Norm-conserving pseudopotentials in the exact-exchange Kohn-Sham formalism

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Abstract. We present a rigorous approach for constructing norm-conserving pseudopotentials within the exact-exchange (EXX) Kohn–Sham density functional formalism. The approach is based on the relativistic EXX scheme within the framework of the optimized potential method. We derive an integral equation that yields the exact local Kohn–Sham exchange potential due to valence electrons. This valence exchange potential is used for constructing ionic pseudopotentials and replaces the standard procedure of unscreening atomic pseudopotentials that is shown to be not applicable in the EXX formalism. The EXX pseudopotentials excellently reproduce the experimental atomic ionization energies and they show a better transferability than the standard pseudopotentials based on the local density approximation (LDA). The relativistic EXX pseudopotentials are shown to lead to the correct ordering of conduction band minima in diamond-structure Ge and reduce the LDA errors in the energetic positions of d bands in solids.

1. Introduction

Density functional theory (DFT) has proven to be a powerful tool for quantum mechanical calculations of the electronic properties of atoms, molecules, and solids [1–3]. The great majority of applications are based on the Kohn–Sham (KS) approach to DFT [4]. The Kohn–Sham equations are single-particle Schrödinger-like equations with an effective *local* potential that consists of the external, the Hartree, the exchange, and the correlation potentials. In conventional KS methods, the exchange and correlation potentials as well as the corresponding energies have to be treated approximately, either within the local density approximation (LDA) or the more sophisticated generalized gradient approximations (GGA) [3]. In a new generation of Kohn–Sham methods, the *exact* expression for the exchange energy has been evaluated, and the *exact local* KS exchange potential has been determined [6–15]. In this approach, termed the exact-exchange (EXX) method hereafter, only the correlation energy and potential need to be approximated. For free atoms and ions, an EXX approach was introduced already quite some time ago and was termed the optimized-effective-potential (OEP) method [6]. It was shown to be superior to the LDA in numerous applications [15–18] and to yield, in particular, the correct asymptotic Kohn–Sham potential ($\sim 1/r$). EXX methods for solids [10, 11, 19] and molecules [12, 13] have only recently been developed and have yielded very encouraging results. The EXX approach for solids has been demonstrated to cure a well known deficiency of the LDA (and GGA), namely the strong underestimation of energy gaps. The major reason

for this success lies in the exact elimination of the unphysical Coulomb self-interaction within the EXX method. In addition, this scheme, combined with GGA correlations, has been shown to yield much better cohesive energies than LDA [11].

The pseudopotential plane-wave method [20] is a well established and efficient technique for solving the Kohn–Sham equations for solids. To attain the quality of all-electron calculations, the ionic pseudopotentials must be generated consistently, i.e., with the same type of Kohn–Sham potentials that are used in the solid state [21–24]. It is known, for example, that LDA-derived ionic pseudopotentials are poorly suited for Hartree–Fock calculations [25]. Therefore, consistent EXX pseudopotentials are needed for the employment of the plane-wave EXX method for solids.

So far, with one exception [**?**], the REXX formalism [15, 17, 33] has only been developed for all-electron calculations on atoms but not for pseudopotential calculations that require a separate treatment of core and valence electrons. An approximate REXX pseudopotential scheme has been reported previously [34, 35], that was based on the Krieger, Li, and Iafrate (KLI) approximation [36] to the OEP.

In this paper, a rigorous method for constructing norm-conserving relativistic EXX (REXX) pseudopotentials is developed. We present a symmetrization scheme for the REXX equations for open-shell atoms that is particularly well adapted for the generation of pseudopotentials. In addition, an implicit scheme for unscreening atomic pseudopotentials is developed that is applicable to density functional schemes—such as EXX—where the explicit dependence of the Kohn–Sham potential on the electron density is not known. In this context, we show that the standard unscreening procedures used for LDA [26–29] or Hartree–Fock pseudopotentials [30–32] are not applicable in the EXX case.

We have generated REXX pseudopotentials for several atoms containing occupied s, p, and d shells. In all cases, these pseudopotentials show a better transferability than LDA pseudopotentials. Finally, we demonstrate that REXX pseudopotentials yield, in contrast to LDA, the correct ordering of energy gaps in crystalline Ge and good agreement with experimental energies of d bands in II–VI compounds. We note that these REXX pseudopotentials have been employed in EXX calculations of cohesive and electronic properties of several semiconductors [10, 11]. REXX pseudopotentials obtained with a closely related approach were recently tested in EXX calculations of diatomic molecules [?].

