Adv. Studies Theor. Phys., Vol. 7, 2013, no. 24, 1157 - 1160
HIKARI Ltd, www.m-hikari.com
http://dx.doi.org/10.12988/astp.2013.3996

The Forming Factors of High Values of Superconducting Transition Temperature T_c in 3*d*-Transition Metal Compounds

V. Particularities of *ab initio* Cluster X_α-discrete Variation Method (X_α-DVM): Exchange Spin-Spin Electron Interaction

[1,2]Elmira Yuryeva

[1]The Ural State College named after I.I. Polzunov, Lenin av. 28
620014 Ekaterinburg, Russia
[2]Ural Technical Institute of Telecommunication and Informatics
Repin str. 15, 620109, Ekaterinburg, Russia
yuryeva55@mail.ru

Anatoliy Yuryev

Ural Federal University, Mira st. 19, 620002 Ekaterinburg, Russia
yurev_anatolii@mail.ru

Abstract

In this article, on an example of the variation of types of exchange-correlation electron - electron interaction, we have traced the genetic relationship between calculated methods Hartree-Fock, Hartree-Fock-Slater, Density Functional Theory.

Keywords: exchange-correlation interaction, Density Functional Theory

The Hartree-Fock-Slater (HFS) method is an effective approach that combines the Hartree-Fock method and methods of Density Functional Theory [1]. Most the Hartree-Fock-Slater method is called X_α-method. In the classical variant of HFS correlation of electrons are neglected, and the exchange potential for electrons with opposite spins can be represented as

$$\begin{aligned} V^{\uparrow}_{X_\alpha}(r1) &= -3[\frac{3}{4\pi}\rho^{\uparrow}(r_1)]^{1/3} \\ V^{\downarrow}_{X_\alpha}(r1) &= -3[\frac{3}{4\pi}\rho^{\downarrow}(r_1)]^{1/3}, \end{aligned} \tag{1}$$

where $\rho^{\uparrow\downarrow}(r_1)$ is the density of electrons with up and down spins. The type of potential (1) is determined through a variation of exchange energy along the electronic density. Using of X_α-method show that this method is suitable for the investigation of different properties not only single atoms but for rather complex molecules and solid states [1].

According [2] the type of approximation for exchange-correlation interaction plays very important role for explanation of properties of condensed matter. Historically the first approximation for exchange potential was expression received by Slater within approximation of free electron which in atomic units ($\hbar = m = e = 1$) can be written as:

$$\begin{aligned} V^{S}_{X}(r1) &= -3[\frac{3}{4\pi}\rho^{\uparrow}(r_1)]^{1/3} = -3[\frac{3}{8\pi}\rho(r_1)]^{1/3} = \\ &= -\frac{3}{2}[\frac{3}{\pi}\rho(r_1)]^{1/3}, \end{aligned} \tag{2}$$

where $\rho^{\uparrow}(r_1) = ½\,\rho$ is the density of electron with spin up and ρ – is total electronic density. In works of Kohn with coauthors [3] was formulated density function theory of electronic density and within approximation of free electrons was received the next expression for exchange potential:

$$V^{K}_{X}(r1) = \frac{2}{3}V^{S}_{X}(r1) = -[\frac{3}{\pi}\rho(r_1)]^{1/3}. \tag{3}$$

Later this contribution became written in total kind according the next expression:

$$V^{K}_{X}(r1) = \alpha\, V^{S}_{X}(r1), \tag{4}$$

and named as X_α-approximation in which α parameter varies within limit from 2/3 up to 1.

From [4] follow that in program code, realized X_α-DV method the approximation of functional of electronic density is used. This approximation was introduced by Hohenberg and Kohn in 1964 [3] and within that the properties of basic state of system are the function of charge density ρ. In particular the total energy of system E_{tot} can be written by the next expression:

$$E_{tot} = T(\rho) + U(\rho) + E_{xc}(\rho)\,, \tag{5}$$

where $T(\rho)$ is the kinetic energy of non interacted particles with density ρ, $U(\rho)$ is the classic electrostatic energy caused by Coulomb electron-electron and electron-nuclear interactions, $E_{xc}(\rho)$ includes many-particles contributions into the total energy, i.e. exchange and correlation energies.

