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From local-density approximation to strong electron correlations

Igor Sandalov[a,b,*], Börje Johansson[a], Olle Eriksson[a]

[a]*Condensed Matter Theory Group, Institute of Physics, University of Uppsala, Box 530, S-75121 Uppsala, Sweden*
[b]*Kirensky Institute of Physics, 630036 Krasnoyarsk, Russia*

Abstract

We formulate a regular approach for ab initio calculations of the band structure, ground state properties ($T = 0$ K) and excitations ($T \neq 0$) which goes beyond the local-density approximation (LDA) for systems with d- and f-electrons. A diagram technique for non-zero temperature both from the itinerant and atomic limits is developed within a non-orthogonal basis which is generated by the calculation in LDA. LDA is taken as a reference point. Local electron correlations are taken into account by exact transformation of total Hamiltonian to many-electron representation. The derived system of equations for Green's functions of coupled conduction and correlated electrons (including angular momenta, etc.) is presented in closed functional form which allows to construct accurately self-consistent approximations. The approach can be used also in particular cases of any non-commutative algebras, like different spin models with strong anisotropy, or models of correlated electrons (Hubbard, Anderson) for multiple on-site orbitals.

Keywords: Beyond LDA; Correlations; Diagram technique; Non-orthogonality

The electrons of open shells (d- or f-s) are treated in band structure calculations (BSC) usually either as localized core electrons, or as delocalized electrons. In the first case two constraints are introduced by "hands": (i) number of in-core f(d)-electrons is fixed, and (ii) mixing of these states with other ones is forbidden. Treating f(d)-electrons as valent ones makes them fully delocalized, while using the same potential for all f(d)-electrons pushes the center of these bands above Fermi energy. Thus, in both ways description of correlated electron systems, say, Kondo systems, Mott insulators, becomes difficult. Zero temperature is the other restriction of BSC. We suggest a regular method to overcome these difficulties. Below we give the essence of our approach.

1. The full Hamiltonian in secondary quantized form $H_{\rm tot} = H_{\rm LDA} + (H_{\rm tot} - H_{\rm LDA})$ is formulated on the basis set of wave functions which are generated by BSC with Hamiltonian $H_{\rm LDA}$. Most convenient methods for our aim are the method of linear muffin-tin orbitals (LMTO) and the method of linear combination of atomic orbitals (LCAO). For certainty we will use LMTO. Since the LMTO basis is non-orthogonal, resulting in a generalized eigenvalue problem with an overlap matrix, $O_{jL,j'L'} = \langle \chi_{jL} | \chi_{j'L'} \rangle$, the anticommutator of corresponding fermionic operators is $\{a_{jL}, a^{\dagger}_{j'L'}\} = (O^{-1})_{jL,j'L'}$. Let us now discuss the case of f-electrons and use for the operator a_{jL} with $L = \{l = 3, m_l, \sigma\}$ the notation $f_{jm_l\sigma}$, whereas all the non-f's are called c_{jL}, $a_{jL} = \delta_{L,(3,m_l\sigma)} f_{m_l\sigma} + (1 - \delta_{L,(3,m_l\sigma)}) c_{jL}$. Then the LDA-LMTO part of the Hamiltonian can be written in the form

$$H_{\rm LMTO} = \sum_{k\lambda} \varepsilon_{k\lambda\sigma} a^{\dagger}_{k\lambda\sigma} a_{k\lambda\sigma} = \sum_{j,L,j',L'} H_{jL,j'L'} c^{\dagger}_{jL} c_{j'L'} + \sum_{j,m_l,\sigma} \varepsilon^0_f f^{\dagger}_{jm_l\sigma} f_{jm_l\sigma} + \sum_{jm_l\sigma j'm_l'} t^{\sigma}_{jm_l,j'm_l'} f^{\dagger}_{jm_l\sigma} f_{j'm_l'\sigma} + \sum_{j,L,j'm_l,\sigma} [H_{jL;j'm_l\sigma} c^{\dagger}_{jL} f_{j'm_l\sigma} + H^{*}_{jm_l\sigma;j'L} f^{\dagger}_{jm_l\sigma} c_{j'L}]. \quad (1)$$

* Correspondence address: Condensed Matter Theory Group, Institute of Physics, University of Uppsala, Box 530, S-75121 Uppsala, Sweden. Tel.: + 46-18-471-35-84; fax: + 46-18-47-35-24; e-mail: igor@fysik.uu.se.

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Here the hopping matrix element and the position of center of f-band are given by [1] $t^{\sigma}_{j,m_i,j',m'_i} = \sum_k e^{ik(R_j - R_{j'})}[H_{m_i,\sigma,m'_i,\sigma}(k) - \delta_{m_i,m'_i}\varepsilon^f_0]$, where $\varepsilon^f_0 = \sum_k H_{m_i\sigma,m_i\sigma}(k)$.

2. Then we rearrange the terms of $H_{\rm tot}$: the on-site Coulomb interactions between the f(d)-electrons are collected and rewritten exactly in the many-electron representation. The latter takes into account the following features of correlations. First, each electron "knows" about the population of all other orbitals in this shell. This is done via the identities of the kind: $\hat{f}_1 = \hat{f}_1[\hat{n}_2 + (1 - \hat{n}_2)][\hat{n}_3 + (1 - \hat{n}_3)] \ldots [\hat{n}_{14} + (1 - \hat{n}_{14})]$. Second, the Pauli principle, $\hat{n}^2_f = \hat{n}_f, \hat{n}_f \equiv \hat{f}^{\dagger}\hat{f}, \hat{f}^2 = 0$ is used. Collecting the terms which have the same operator structure we come to an atomic-like zero on-site f(d)-electron Hamiltonian which can be diagonalized in Hubbard's operators, X^b. Third, kinematic interactions arise from non-trivial commutation relations of Hubbard operators. The bare delocalized electrons are still described by LDA Hamiltonian.