The paper is organized as follows. In section 2, the main equations of the relativistic exact-exchange (REXX) method for atoms are briefly summarized to set up the notation. We introduce the generalized configuration-averaging procedure for open-shell atoms in section 2.1, used to obtain spherically symmetric equations that are suitable for pseudopotentials. In section 3 it is first pointed out that none of the known unscreening procedures is adequate for generating REXX pseudopotentials. Then we show how one can generate an ionic pseudopotential without knowing the explicit dependence of the exchange and correlation functional on the valence electron density. In section 4, the REXX and RLDA pseudopotentials are compared with one another, and, finally, the key results are summarized in section 5. Generally, Rydberg units are used throughout the paper ($\hbar = 2m_e = e^2/2 = 1$), but we have explicitly included these constants in some cases for the sake of clarity. The code for generating the present pseudopotentials, together with additional technical details, is available on the Internet (www.wsi.tum.de).

2. Relativistic exact-exchange calculations for atoms

The present analysis is based upon the relativistic Kohn–Sham formalism in the framework of the exact-exchange scheme (REXX) [15, 17, 33]. In the context of atoms, this scheme

is conventionally referred to as the relativistic optimized-effective-potential (ROEP) method [15,17,33] but we shall nevertheless consistently use the former term which is more widely used for solids. In the absence of magnetic fields, the zeroth component $\rho(\vec{r})$ of the ground-state four-current density determines the external potential $v_{ext}(\vec{r})$ (for atoms $v_{ext}(r) = -Ze^2/r$; Z is the atomic number) and the ground-state wave function uniquely. Consequently, only a scalar effective potential v_s acts on the four-component spinors $\phi_k(\vec{r})$ in the relativistic Kohn–Sham equations. For easier comparison with the non-relativistic (and pseudopotential) case, we use the convention that energy $\epsilon_k = 0$ refers to the energy of one free electron at rest, which is $m_e c^2$ with respect to the vacuum ($\epsilon_k = \epsilon'_k - m_e c^2$). The resulting longitudinal relativistic Kohn–Sham equations for the four-component spinors $\phi_k(\vec{r})$ read [15,17,33]

$$(-\mathrm{i}c\hbar\hat{\vec{\alpha}} \cdot \vec{\nabla} + (\hat{\beta} - 1)m_e c^2 + v_s(\vec{r}))\phi_k(\vec{r}) = \epsilon_k \phi_k(\vec{r}) \tag{1}$$

where $\hat{\vec{\alpha}}$ and $\hat{\beta}$ are the Dirac matrices [37], and the scalar effective Kohn–Sham potential $v_s = v_{ext} + v_H + v_x + v_c$ is a sum of the external, Hartree, exchange, and correlation potentials. Each of these terms is a functional of the density $\rho(\vec{r}) = \sum_k^{occ} \phi_k^\dagger(\vec{r})\phi_k(\vec{r})$. In the REXX formalism, the *local* Kohn–Sham exchange potential $v_x(\vec{r})$ is determined exactly whereas the correlation potential is treated approximately. In the present work, we have employed the LDA for the latter throughout [38]. The Kohn–Sham exchange potential is determined by the following integral equation that must be solved simultaneously with equation (1) [17]:

$$\sum_k \int \mathrm{d}^3 r' \left(\phi_k^\dagger(\vec{r}')v_x(\vec{r}') - \frac{\delta E_x}{\delta \phi_k(\vec{r}')} \right) G_{sk}(\vec{r}', \vec{r})\phi_k(\vec{r}) + \text{c.c.} = 0 \tag{2}$$

with

$$G_{sk}(\vec{r}', \vec{r}) = \sum_{j \neq k} \frac{\phi_j(\vec{r}')\phi_j^\dagger(\vec{r})}{\epsilon_k - \epsilon_j} \tag{3}$$

where $G_{sk}(\vec{r}, \vec{r}')$ is the Green function of the relativistic Kohn–Sham equation (1) projected onto the subspace orthogonal to $\phi_k(\vec{r})$. The exchange energy functional is given explicitly by the relativistic Fock term in terms of the spinors $\phi_k(\vec{r})$.

