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2009 J. Phys.: Condens. Matter 21 064208

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Relativistic optimized effective potential method—application to alkali metals

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Received 27 June 2008, in final form 7 August 2008

Published 20 January 2009

Online at stacks.iop.org/JPhysCM/21/064208

Abstract

We present a relativistic formulation of the optimized effective potential method (ROEP) and its implementation within the Korringa–Kohn–Rostoker multiple scattering formalism. The scheme is an all-electron approach, treating core and band states formally on the same footing. We use exact exchange (EXX) as an approximation to the exchange correlation functional. Numerical four-component wavefunctions for the description of core and valence electrons and the corresponding ingredients of the ROEP integral equation are employed. The exact exchange expression for the valence states is reformulated in terms of the electronic Green's function that in turn is evaluated by making use of multiple scattering formalism. We present and discuss the application of the formalism to non-magnetic alkali metals.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years density functional theory (DFT) [1, 2] as the most popular and versatile theory used in describing the electronic structure of solids has been continuously developed. Its success hinges on the approximation to the exchange–correlation functional. In tailoring appropriate functionals, recently, so-called orbital functionals on the level of exact exchange (EXX) are studied intensively [3–10]. Using orbital functionals requires the use of the optimized potential (OPM) method to calculate the effective potential (for that reason the term ‘optimized effective potential (OEP)’ is synonymously used in the literature). The starting point of this development was a non-relativistic formulation [11] which was later extended to a spin-polarized [12] and relativistic, albeit non-spin-polarized, form [13, 14]. Here we use a recent extension of this approach [10] to a relativistic formulation, being able to take spin polarization into account.

In this work we treat the electronic structure problem of the solid using the spin-polarized relativistic Korringa–Kohn–Rostoker (KKR) multiple scattering formalism [15]. For the exchange–correlation contribution we employ the exact exchange approximation. Treatment of the core states uses the approach for atoms given in [10] with an appropriate treatment

of the boundary problem. The mentioned approach is also used to treat the free atom case allowing for checks and comparison. Valence states are treated using multiple scattering theory. Earlier work in the non-relativistic context using LMTO [3] or KKR [4], respectively, employed *numerical* variations of the exchange energy functional with respect to the density. In contrast, we here perform the variations analytically and determine explicitly the involved functional derivatives.

At the moment pseudo-potentials are frequently used in OEP studies [9, 16, 17] when solving the electronic structure problem, and their reliability has been disputed [18]. In contrast, we here make use of an all-electron approach, treating core and valence electrons on the same footing. Further, when constructing the Green's function we avoid the so-called sum over states approach, whose application leads to problems, especially when having in mind inclusion of correlation effects [19].

This paper is organized as follows—first, we present the ROEP equations, treating core and valence states formally on the same footing. Then we give details on the calculation of simple metals. Finally, we present results and compare the resulting exchange potentials for the solid to corresponding exchange potentials obtained from free atom calculations.

2. Theory

The starting point is the Dirac equation within relativistic Kohn–Sham (KS) spin-DFT (see, e.g., [20]):

$$\left[-ic\boldsymbol{\alpha} \cdot \nabla + \frac{c^2}{2}\beta + V_{\text{KS}}(\mathbf{r}) \right] \phi_k(\mathbf{r}) = \epsilon_k \phi_k(\mathbf{r}), \quad (1)$$

where k specifies a set of quantum numbers for either core (c) or band (v) states. The single-particle orbitals are expanded in terms of relativistic spin-angular functions labeled by a combined index $\Lambda = (\kappa, \mu)$, with κ and μ being the spin–orbit and magnetic quantum numbers (more details of the coupling scheme used can be found in [15]). When restricting to a magnetic field in the z direction and a magnetization density collinear to the magnetic field we have

$$V_{\text{KS}}(\mathbf{r}) = \bar{V}_{\text{KS}}(\mathbf{r}) + \beta \Sigma_z B_{\text{xc}}(\mathbf{r}) \quad (2)$$

$$= V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + \bar{V}_{\text{xc}}(\mathbf{r}) + \beta \Sigma_z B_{\text{xc}}(\mathbf{r}), \quad (3)$$