3. Large energy separation of the terms with different numbers of f(d)-electrons allows to neglect the contributions from the states which differ from the valent one by more than two localized electrons. If we adopt the assumption that the Coulomb interaction of f(d)-electrons with others is treated by LDA suffciently, then we obtain the periodical Hubbard–Anderson model.

4. The Matsubara Green' functions (GFs) $\langle \eta(\tau)\eta^{\dagger}(0)\rangle$ with $\eta^{\dagger}_{j\lambda} = (c^{\dagger}_{jL_1}, \ldots, c^{\dagger}_{jL_n}, X^{\dagger b_1}_j, \ldots, X^{\dagger b_m}_j)$ are introduced. Here c describes conduction electrons. The commutation relations between η-operators have been calculated by making use of their explicit form in terms of f-operators and known anticommutators $\{c_{iL}, f^{\dagger}_{jm_i\sigma}\} = (O^{-1})_{iL,jm_i\sigma}$, where O^{-1} is the inversed overlap matrix.

5. Then we develop a diagram technique for these and boson-like GFs. The advantage of the suggested from of technique is that it can work with non-orthogonal basis and is developed for a many-orbital problem within Hubbard's operators. The idea [2–4] consists of introducing the S-matrix with external fields $\int UM$ where the operators M are the ones which were generated by the equation of motion for the GFs. Schematically, the resulting (in martix form) equation can be written as

$$[I(i\partial_t - \varepsilon 1_0) - C_1\mathscr{U}]\langle T\eta\eta^{\dagger}\rangle_u = i\delta(t - t')\langle\{\eta, \eta^{\dagger}\}\rangle_u + O^{-1}V\langle TM\eta\eta^{\dagger}\rangle_u. \quad (2)$$

and, in the next step, making use of the Schwinger's trick (ST) $\langle TM\eta\eta^{\dagger}\rangle_u = (\langle TM\rangle_u + i\delta/\delta\mathscr{U})\langle T\eta\eta^{\dagger}\rangle_u$. Introducing the self-energy operator Σ by the relation $O^{-1}V(\langle T\hat{M}\rangle + \delta/\delta\mathscr{U})G \equiv \Sigma G$ with $G \equiv \langle T\eta\eta^{\dagger}\rangle_u$, we can rewrite Eq. (1) in the form

$$(D_0^{-1} - \Sigma)G = P, \quad D_0^{-1} \equiv (Ii\partial_t - \hat{\Omega}_0 - \hat{C}\mathscr{U})^{-1}. \quad (3)$$

In order to separate the standard fermion-like contributions in the solution to Eq. (2) from those coming from non-trivial commutation relations, we look for solutions to Eqs. (2) and (3) in the form $G = DP$. Iterations of Eq. (2) in the form (2) give the diagram technique with the vertices, defined as $\Gamma_{\rm f} \equiv \delta D^{-1}/\delta\mathscr{U}$ and $\Gamma_{\rm b} \equiv \delta P/\delta\mathscr{U}$. The derivatives of diagonal operators $\delta P/\delta\mathscr{U}$ are cumulants and describe dressing of populations numbers, while the derivatives of non-diagonal ones are response functions. Similar procedure is used for bose-type of transitions. The equation for the set of $\langle TM\rangle_u$ is obtained from its averaged equation of motion and ST. Known in the earlier versions of diagram techniques is the problem of a non-unique set of diagrams (dependence on the way of Wick-like decoupling) which is also solved by this construction. It should be noted that the usual statistical method to construct diagram technique does not work due to $\{c, X\} \neq 0$ (we are not able to calculate in explicit form the time dependence of operators in the interaction picture).

The lowest, Hubbard-I approximation is obtained by putting $\delta G^{-1}/\delta\mathscr{U}$ in self-energy Σ. This approximation leads to separation of f(d)-electron shell into delocalized and localized subsystems, narrower bands, reduced mixing and satellites in density of states below and above Fermi energy. The population numbers N_Γ of many-electron states of ion $|\Gamma\rangle$ should be found additionally to the usual self-consistency loop in LDA. Next, mean field approximation arises if we take into account zero vertex $\Gamma^0_f = \delta G_0^{-1}/\delta\mathscr{U} \neq 0$, but add no higher corrections to it, $\delta\Sigma/\delta\mathscr{U} = 0$. Here the Hubbard U is slightly split [5] into few different values and is decreased due to kinematic interactions. The latter comes from mixing interaction and hopping. The screening of kinematic interactions arises in the random phase approximation (RPA). It is obtained with the help of transformation to description in terms of effective field, $\delta/\delta\mathscr{U} \to (\delta\mathscr{U}_{\rm eff}/\delta\mathscr{U})\delta/\delta\mathscr{U}_{\rm eff}$. RPA gives small corrections to quasi-fermion quasiparticles, (fermion-like excitations), while it is important for the local moment dependence on temperature (bose-like excitations). We emphasize that this RPA is different from the common one arising in the theory of electron gas.

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