The resulting REXX equations are valid for arbitrary open-shell systems with non-spherical electron density $\rho(\vec{r})$. In this form, however, they are not well adapted to the construction of transferable pseudopotentials. 'Good' pseudopotentials describe the interaction of extended valence states with a closed-shell ion core and should not depend on the detailed valence electron configuration that they are embedded into. Therefore, it is necessary to employ an appropriate symmetrization scheme that transforms the open-shell atoms into species with spherical symmetry, characterized by a spherical electronic density $\rho(r)$ and a spherical Kohn–Sham potential $v_s(r)$. Once this spherical symmetrization has been performed, the relativistic Kohn–Sham equation for the four-component spinors reduces to the following equation for the two-component radial spinor $\Psi_\alpha(r) := (f_\alpha(r), g_\alpha(r))^\top$ that we specify here for later reference:

$$\left(-c\mathrm{i}\sigma_2 \frac{\mathrm{d}}{\mathrm{d}r} + \frac{c\kappa}{r}\sigma_1 + \frac{c^2}{2}\sigma_3 + v_s(r) - \frac{c^2}{2} - \epsilon_\alpha \right)\Psi_\alpha(r) = 0 \tag{4}$$

where σ_k ($k = 1, 2, 3$) are 2×2 Pauli matrices [39], and $\kappa = l$ for the total-angular-momentum quantum number $j = j_- := l - 1/2$, and $\kappa = -(l + 1)$ for $j = j_+ := l + 1/2$. Here, l is the spatial angular momentum quantum number. The quantum numbers (nlj) of a given shell have been lumped together into a single Greek index α.

2.1. Spherical symmetrization for open-shell atoms

In this section, we show how to convert the relativistic Kohn–Sham equations for open-shell atoms with the exact exchange potential into rotationally invariant equations of the form of equation (4). In the LDA, the symmetrization of the one-electron density and the Kohn–Sham potential in open-shell atoms is achieved simply by occupying all open shells with fractional electron numbers. Since, by contrast, we treat the exchange interaction exactly, we must explicitly calculate the energy and density for different electron configurations and perform the averaging procedure over angular degrees of freedom subsequently. In this paper, we show that a 'generalized configuration-averaging principle' [40], that has previously been developed for hyper-Hartree–Fock–Dirac calculations, can be adapted effectively for the REXX formalism.

We consider an atom with a certain number of closed shells and one open (nl)-shell. The latter consists of two j-subshells j_- and j_+ containing $2l$ and $2l + 2$ orbitals, respectively. In the standard Slater averaging scheme [41, 42], one averages only over electron configurations within each j-subshell. By contrast, we average over *all* possible electronic configurations within the open (nl)-shell. This generalized configuration average has the advantage of yielding observables that no longer depend on atomic subshell indices. For an observable O, its generalized average is denoted by $\overline{O}$ and is evaluated in two steps. Let us consider the different possible distributions of the N electrons in the atom over the available subshells $\alpha = (nlj)$. Each distribution defines a sub-configuration M and may be characterized by the occupation numbers n_α^M for all subshells, including the closed shells. Let S_M be the statistical weight of this distribution and $\mathcal{N}_M$ the number of occupied subshells. In the first step, we compute the standard intra-subshell Slater average [41, 42] O_M of the observable O for each sub-configuration M. Then, in the second step, the average over all sub-configurations M yields the generalized average, $\overline{O} = \sum_M S_M O_M$. The first step yields the spherical electron density ρ_M and the exchange energy E_x^M for each configuration M in the forms

$$\rho_M(r) = \frac{1}{4\pi r^2} \sum_{\alpha=1}^{\mathcal{N}_M} n_\alpha^M \Psi_\alpha^\top(r) \Psi_\alpha(r) \tag{5}$$

$$E_x^M = -\frac{1}{2} \sum_{\alpha=1}^{\mathcal{N}_M} \int_0^\infty \mathrm{d}r \ \Psi_\alpha^\top(r) X_\alpha^M(r) \tag{6}$$

with

$$X_\alpha^M(r) = \frac{1}{2} \sum_{\beta=1}^{\mathcal{N}_M} \sum_L C_{\alpha\beta L} \Psi_\beta(r) \int_0^\infty \mathrm{d}r' \ \Psi_\beta^\top(r') \, \mathrm{v}_L(r, r') \Psi_\alpha(r') \tag{7}$$

