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Validity of Anderson and Hubbard model for the description of Ce metal and cerium heavy fermion compounds

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The importance of taking into account inter-site $f-f$ hybridization in electron structure calculations for Ce metal and cerium heavy fermion compounds was studied. We demonstrate that for heavy-fermion systems such as cerium compound $CeCu_2Si_2$ $f-f$ hybridization can be neglected and Anderson model application is well justified. On another hand for cerium metal $f-f$ hybridization is strong enough to provide the contribution to hybridization function comparable to hybridization between $4f$ and itinerant electrons. We argue that in the case of Ce only the most general Hamiltonian combining Hubbard and Anderson models should be used.

The mysterious properties of metallic Ce, which has paramagnetic phase with the local magnetic moments at ambient pressure and room temperature (Ce$-\gamma$ phase), and show the absence of local moments and Pauli paramagnetism below $\sim$100 K (Ce$-\alpha$ phase) rivet attention of the researchers [1]. For decades the electronic and magnetic properties of metallic Ce and heavy fermion cerium compounds were considered in the frameworks of the single impurity problem mainly using Anderson impurity model [2]:

$$\hat{H}_{SIAM} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \hat{c}^{\dagger}_{\mathbf{k}\sigma} \hat{c}_{\mathbf{k}\sigma} + \varepsilon_f \sum_{\sigma} \hat{f}^{\dagger}_{\sigma} \hat{f}_{\sigma} + U \hat{n}_{f\uparrow} \hat{n}_{f\downarrow} + \\ + \sum_{\mathbf{k}\sigma} \left(V_{\mathbf{k}} \hat{c}^{\dagger}_{\mathbf{k}\sigma} \hat{f}_{\sigma} + V^{*}_{\mathbf{k}} \hat{f}^{\dagger}_{\sigma} \hat{c}_{\mathbf{k}\sigma} \right), \quad (1)$$

where localized f-electrons with on-cite Coulomb interaction term $U\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}$ hybridize with itinerant c-electrons described by dispersion $\varepsilon_{\mathbf{k}}$ with a hybridization strength parameter $V_{\mathbf{k}}$.

One can introduce noninteracting Green function $\mathcal{G}_0$ (defined as Green function with Coulomb interaction switched off):

$$\mathcal{G}_0(i\omega_n) = (i\omega_n + \mu - \epsilon_d - \Delta(i\omega_n))^{-1}, \quad (2)$$

where $\omega_n = (2n+1)\pi T$, $n = 0, \pm 1, \pm 2, \ldots$ are Matsubara frequencies and hybridization function $\Delta(i\omega_n)$ is defined as:

$$\Delta(i\omega_n) = \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}}|^2}{i\omega_n - \epsilon_{\mathbf{k}} + \mu}. \quad (3)$$

Then the problem that should be solved is to describe f-electrons with on-cite Coulomb interaction in an effective media defined by noninteracting Green function $\mathcal{G}_0$ (2) where interaction with effective media is determined by hybridization function $\Delta(i\omega_n)$ (3).

The calculations performed using this model allowed to obtain consistent description of the evolution of magnetic and electronic properties as due to appearance of the Kondo scattering in $\alpha-$phase of Ce. The impurity models were applied for the study of the magnetic susceptibility [3], specific heat [3] and different types of spectra (photoemission [4], Bremsstrahlung isochromatic [5], electron-energy-loss [6]). Fitting of the theoretical result obtained within impurity models to different experimental data (protoemission spectra, susceptibility etc.) allows to extract the most important parameters in Kondo physics – Kondo temperature T_K [5].

While Anderson impurity model (1) has allowed to capture main energy scale in heavy-fermion physics – Kondo temperature T_K, it cannot describe coherence effects when at low temperatures rich phase diagram appears with long-range magnetic ordering and superconductivity. Basic model used to describe such effects for f-systems is periodic Anderson model (PAM) with Hamiltonian:

$$\hat{H} = \varepsilon_c \sum_{i\sigma} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma} + \sum_{ij\sigma} t_{ij} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} + \varepsilon_f \sum_{i\sigma} \hat{n}^{f}_{i\sigma} + \\ + U \sum_{i} \hat{n}^{f}_{i\uparrow} \hat{n}^{f}_{i\downarrow} + \sum_{ij\sigma} \left(V_{ij} \hat{c}^{\dagger}_{i\sigma} \hat{f}_{j\sigma} + V^{*}_{ij} \hat{f}^{\dagger}_{j\sigma} \hat{c}_{i\sigma} \right). \quad (4)$$

It deals with localized f-electrons on all sites embedded in itinerant c-electrons bath with a term responsible for hybridization between localized and itinerant electrons.