where the spin-averaged (\bar{V}_{xc}) and spin-dependent exchange–correlation (B_{xc}) potentials are given as functional derivatives of E_{xc} :

$$\bar{V}_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n, m]}{\delta n(\mathbf{r})} \quad B_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n, m]}{\delta m(\mathbf{r})} \quad (4)$$

with respect to the electron density and spin magnetization, respectively, given by

$$n(\mathbf{r}) = \frac{1}{2} \sum_k^{\text{occ}} \phi_k^\dagger(\mathbf{r}) \phi_k(\mathbf{r}) + \text{c.c.} \quad (5)$$

$$m(\mathbf{r}) = \frac{1}{2} \sum_k^{\text{occ}} \phi_k^\dagger(\mathbf{r}) \beta \Sigma_z \phi_k(\mathbf{r}) + \text{c.c.} \quad (6)$$

The relativistic optimized effective potentials are given as the solution of the ROEP integral equation:

$$\int d^3r' \begin{pmatrix} \bar{V}_{\text{xc}}(\mathbf{r}') \\ B_{\text{xc}}(\mathbf{r}') \end{pmatrix}^T \chi(\mathbf{r}', \mathbf{r}) = \begin{pmatrix} I_{\text{V}}(\mathbf{r}) \\ I_{\text{B}}(\mathbf{r}) \end{pmatrix}^T. \quad (7)$$

In the following we give details of the evaluation of the inhomogeneities and the static non-interacting Kohn–Sham response function χ needed to invert the latter equation. Both inhomogeneities and response are partitioned into core and valence contributions.

The response is given by the sum of core (c) and valence (v) contributions, respectively:

$$\chi(\mathbf{r}, \mathbf{r}') = \chi^{(\text{c})}(\mathbf{r}, \mathbf{r}') + \chi^{(\text{v})}(\mathbf{r}, \mathbf{r}'). \quad (8)$$

Partitioning the expression for the exchange–correlation energy results into four terms associated with core–core (cc), core–valence (cv), valence–core (vc) and valence–valence (vv) contributions:

$$E_{\text{xc}} = E_{\text{xc}}^{(\text{cc})} + E_{\text{xc}}^{(\text{cv})} + E_{\text{xc}}^{(\text{vc})} + E_{\text{xc}}^{(\text{vv})}. \quad (9)$$

The inhomogeneities I_{V} and I_{B} of equation (7) have to be formulated accordingly using expressions for core and band states, respectively. In what follows we use exact exchange (EXX, E_x) as an approximation to the exchange–correlation functional and give the terms needed for solving equation (7) according to the partitioning given in equations (8) and (9).

2.1. Core–core contributions

We here derive the expressions along the lines of the formalism [10] developed for the free atom case.

Using the chain rule for functional derivatives the inhomogeneities are obtained as

$$I_{\text{V}}^{(\text{cc})}(\mathbf{r}) = \int d^3r' \sum_k \frac{\delta \phi_k^\dagger(\mathbf{r}')}{\delta \bar{V}_{\text{KS}}(\mathbf{r})} \frac{\delta E_x^{\text{cc}}[n, m]}{\delta \phi_k^\dagger(\mathbf{r}')} + \text{c.c.} \quad (10)$$

$$I_{\text{B}}^{(\text{cc})}(\mathbf{r}) = \int d^3r' \sum_k \frac{\delta \phi_k^\dagger(\mathbf{r}')}{\delta B_{\text{xc}}(\mathbf{r})} \frac{\delta E_x^{\text{cc}}[n, m]}{\delta \phi_k^\dagger(\mathbf{r}')} + \text{c.c.} \quad (11)$$

Given the EXX expression for E_x

$$E_x = - \sum_{kl}^{\text{occ}} \int d^3r \int d^3r' \frac{\phi_k^\dagger(\mathbf{r}) \phi_l(\mathbf{r}) \phi_l^\dagger(\mathbf{r}') \phi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (12)$$

as an explicit functional of the spinor–orbitals these can be readily determined. The variations of the orbitals with respect to changes in the KS potentials are obtained from first-order perturbation theory as

$$\frac{\delta \phi_k^\dagger(\mathbf{r}')}{\delta \bar{V}_{\text{KS}}(\mathbf{r})} = \phi_k^\dagger(\mathbf{r}) G_k^{(\text{c})}(\mathbf{r}, \mathbf{r}') \quad (13)$$

$$\frac{\delta \phi_k^\dagger(\mathbf{r}')}{\delta B_{\text{xc}}(\mathbf{r})} = \phi_k^\dagger(\mathbf{r}) \beta \Sigma_z G_k^{(\text{c})}(\mathbf{r}, \mathbf{r}').$$