where $\mathrm{v}_L(r, r') = e^2 \min(r, r')^L / \max(r, r')^{L+1}$ results from the expansion of the Coulomb potential $e^2/|\vec{r} - \vec{r}'|$ into spherical harmonics. The coefficients $C_{\alpha\beta L}$ may be derived from references [41, 42]. The index L in equation (7) ranges through all integers which simultaneously obey the following conditions: (i) $L + l_\alpha + l_\beta$ is even, (ii) $|l_\alpha - l_\beta| \leqslant L \leqslant l_\alpha + l_\beta$, and (iii) $|j_\alpha - j_\beta| \leqslant L \leqslant j_\alpha + j_\beta$ for the two subshells α and β. The total energy of the sub-configuration M is given by

$$E_{tot}^M = \sum_{\alpha=1}^{\mathcal{N}_M} n_\alpha^M \epsilon_\alpha - 4\pi \int_0^\infty \mathrm{d}r \ r^2 \rho_M(r) v_s(r) + 4\pi \int_0^\infty \mathrm{d}r \ r^2 \rho_M(r) V_{ext}(r)$$
$$+ \frac{4\pi}{2} \int_0^\infty \mathrm{d}r \ r^2 \rho_M(r) V_H(r) \ + E_x^M + E_c[\rho_M]. \tag{8}$$

Note that the one-particle energies ϵ_α and spinors Ψ_α do not depend on the sub-configuration M in these equations, since they fulfil equation (4) with the spherical effective potential $v_s(r)$

that is determined by the generalized average of the density $\overline{\rho}(r) = \sum_M S_M \rho_M(r)$:

$$v_s([\overline{\rho}]; r) = v_{ext}(r) + v_H([\overline{\rho}]; r) + v_x([\overline{\rho}]; r) + v_c([\overline{\rho}]; r). \tag{9}$$

In order to generate the exchange potential $v_x[\overline{\rho}]$ exactly, we insert the generalized configuration average of the exchange energy $\overline{E}_x$ together with the radial spinors into the integral equation (2). This leads to the following inhomogeneous linear Fredholm integral equation of the first kind for the radial exact exchange potential $v_x(r)$:

$$\int_0^\infty \mathrm{d}r' \, \overline{K}(r, r') v_x(r') = \overline{F}(r) \tag{10}$$

with the kernel $\overline{K}(r, r')$:

$$\overline{K}(r, r') = \sum_M S_M K_M(r, r') = \sum_M S_M \sum_{\alpha=1}^{\mathcal{N}_M} n_\alpha^M \Psi_\alpha^\top(r) \, G_\alpha(r, r') \Psi_\alpha(r') \tag{11}$$

and the inhomogeneity $\overline{F}(r)$:

$$\overline{F}(r) = \sum_M S_M \sum_{\alpha=1}^{\mathcal{N}_M} \int_0^\infty \mathrm{d}r' \, (X_\alpha^M)^\top(r') \, G_\alpha(r', r) \Psi_\alpha(r) + \Delta F(r) \tag{12}$$

with

$$\Delta F(r) = \sum_M S_M \int_0^\infty \mathrm{d}r' \, K_M(r, r') \Big[v_H([\rho_M]; r') + v_c([\rho_M]; r') - v_H([\overline{\rho}]; r') - v_c([\overline{\rho}]; r') \Big] \tag{13}$$

where $G_\alpha(r, r')$ are 2×2 matrices that obey the equations

$$\left(-c\mathrm{i}\sigma_2 \frac{\mathrm{d}}{\mathrm{d}r} + \frac{c\kappa}{r} \sigma_1 + \frac{c^2}{2} \sigma_3 + v_s(r) - \frac{c^2}{2} - \epsilon_\alpha \right) G_\alpha(r, r') = -\delta(r - r') + \Psi_\alpha(r) \Psi_\alpha^\top(r'). \tag{14}$$

Practical hints concerning the calculation of $G_\alpha(r, r')$ may be found in reference [15]. Note that the correction term $\Delta F(r)$ in equation (13) vanishes if the standard ROEP method for atoms is invoked [15] where only a single sub-configuration (with weight equal to 1) is used in calculating the spherical average.