In both impurity (1) and periodic (4) Anderson models hybridization between f-electrons on different lattice sites is assumed to be absent in contrast to Hubbard model where competition between inter-site $f-f$ hybridization and Coulomb on-site interaction is explicitly defined:

$$\hat{H} = \sum_{ij\sigma} t^f_{ij} \hat{f}^\dagger_{i\sigma} \hat{f}_{j\sigma} + \varepsilon_f \sum_{i\sigma} \hat{n}^f_{i\sigma} + U \sum_i \hat{n}^f_{i\uparrow} \hat{n}^f_{i\downarrow}.$$

If one cannot neglect inter-site $f-f$ hybridization then the most general Hamiltonian combining Hubbard and Anderson models should be defined and studied:

$$\hat{H} = \varepsilon_c \sum_{i\sigma} \hat{c}^\dagger_{i\sigma} \hat{c}_{i\sigma} + \sum_{ij\sigma} t_{ij} \hat{c}^\dagger_{i\sigma} \hat{c}_{j\sigma} + \\ + \sum_{ij\sigma} t^f_{ij} \hat{f}^\dagger_{i\sigma} \hat{f}_{j\sigma} + \varepsilon_f \sum_{i\sigma} \hat{n}^f_{i\sigma} + U \sum_i \hat{n}^f_{i\uparrow} \hat{n}^f_{i\downarrow} + \\ + \sum_{ij\sigma} \left(V_{ij} \hat{c}^\dagger_{i\sigma} \hat{f}_{j\sigma} + V^*_{ij} \hat{f}^\dagger_{j\sigma} \hat{c}_{i\sigma} \right). \quad (5)$$

In the present paper we investigate the problem of applicability of Anderson model to study cerium and cerium compounds and estimate the strength of inter-site $f-f$ hybridization. We demonstrate that while for heavy-fermion systems such as cerium compound $CeCu_2Si_2$ $f-f$ hybridization can be neglected and Anderson model (4) application is well justified, for cerium metal inter-site $f-f$ hybridization is strong enough giving contribution to hybridization function (3), which is comparable to hybridization of f-electrons with itinerant electrons. In the last case only the most general Hamiltonian (5) should be used.

With the use of the Linear muffin-tin orbitals (LMTO) method [7] and the Local density approximation (LDA) we show that Ce-4f states in metallic Ce should not be described simply as impurity levels. These states do form bands and $f-f$ hopping matrix elements between different Ce sites are sizable. In contrast the f-states in Ce compounds are more localized and do not show significant band dispersion.

We start from the Ce-4f partial Density of states (DOS) for Ce-α, Ce-γ and $CeCu_2Si_2$ presented in Fig.1. One may see that the widths of the DOS are comparable for all three systems and hence it may be expected that the band characteristics of f-states in these compounds are similar. Since the similarity in the position, width and shape of partial DOS is most pronounced for Ce-γ and $CeCu_2Si_2$ we will use these two systems to compare band effects.

The real band structures obtained in the self-consistent LDA calculation for Ce-γ is shown by dashed curves in Fig.2. Seven Ce-4f are spread over wide energy [-0.4 eV, 1 eV] (compare with Fig.1).

In order to check whether Ce-4f states can be treated as independent impurity states we remove (set zero) all the matrix elements from the self-consistent LDA hamiltonian except Ce-4f. The self-consistent potential for the real material is still used, so that the resulting band structure is *not* the same as for hypothetical "Ce-f-only ions" in Ce-γ type lattice. The band structure obtained within this method can be thought as the actual dispersion of Ce$-f$ states in real Ce$-\gamma$, where hybridization with Ce$-s,p,d$ states was switched off. The same procedure was previously applied for the analysis of the chemical bonding in Ag_2NiO_2 [8].

The comparison of full-orbital LDA bands structure and one obtained removing Ce-s,p,d states from the basis set is shown in Fig.2. One may see that the band dispersion of Ce-4f states is quite similar, and that these states still form the real bands, rather than atomic levels. The band-width $W_{f-only} \sim 0.75$ eV in Ce$-\gamma$.