Here $G_k^{(\text{c})}$ is the orthogonal Green’s function whose construction in the relativistic case is much more involved than in the non-relativistic case and is given in [10, 21]

Using the operators $O^v \in \{\mathbb{I}_4, \beta \Sigma_z\}$, where $v = n, m$ denotes the association with the charge density and magnetization, respectively, the static KS response functions can be written as a sum over occupied core states:

$$\chi_{\mu\nu}^{(\text{c})}(\mathbf{r}', \mathbf{r}) = \sum_k^{\text{occ}} \phi_k^\dagger(\mathbf{r}') O^\mu G_k^{(\text{c})}(\mathbf{r}', \mathbf{r}) O^\nu \phi_k(\mathbf{r}). \quad (14)$$

2.2. Valence–valence contributions

The valence properties of the paramagnetic ground state are represented within the relativistic KKR method by the multiple scattering Green’s function [22]:

$$G^{(\text{v})}(\mathbf{r}, \mathbf{r}', E) = \sum_{\Lambda\Lambda'} Z_{\Lambda}^n(\mathbf{r}, E) \tau_{\Lambda\Lambda'}^{nn'}, Z_{\Lambda'}^{n'\times}(\mathbf{r}', E) - \sum_{\Lambda} [Z_{\Lambda}^n(\mathbf{r}, E) J_{\Lambda}^{n\times}(\mathbf{r}', E) \Theta(r' - r) + J_{\Lambda}^n(\mathbf{r}, E) Z_{\Lambda}^{n'\times}(\mathbf{r}', E) \Theta(r - r')] \delta_{nn'}, \quad (15)$$

where Z_{Λ}^n and J_{Λ}^n are four-component wavefunctions, being regular and irregular solutions, respectively, of the single-site Dirac equation at a site n , and $\tau_{\Lambda\Lambda'}^{nn'}$ is the scattering path operator subsuming the multiple scattering events in the solid. Using $G^{(\text{v})}$ the relativistic exact exchange functional can be written as

$$E_x^{(\text{vv})}[n] = -\frac{1}{\pi^2} \int d^3r \int d^3r' \frac{\text{Tr} [\text{Im} \int dE G^{(\text{v})}(\mathbf{r}, \mathbf{r}', E)] [\text{Im} \int dE' G^{(\text{v})}(\mathbf{r}', \mathbf{r}, E')]}{|\mathbf{r} - \mathbf{r}'|}, \quad (16)$$