The present generalized configuration-averaging procedure eliminates the explicit dependence of the Kohn–Sham potential on atomic subshells which is a prerequisite for constructing transferable pseudopotentials for solid-state applications as mentioned before. The independence of the Kohn–Sham potential of j also greatly facilitates taking the non-relativistic limit of the Dirac–KS equation (4). Note, however, that the wave functions and eigenvalues in equations (4) and (14) still depend on j via the factor κ; only the Kohn–Sham potential itself no longer depends on j.

Finally, we need to show that the present averaging procedure preserves the correct asymptotic behaviour of the exact exchange potential v_x. Following arguments analogous to those for the non-relativistic case [18, 43], it is easy to show that, for $r \to \infty$,

$$v_x(r) \to -\frac{\overline{X}_\tau(r)}{\overline{n}_\tau f_\tau(r)} \to -\frac{e^2}{r} \tag{15}$$

where f_τ denotes the large component of the one-electron orbital τ with the highest energy eigenvalue among the occupied orbitals (e.g., the $4p_{3/2}$ orbital in Ge). The quantity $\overline{X}_\tau$ is the generalized average of X_τ^M of equation (7) and $\overline{n}_\tau$ denotes the generalized average occupation number of this orbital. Therefore, the relativistic exact exchange Kohn–Sham (REXX-KS) potential has the correct asymptotic behaviour, in contrast to the relativistic local density approximation (RLDA) KS potential. The latter tends to zero exponentially.

3. Relativistic exact exchange pseudopotentials

The atomic REXX equations in the previous section form the starting point for generating norm-conserving pseudopotentials. Since the Kohn–Sham potential correctly tends to $-e^2/r$ asymptotically in the REXX method, one eliminates the following ambiguity that plagues the LDA. The construction of pseudopotentials often requires one to include states that are unoccupied in the free atom (such as the 4d states in Ga, Ge, or As, for example). In LDA or GGA, the unoccupied states are unbound in most cases and must be converted to bound states either by using ions as reference systems [26] or by normalizing the unbound states to some suitably chosen radius (Hamann's procedure [28]). Both approaches clearly limit the transferability of the pseudopotentials generated. By contrast, the REXX-KS potential v_s supports bound unoccupied states. This is illustrated for the Kr atom in figure 1. This important property of v_s allows one to treat the occupied and unoccupied states on an equal footing.
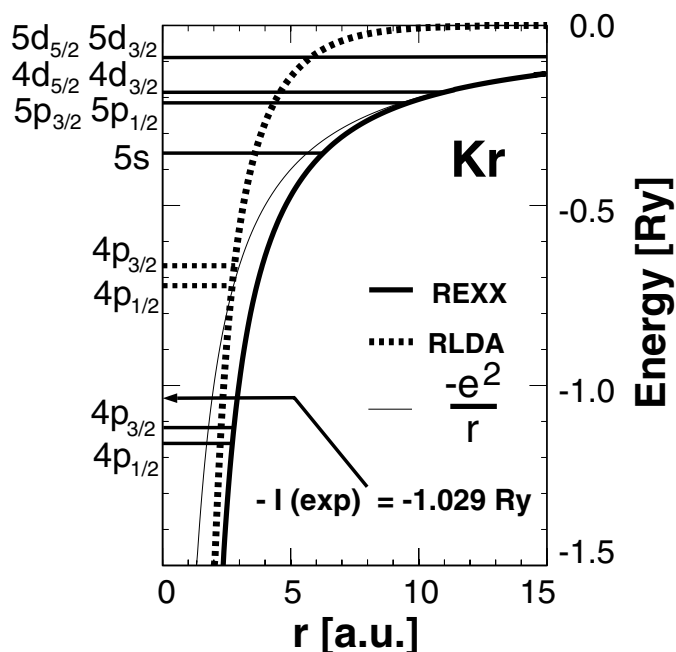

Figure 1. The effective Kohn–Sham potential in rydbergs of the neutral krypton atom in the relativistic LDA (RLDA, dotted line) and relativistic exact-exchange (REXX, continuous line) methods, as functions of the distance in atomic units. For comparison, the thin line shows the Coulomb potential. The energies of the highest occupied (4p$_{3/2}$, 4p$_{1/2}$) valence states and several unoccupied states are also depicted. In RLDA, only the 4p states are shown since all unoccupied states are unbound. The arrow indicates the experimental value of the ionization energy I.

