_{m}(\epsilon)]/\pi$ [3], is obtained from the local Green’s function of the impurity $G_{m}(\epsilon)$. In the space of Matsubara frequencies, the local Green’s function $G_{m}$ can be expressed in terms of the corresponding density of states (DOS) $\rho_{m}(\epsilon)$,

$$G_{m}(i\omega) = \int_{-\infty}^{D} d\epsilon \frac{\rho_{m}(\epsilon)}{i\omega_n - \epsilon - \epsilon_d - h_{CF}^{m}} = \frac{1}{\omega_n - \epsilon_d - h_{CF}^{m} - \Delta_{m}(i\omega_n)},$$

where $\rho_{m}(\epsilon)$ is calculated in the local density approximation using the full-potential linearized augmented plane wave method (FLAPW) [4, 5]. Note that in order to achieve the correct analytic behavior of $G(i\omega)$, the DOS has to be properly normalized, so that $\int_{-\infty}^{D} \rho_{m}(\epsilon) = 1$ for the chosen upper cutoff $D$. The crystal field of each block was determined as the first moment of the DOS. The crystal field energies were found to be $h_{CF}^{t_{2g}} = 0.039$ eV and $h_{CF}^{e_g} = -0.059$ eV.

The Matsubara frequency hybridization function of the discrete Anderson model in eq. (1) is $\Delta_{m}(i\omega_n) = \sum_{k=1}^{K} V_{km}^2/(i\omega_n - \epsilon_{km})$. The parameters $\epsilon_{mk}$ and $V_{mk}$ were obtained by fitting this expression to the continuous hybridization function appearing in Eq. (2) by minimizing the residual function $f_{m}((\epsilon_{km}, V_{km})) = \sum_{n=1}^{N_{\omega}} \frac{1}{\sqrt{\omega_n}} |\tilde{\Delta}_{m}(i\omega_n) - \Delta_{m}(i\omega_n)|^2$ [6], with $N_{\omega} = 637$. The parameter $K$ defines the number of “bath” orbitals included in the discrete model: 30 spin-orbitals for $K = 3$ (model III), and 40 spin-orbitals for $K = 4$ (model IV).

The interaction term in Eq. (1) was parametrized with the Slater integrals $F_0 = 4.0$ eV, $F_2 = 7.75$ eV and $F_4 = 4.85$ eV, which correspond to an intra-orbital repulsion $U = 4.0$ eV and to an exchange interaction $J = 0.9$ eV, the characteristic values for 3d metals [7]. In order to correct for the double counting of the Hartree-like contribution in the interaction term of eq. (1), the parameter $\mu$ needs to be subtracted from the energy of each spin-orbital. This parameter defines the value of $\epsilon_d$ in eq. (1) in the ED calculations, and was set to the three values used in ref. [1], namely 26 eV, 27 eV and 28 eV.

The exact diagonalization was performed using the Lanczos method in a reduced many-body Hilbert space, which includes only states with a limited number of excitations (in the
Table 2. The total occupation $\langle N \rangle$, impurity occupation $\langle n_d \rangle$ and impurity spin as functions of $\mu$, calculated by the exact diagonalization and compared to the QMC calculations from ref. [1].

| $\mu$ (eV) | $\langle N \rangle$ | $\langle n_d \rangle$ | $S$ | $Z_{t_2g}$ | $Z_{e_g}$ |
|---|---|---|---|---|---|
| 26 | 21.93 | 7.47 | 1.13 | 0.06 | 0.25 |
| 27 | 22.31 | 7.77 | 0.99 | 0.10 | 0.23 |
| 28 | 23.67 | 8.17 | 0.79 | 0.31 | 0.34 |
| 26 | 28.02 | 7.46 | 1.14 | 0.12 | 0.29 |
| 27 | 28.71 | 7.77 | 0.99 | 0.30 | 0.23 |
| 28 | 29.92 | 8.20 | 0.79 | 0.43 | 0.40 |
| 26 | 7.51 | 1.02 | 0.38 | 0.39 |
| 27 | 7.78 | 0.92 | 0.42 | 0.47 |
| 28 | 8.06 | 0.82 | 0.48 | 0.56 |

3. Results

The bath parameters shown in table 1 were used to create six discrete Anderson models – three $\mu$ values of 26 eV, 27 eV and 28 eV for each of the models III and IV. For each model, several observables were measured as grand canonical averages – the total number of electrons, the occupation of the impurity $d$ shell, and the spin moment in the $d$ shell. The observables have been measured at room temperature, $\beta = 1/k_B T = 40$ eV$^{-1}$. The spin moment $S$ was found using the expectation value $\langle S^2 \rangle = S (S + 1)$. The results are shown in table 2. For every value of $\mu$, the observables of models III and IV are in good agreement with each other, which demonstrates convergence with respect to the bath-size parameter $K$. The observables of all models are in good agreement with the corresponding DFT+QMC results as well.

The self-energy $\Sigma(\omega)$ was computed from the Green’s function of the Anderson impurity model as $\Sigma(\omega) = \omega - H^{(0)}_{\text{imp}} - G^{-1}_{\text{imp}}(\omega)$ where $H^{(0)}_{\text{imp}}$ is the impurity Hamiltonian without the Coulomb term [8]. It was used to calculate the quasi-particle weight of each orbital, $Z_m = \left(1 - \text{Re} \left[ \frac{\partial \Sigma_m(\omega)}{\partial \omega} \right] \right)^{-1}$, which was used in ref. [1] to estimate the Kondo temperature.

The results are shown in table 2 together with the results from ref. [1]. For the $t_2g$ states, our quasi-particle weights behave qualitatively similar to the ones calculated by QMC, increasing with $\langle n_d \rangle$. For the $e_g$ states, the quasi-particle weight for $\mu = 27$ eV breaks the pattern, as it is slightly lower than for $\mu = 26$ eV.

The spectral function of each discrete model was calculated from the impurity’s Green’s function. The spectra are depicted in figure 1. For each value of $\mu$, the spectra of model III and IV are largely in agreement with each other. However, the DOS for $\mu = 27$ eV does not match the corresponding plot from ref. [1] very well. The discrepancy between the spectra and quasi-particle weights found by ED and QMC is an artifact of the relatively sparse discretization of the impurity model used in the ED method. Clearly, the energy-resolved quantities are much more susceptible to the discretization errors than averaged quantities like occupations and spin moments discussed above.
Figure 1. Density of states of the $t_{2g}$ and $e_g$ orbitals for model III and IV, for $\mu$ values of 26 eV, 27 eV and 28 eV. Lorenzian broadening with FWHM of 0.2 eV was applied.

4. Summary
We present DFT+ED calculations performed on a model of a Co impurity in a Cu bulk. The material is described with an Anderson impurity model, parameters of which have been found by DFT in the local density approximation. Two bath sizes and three double-counting parameters have been used in our study. The reported impurity occupations and spin moments are found to be essentially converged with respect to the size of the bath and to agree with the DFT+QMC calculations [1]. The convergence of the spectral functions (and related quantities like the quasi-particle weights) is not as good. Still, the qualitative behavior of the quasi-particle weights is mostly in agreement with DFT+QMC as well. Our research indicates that DFT+ED is a useful method for studying the electronic structure of systems with magnetic impurities.

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