Particularity of DV approach is the calculation of matrix elements of one electron Hamiltonian without expansion on to integrals calculated on the basic functions and without limits imposed for example in “tight-binding” approximation [5].

According to [4] Coulomb interaction exists between electrons also. This interaction should lead to a decrease in the probability of finding the electrons at close quarters, resulting in a one-electron wave function must depend on the position of the other electrons. This effect in Hartree-Fock method did not take to account because the influence of remaining electrons is calculated exactly. The deferent corrections to exchange potential which turn it to exchange-correlation potential are developed by to account Coulomb correlation in approximate approaches. For example given potential may be written as Slater potential with factor α(r_s) which depend from r_s parameter and is not a constant:

$$\mathrm{V}_{X\alpha}^{S} = -\alpha(r_s)[\mathrm{V}_{Xi}^{HF}(r_1)]_{mean}\,, \tag{6}$$

where $\alpha(r_s)$ can be written for example in commonly practiced form introduced by Hedin-Lundqvist [6] which reflect the fact that $\alpha(r_s)=\frac{2}{3}$ at $r_s=0$ and α(r_s) grows with growing of r_s:

$$\alpha(r_s) = \frac{2}{3} + 0.0211 r_s \ln\left(1 + \frac{24.3}{r_s}\right) \tag{7}$$

Within this work we used the exchange-correlation potential in Gunnarsson-Lundqvist [7] form:

$$\alpha(r_s) = 1 + 0.0545 r_S \ln(1 + \frac{11.4}{r_S}) \pm \frac{1}{3}(1 - 0.036 r_S - \frac{1.36 r_S}{1 + 10 r_S})\frac{S}{1 \pm 0.297 S}\,, \tag{8}$$

where $r_S = [\frac{3}{4\pi(\rho^{\uparrow} + \rho^{\downarrow})}]^{1/3}$, $S = \frac{\rho^{\uparrow} - \rho^{\downarrow}}{\rho^{\uparrow} + \rho^{\downarrow}}$, and the upper signs in (8) correspond to the potential for the electrons with spin up, and the lower - for the electrons with spin down.

The results show that the position of the minimum of the total energy depends on the choice of the kind of the electron-electron exchange-correlation potential.

REFERENCES

[1]. V.G. Tsirelson, Qvantovaja khimija. Moleculy, moleculjarnye sistemy i tverdye tela, BINOM. Laboratorija znanii, Moskva, 2010. [in Russian]

[2]. V.A. Krashaninin, A.A. Yuryev, Vlijanie vybora priblizhenija dlja ucheta obmenno-korreljatsionnogo vzaimodeistvija electronov provodimosti s ostovnymi electronami na paschet svoistv metallov v metode psevdopotentsiala, Trudy XII Possiiskoi konferentsii «Stroenie I svoistva metallicheskih I shlakovyh rasplavov». T.1. Modelirovanie I raschet structury I svoistv neuporjadochennyh system v kondensirovannom sostojanii, UrO RAN, Ekaterinburg, 2008. [in Russian]

[3]. P.Hohenberg, W. Kohn, Inhomogeneous electron gas, Phys. Rev, 136 (1964), B864 – B871.

[4]. Yu.V. Chshapova, E.I. Yuryeva, M.V. Ryzhkov, A.L. Ivanovskii, V.N. Bykov, S.L. Votjakov, Kvantovo-himicheskie raschety v mineralogii: modelirovanie electronnogo stroenija I parametry messbauerovskih spektrov, Miass: IMin UrO RAN, 2000, 1 - 90. [in Russian]

[5]. D.E. Ellis, G.S. Painter, Discrete variation method for the energy-band-problem with general crystal potentials, Phys. Rev. B, 2 (1970), 2887 – 2898.

[6]. L. Hedin, B.I. Lundqvist, On local density schemes, J. Phys. C, 33 (1972), 73-81.

[7]. O. Gunnarsson, B.I. Lundqvist, Exchange and correlation in atoms, molecules, and solids by spin-density-functional formalism, Phys. Rev. B, 13 (1976), 4274 - 4298.

Received: August 26, 2013