In the first step of calculating pseudopotentials, neutral atomic pseudopotentials are generated in close analogy to the standard method of Troullier and Martins [27]. The atomic all-electron calculations are performed in the generalized configuration average corresponding to the ground state of the neutral atom. This yields the one-electron energies ϵ_{nlj} and radial spinors $(f_{nlj}, g_{nlj})^\top$. In the next step, we construct the pseudo-wave functions φ_{lj} for the valence electrons. Beyond the cut-off radius r_c^l we set them equal to the large component of the corresponding all-electron wave function, $\varphi_{lj}^{ps}(r) = f_{lj}(r)$ and nodeless for shorter distances, following reference [27]. In addition, we require the norm of φ_{lj}^{ps}, integrated up to

r_c^l, to be equal to the norm of the corresponding two-component radial spinor. The neglect of the small component outside the core leads to a negligible error of the order of α^2 [44], where $\alpha \approx 1/137$ is the fine-structure constant. Note that the index n has been dropped here, since the orbital quantum numbers (lj) uniquely determine the pseudo-valence states. The pseudo-wave functions φ_{lj}^{ps} obey the pseudopotential Schrödinger equation with eigenvalues equal to the l- and j-dependent all-electron energies of the valence electrons:

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{lj}^{ps}(r) - \epsilon_{lj} \right) \phi_{lj}^{ps}(r) = 0. \tag{16}$$

In the next step, the *screened* pseudopotential with components $V_{lj}^{ps}(r)$ is obtained by inverting this equation [27]. Note that it is this inversion that causes the pseudopotential to be lj-dependent despite the fact that the all-electron Kohn–Sham potential is lj-independent. The remaining task is to determine the ionic pseudopotential V^{ion}, i.e. the potential of a single valence electron in the field of the atomic core. It needs to be extracted from V_{lj}^{ps} through elimination of the electron–electron interaction between the pseudo-electrons. This so-called unscreening procedure turns out to be the major non-trivial step in the REXX scheme and is discussed in the next section.

3.1. The unscreening procedure for the exact exchange pseudopotentials

In the neutral pseudo-atom, the pseudo-electrons move in an effective potential that may be written as a sum of the ionic pseudopotential V^{ion} and a screening potential V_{screen}^{ps}:

$$V_{lj}^{ps}(r) = V_{lj}^{ion}(r) + V_{screen}^{ps}([\rho^{ps}]; r) \tag{17}$$

$$V_{screen}^{ps}([\rho^{ps}]; r) = v_H^{ps}([\rho^{ps}]; r) + v_x^{ps}([\rho^{ps}]; r) + v_c^{ps}([\rho^{ps}]; r). \tag{18}$$

The potential V_{screen}^{ps} is a functional of the pseudo-electron density ρ^{ps} and contains the same density functionals as the ones entering the all-electron calculation. In the LDA (or GGA) scheme, the Hartree potential v_H, the correlation potential v_c, as well as the exchange potential v_x are known explicit functions of the pseudo-electron density. In such a case, the unscreening of the atomic pseudopotentials can be performed straightforwardly by subtracting V_{screen}^{ps} from V_{lj}^{ps} [26, 27]. Similarly, the ionic pseudopotentials in the Hartree–Fock method [30–32] can be obtained simply by subtracting from V^{ps} the Coulomb and non-local exchange contribution due to the valence electrons. This contribution is an explicit known functional of the pseudo-orbitals and has the same form as its all-electron counterpart because the Hartree–Fock Coulomb and exchange potential consists of additive contributions of all occupied orbitals. Similar arguments apply to other pseudopotential methods where the explicit dependence of the screening potential on the orbitals is known, such as the self-interaction-corrected LDA (SIC-LDA) [38]. *In the REXX formalism, on the other hand, these standard methods of unscreening are not applicable, since neither the explicit dependence of v_x on the density nor that on the orbitals is known.* We have therefore developed an alternative method to construct V_{lj}^{ion} that does not require the explicit knowledge of v_x^{ps} as a function of ρ or the orbitals.