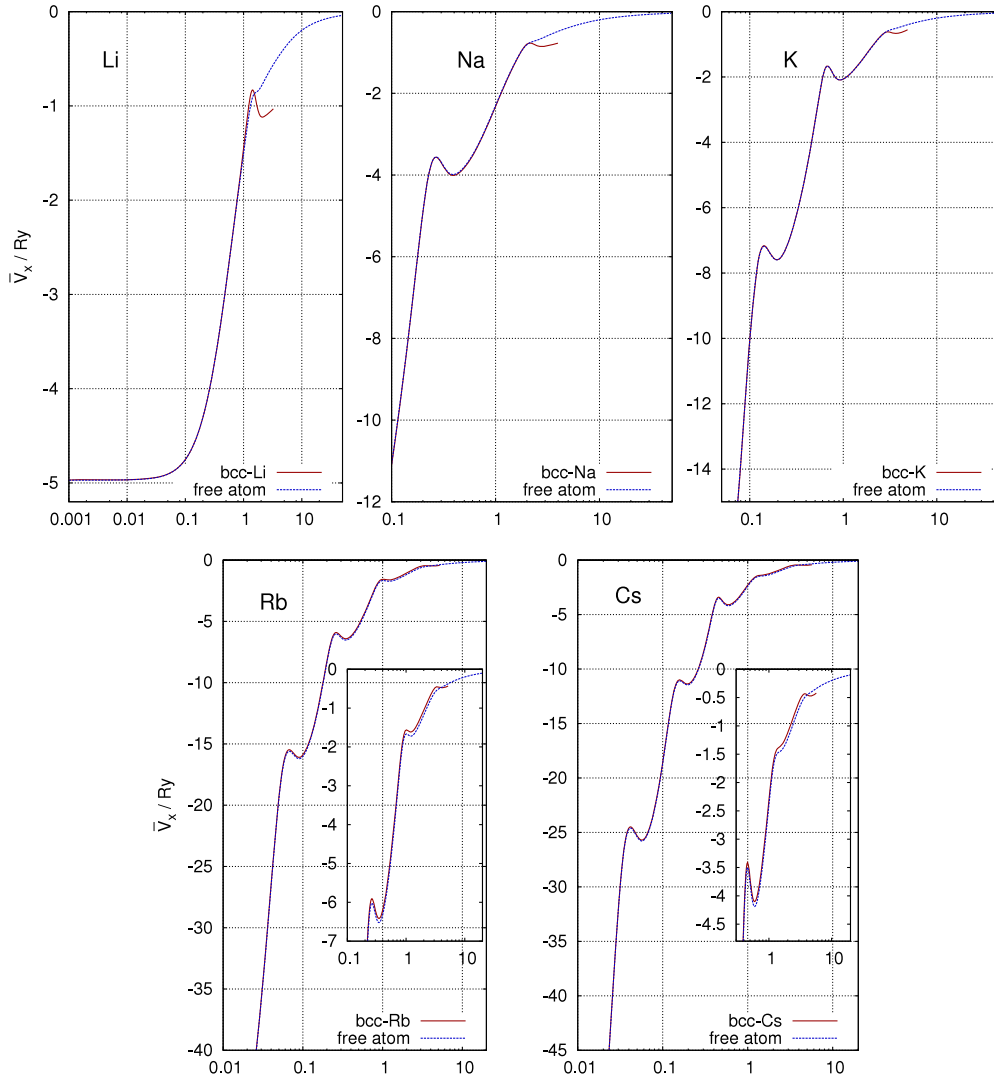


Figure 1. (Spin-averaged) exchange potentials for alkali metals in the solid state and their free atom counterparts calculated using the spin-polarized (in the case of atoms) relativistic optimized effective potential method. Note that the exchange potentials for the solid extend to the WS radius only. The exchange potentials for the solid have been shifted in energy and aligned with those from the atom to allow comparison. The insets shown for Rb and Cs show an enlarged part of the valence region.

where use has been made of the expression for the density matrix $n^{(v)}(\mathbf{r}, \mathbf{r}')$ in terms of $G^{(v)}$:

$$n^{(v)}(\mathbf{r}, \mathbf{r}') = -\frac{1}{\pi} \text{Im} \int dE G^{(v)}(\mathbf{r}, \mathbf{r}', E). \quad (17)$$

To determine the contribution of the valence states to the inhomogeneity in equation (7), equation (16) is varied with respect to $\bar{V}_{KS}(\mathbf{r})$ which gives

$$\begin{aligned} I_V^{(vv)}(\mathbf{r}) &= \frac{\delta E_x^{(vv)}}{\delta \bar{V}_{KS}(\mathbf{r})} \\ &= -\frac{2}{\pi^2} \int d^3 r' \int d^3 r'' \left\{ \text{Tr} \left[\text{Im} \int dE G^{(v)}(\mathbf{r}', \mathbf{r}'', E) \right] \right. \\ &\quad \times \left. \left[\text{Im} \int dE' G^{(v)}(\mathbf{r}'', \mathbf{r}, E') G^{(v)}(\mathbf{r}, \mathbf{r}', E') \right] \right\} \{|\mathbf{r}' - \mathbf{r}''|\}^{-1}. \end{aligned} \quad (18)$$

The contribution of the valence states to the response function is determined using $G^{(v)}$ as [23, 24]

$$\chi^{(v)}(\mathbf{r}, \mathbf{r}') = -\text{Tr} \int dE G^{(v)}(\mathbf{r}, \mathbf{r}', E) G^{(v)}(\mathbf{r}', \mathbf{r}, E). \quad (19)$$

2.3. Valence-core contributions

The inhomogeneities $I_V^{(vc)}$ and $I_V^{(cv)}$ are obtained by adopting equation (16), replacing the appropriate parts by the core density matrix $n^{(c)}(\mathbf{r}, \mathbf{r}')$ and varying with respect to $\bar{V}_{KS}(\mathbf{r})$.