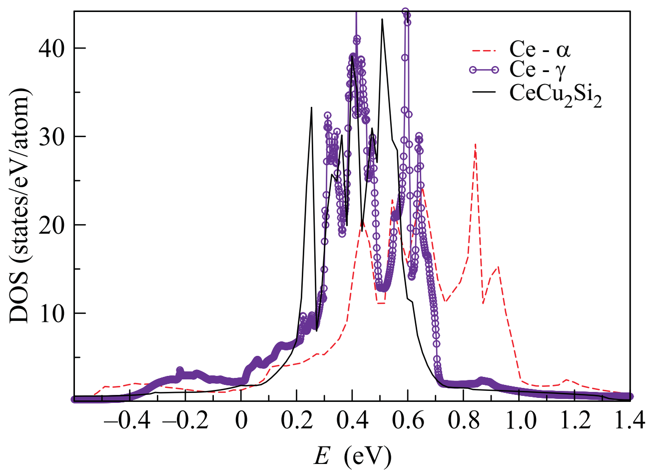

Fig.1. (Color online). LDA Ce$-4f$ partial DOS for Ce-α (dashed, red), Ce-γ (solid with circles, violet) and $CeCu_2Si_2$ (solid, black). The Fermi level is in zero

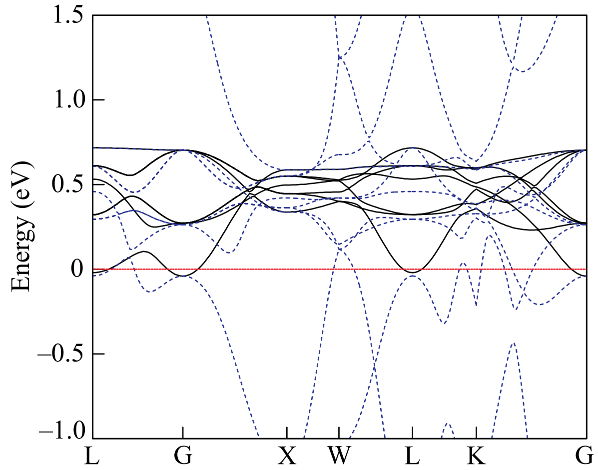

Fig.2. (Color online). Full orbital LDA band structure for Ce-γ is shown by blue dashed curve. The band structure obtained by removing Ce$-s,p,d$ states from the self-consistent LDA hamiltonian is shown in black. They are more localized, but still cannot be considered as atomic levels. The Fermi level corresponds to zero energy

In order to show that this situation is specific to Ce we performed the same calculations for $CeCu_2Si_2$. The results are presented in Fig.3. In contrast to the case

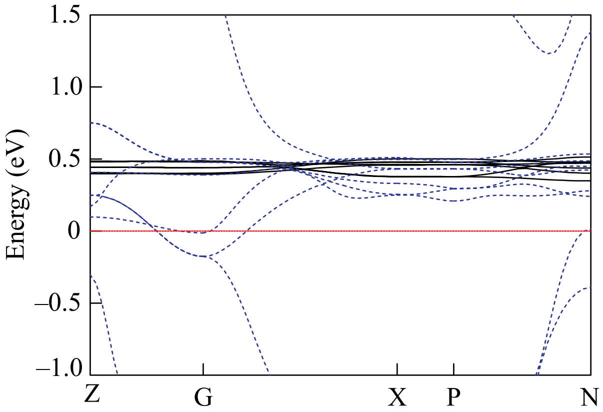

Fig.3. (Color online). Full orbital LDA band structure for $CeCu_2Si_2$ is shown by blue dashed curve. The band structure obtained by removing Ce$-s, p, d$ states from the self-consistent LDA hamiltonian is shown in black. The Fermi level corresponds to zero energy

of metallic Ce the absence of the hybridization between Ce$-4f$ and Ce-s, p, d states leads to the loss of band dispersion. The reason for such a different behavior of metallic Ce and $CeCu_2Si_2$ is rather obvious: in the last case Ce ions are separated by Cu and Si, direct $f-f$ hopping and corresponding effective bandwidth is small ($W_{f-only}\sim 0.1$ eV) and the bands are dispersionless like atomic levels. However, the presence of sizable band dispersion for metallic Ce was not taken into account in previous model calculations.

The value of the Ce $f-f$ hopping parameters estimated from the band-width and tight-binding parametrization or more sophisticated Wannier projection procedure [9] results in t_{ff} ~30 meV. The presence of small, but finite $f-f$ hopping may lead to a number of consequences. The most obvious is a direct antiferromagnetic exchange interaction between Ce ions proportional to $2t_{ff}^2/U$. Together with indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange this interaction will act against formation of a coherent state.