We start by determining v_H^{ps} and v_c^{ps}. To this end we compute the generalized averaged pseudo-electron density ρ^{ps} analogously to the all-electron density by a generalized configuration averaging, which reads

$$\rho^{ps}(r) = \sum_M S_M \rho_m^{ps}(r) = \sum_M S_M \sum n_{lj}^M (\varphi_{lj}^{ps}(r))^2 \tag{19}$$

where n_{lj}^M are the occupation numbers of the orbitals lj in different sub-configurations M as defined in section 2. This procedure guarantees that $\rho^{ps}(r) = \overline{\rho}(r)$ for $r > r_c$, where

$r_c = \max_l(r_c^l)$. Since the Hartree and LDA or GGA correlation pseudopotentials in the screening potential are known functionals of the density, they can be calculated directly—in contrast to v_x^{ps}. In order to determine the latter within the REXX scheme, we again follow the procedure of calculating v_x for an atom (section 2) but now apply it to a pseudo-atom. In particular, the integral equation for v_x^{ps} reads

$$\int_0^\infty dr' \, K^{ps}(r, r') v_x^{ps}(r') = F^{ps}(r) \tag{20}$$

where the kernel $K^{ps}(r, r')$ and the inhomogeneity $F^{ps}(r)$ are defined analogously to their all-electron counterparts. To be precise, the pseudo-wave functions φ_{lj}^{ps} are assumed to correspond to the major components of the radial spinors, and we obtain $K^{ps}(r, r')$ and $F^{ps}(r)$ from equations (11) and (12) by neglecting the minor components. In accord with the other steps in constructing valence pseudopotentials, this introduces errors of the order of $(1/137)^2$. The pseudo-Green function in the kernel $K^{ps}(r, r')$ obeys a Schrödinger-type equation of the form given in equation (14) with v_s and Ψ_α replaced by V_{lj}^{ps} and φ_{lj}^{ps}, respectively.

Thus, this unscreening procedure does not require the solution of an entirely different set of equations but can be carried out with basically the same equations as are used in the all-electron problem. This method can therefore be implemented easily. An alternative way to solve or, rather, to avoid the unscreening procedure altogether is to generate the pseudopotential from all-electron calculations for positive ions with only a single valence electron. This approach has been used with some success in the Hartree–Fock scheme before [23, 45] but not in LDA, where these pseudopotentials are known to reproduce neutral atoms and atoms in solids rather poorly [23]. We have nevertheless tested this procedure within the REXX scheme for Si, Ga, and Ge and obtained a fairly accurate pseudopotential for Si, but not for the heavier atoms Ga and Ge.

We note that this unscreening procedure can easily be generalized to construct consistent pseudopotentials for the case of orbital-dependent exchange–correlation functionals, such as the meta-GGA functionals [46]. These functionals are currently considered to be a particularly promising development in the DFT.

Since solid-state calculations are often performed scalar relativistically, it is useful to define the spin-averaged pseudopotential [26]:

$$\overline{V}_l^{ion}(r) = \frac{l+1}{2l+1} V_{l,l+1/2}^{ion}(r) + \frac{l}{2l+1} V_{l,l-1/2}^{ion}(r). \tag{21}$$

Whenever we refer to results involving this potential, we will refer to the EXX (rather than REXX) method.

3.2. Intermediate-range tails of exact exchange pseudopotentials

Both the relativistic REXX and the scalar relativistic ionic EXX pseudopotential $\overline{V}_l^{ion}(r)$ asymptotically approach the correct limit $-Z_v e^2/r$, with Z_v being the number of valence electrons. However, they deviate from the asymptotic limit at intermediate distances $r > r_c$, as can be seen in figure 2. While the magnitude of this deviation is small, such a tail nevertheless limits the transferability of a pseudopotential and is undesirable in solid-state calculations.

The deviation from $-Z_v e^2/r$ for intermediate distances $r > r_c$ in the ionic EXX pseudopotential originates in the difference between the all-electron potential V_{screen} and the pseudo-electron screening potential V_{screen}^{ps} outside the core region (cf. equations (17) and (18)) [31]. In the Hartree–Fock method, both the all-electron and the pseudo-electron screening potentials are non-local. This non-locality transports the gross differences between the all-electron wave functions and pseudo-wave functions within the core region to the area outside

the core, even though the real and pseudo-wave functions themselves are equal for $r > r_c$. This effect leads to large long-range tails in Hartree–Fock pseudopotentials [31, 32, 47].
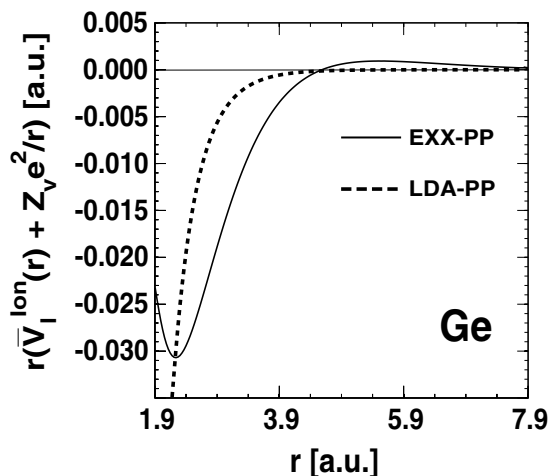