More details on the analytical treatment of the functional variation of E_x in terms of the Green's function for the valence states will be published elsewhere [25].

3. Details of the calculation

The effective potentials as a solution of the ROPM equation (7) are obtained by a discretization of the inhomogeneities and

the response function on real space meshes and subsequent matrix inversion. Choosing the effective potentials to be spherically symmetric, corresponding spherically averaged inhomogeneities and response functions are used in the procedure.

For the atomic calculation the range of the radial mesh depends on the system and is chosen such that numerical stability as well as high accuracy of the result is guaranteed. The meshes in this case typically extend to about 30–50 au. Outer boundary conditions are imposed using the procedure given in [10], by using a spin-projected representation of the potentials and using the exact result for $r \rightarrow \infty$.

Determining the effective potentials for the solid, the computationally most demanding part is the evaluation of the Coulomb integrals in equation (18) on a double energy mesh (E, E'). In contrast to a former KKR implementation, where the variations are computed numerically we do the variation in equation (18) analytically. As done in a previous non-relativistic implementation of the OPM by means of the KKR [4] the energy integration is done on a complex energy path.

We use the atomic sphere approximation (ASA) and the inversion is done on an exponential radial mesh spanning the Wigner–Seitz (WS) radius. The boundary condition at the WS radius is chosen as in [4] and we obtain the δ -like feature of V_x , as reported there.

For the non-magnetic metals Li, Na, K, Rb and Cs we used lattice constants of 6.63, 8.11, 9.87, 10.55 and 11.61 au, respectively. The structure has been assumed to be body-centered cubic (bcc) for all metals considered here.

4. Results and discussion

In figure 1 the exchange potentials for the stable elemental alkali metals are shown. In addition, to allow comparison, the spin-averaged exchange potentials of the corresponding free atoms are plotted (note that the free atoms are magnetic and, further, that for the solid the exchange potentials extend to the WS radius only). All of them show a pronounced shell structure. As expected, especially for the elements with high atomic number the exchange potentials for the atoms and their solid counterpart are very similar in the nuclear near regime. As a result of the different boundary condition systematic changes in the valence regions are visible.

For the open-shell free atoms the exchange fields B_x are shown in figure 2. They have a generic structure showing the typical bump of the outer s electron and are non-vanishing near the nucleus (as opposed to exchange fields obtained in the local density approximation). With increasing atomic number the exchange fields show a fine structure near the nucleus associated with the shell structure of the atom.

In summary, we have devised a relativistic optimized effective potential method implemented in KKR multiple scattering theory. Core and valence electrons are treated on the same footing in an all-electron approach. Results for non-magnetic alkali metals demonstrate the future potential of this approach. Ongoing work is devoted to the application of this formalism to magnetic solids and the inclusion of correlations.

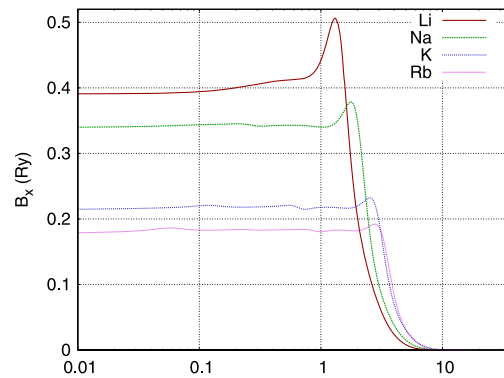


Figure 2. Spin-dependent exchange potentials for free open-shell alkali atoms calculated using the spin-polarized relativistic optimized effective potential method.

Acknowledgments

Financial support by the German DFG within the priority program SPP 1145 is gratefully acknowledged. In addition, one of the authors (HE) would like to thank Professor J Kanamori for his hospitality during a stay at the International Institute for Advanced Studies (IIAS, Kyoto).

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