The most direct investigation of the effects connected with the presence of finite $f-f$ hoppings in pure Ce can be performed by a numerical solution of (5), using for instance Dynamical mean-field theory (DMFT) or its cluster extension [10]. However, already on the LDA level one may show that these effects should be important. In order to demonstrate it the hybridization function on the real energy axis was constructed with and without $f-f$ hopping. On the first step of this procedure one obtains Hamiltonian in the basis of Wannier functions in real space as described in ref. [9]. Then one makes zero corresponding off-diagonal matrix elements, performs back Fourier transform to reciprocal space, calculates density of states using tetrahedron method and constructs hybridization function $\Delta(\varepsilon)$ using formalism developed in ref. [11]:

$$\Delta(\varepsilon) = -Im\sum_{\nu}\Big(\int\frac{\rho_{\nu}(\varepsilon')}{\varepsilon-\varepsilon'-i\theta}d\varepsilon'\Big)^{-1}, \qquad (6)$$

where $\rho_{\nu}(\varepsilon)$ is a partial DOS, and ν – orbital index. To avoid numerical errors partial DOS were normalized on unity before apply (6).

The plot of the hybridization function obtained in this way in comparison with $\Delta(\varepsilon)$ from conventional LDA calculation is presented in Fig.4. One may see that

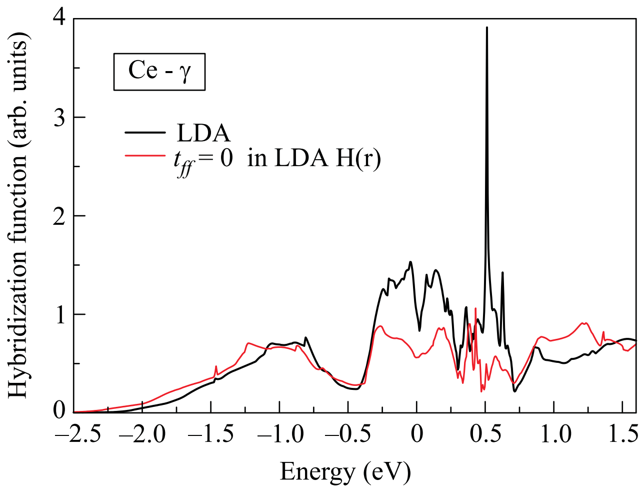

Fig.4. (Color online). Total hybridization function $\Delta(\varepsilon)$ for Ce$-\gamma$ as defined in (6) calculated in conventional LDA and in LDA, where in self-consistent Hamiltonian off-diagonal inter-site $f-f$ matrix elements were put to zero. The Fermi level corresponds to zero energy

the most significant changes in frequency are observed near the Fermi level. The full description of the electronic properties of the system with given hybridization can be obtained only by numerical solution of many-body problem. However, already on the LDA level we obtain that the ratio $\bar{\Delta}_{LDA}(\varepsilon)/\bar{\Delta}_{t_{ff}=0}(\varepsilon)$ is of order 2 for Ce and 1.2 for $CeCu_2Si_2$, where $\bar{\Delta}(\varepsilon)$ is averaged over the region of 1 eV around the Fermi level total hybridization function. This demonstrates an importance of the account of direct $f-f$ hopping matrix elements in a real many-body calculation

To sum up, in the present paper we've shown that there is sizable $f-f$ hopping matrix element in the metallic Ce. This implies that the full description of the electronic properties of Ce should be obtained not within the frameworks of the single impurity, but rather in lattice models, where hopping parameters between different f-sites are implicitly taken into account. Thus, multi-band Hubbard model is one of the models suitable for such an investigation.

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1. See review D. C. Koskenmaki and K. A. Gschneider, Jr. in *Handbook on the Physics and Chemistry of the Rare Earths*, Eds. K. A. Gschneider and L. Eyring (North-Holland, Amsterdam, 1978), Vol. 1, Chap. 4.
2. P. W. Anderson, Phys. Rev. **124**, 41 (1961).
3. V. T. Rajan, Phys. Rev. Lett **51**, 308 (1983).
4. F. Patthey, J.-M. Imer, W.-D. Schneider et al., Phys. Rev. B **42**, 8864 (1990).
5. L. Z. Liu, J. W. Allen, O. Gunnarsson et al., Phys. Rev. B **45**, 8934 (1992).
6. E. Wuilloud, H. R. Moser, W.-D. Schneider, and Y. Baer, Phys. Rev. B **28**, 7354 (1983).
7. O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).
8. M. D. Johannes, S. V. Streltsov, I. I. Mazin, and D. I. Khomskii, Phys. Rev. B **75**, 180404 (2007).
9. S. V. Streltsov, A. S. Mylnikova, A. O. Shorikov et al., Phys. Rev. B **71**, 245114 (2005).
10. A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
11. O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B **39**, 1708 (1989).