Figure 2. Deviations of the EXX and LDA pseudopotentials for Ge from their asymptotic limit outside the cut-off radius $r_c = 1.9$ (in atomic units). The potentials have been multiplied by the distance r and all quantities are given in atomic units. The results are shown without the tail cut-off.

In the LDA, on the other hand, the locality of both V_{screen} and V_{screen}^{ps} guarantees that the ionic pseudopotential $\overline{V}_l^{ion}$ reaches $-Z_v e^2/r$ very quickly outside the core radius. Nevertheless, a small deviation from $-Z_v e^2/r$ for $r > r_c$ occurs even in the LDA as can be deduced from figure 2. This is due to the neglect of the minor component of the all-electron wave function for $r > r_c$ in the pseudopotential construction [27].

In the EXX method, the exact exchange potential is local, but the integral equations that determine this exchange potential for the atom (equation (10)) and for the pseudo-atom (equation (20)) are of non-local character. In particular, the non-local kernels K in equations (10) and (20) differ inside the core. Therefore, the intermediate-range pseudopotential tails are larger in the EXX method than in the LDA scheme but significantly smaller than in the Hartree–Fock one. We note that similar effects have been previously discussed for pseudopotentials that are based on the KLI approximation of the OEP method [34, 35]. In fact, we followed the procedure of reference [34] and smoothly cut off the tails beyond a certain ionic radius r_0 that is set to approximately half bond length ($r_0 \geqslant 2.0\, a_B$) of a typical semiconductor. Fortunately, the cohesive and electronic properties of semiconductors are insensitive to the choice of r_0 [11].

Finally, we would like to make two remarks. First, the present relativistic and non-relativistic EXX pseudopotentials can easily be cast into the separable Kleinman–Bylander form by following the standard procedures [48, 49]. Secondly, the Kohn–Sham formalism is strictly valid only for local external potentials. In principle, pseudopotentials violate this condition since they contain an orbital-dependent projection operator—be it the LDA, GGA, or EXX. Nevertheless, the generation of pseudopotentials can be rigorously justified within the framework of the generalized Kohn–Sham scheme [50].

4. Results and properties of REXX pseudopotentials

With the procedure described in section 3, we have generated REXX pseudopotentials for several atoms. Here, we present results for some typical examples, and compare them with standard LDA pseudopotentials. We also discuss results for band structures in semiconductors.

First, we compare REXX and RLDA results for atomic all-electron properties. Table 1 summarizes results of RLDA and REXX calculations for the highest occupied Kohn–Sham orbital energies, the first and fourfold ionization energies of C, Si, and Ge atoms, and compares these results with experiment. Most strikingly, the moduli of the highest occupied orbital energy and the ionization energy agree with one another almost perfectly in the REXX method, in accord with the exact Kohn–Sham theory [51]. By contrast, these quantities differ by almost a factor of two in the RLDA, as is well known. In addition, the REXX ionization energies are in much better agreement with experiment. We have also included pseudopotential results in table 1 in order to show that the all-electron properties are faithfully reproduced by the present pseudopotential method.

Table 1. Atomic and pseudopotential ionization energies for C, Si, and Ge calculated within the REXX and RLDA methods and compared to experiment. The LDA correlation energy functional has been used in both cases. ϵ_I is the one-particle energy of the highest occupied orbital, whereas E_I and E_{IV} denote the first and the fourfold ionization energies, respectively. The RLDA and REXX pseudopotentials have been generated with cut-off radii r_c (for all angular momentum components) equal to 1.5, 2.2, and 1.9 a_B, for C, Si, and Ge, respectively. All energies are in rydbergs and the experimental values are from reference [61].

| Element | Energy | RLDA | | REXX | | |
		Atom	Pseudo-atom	Atom	Pseudo-atom	Experiment
C	$-\epsilon_I$	0.3982	0.3982	0.9061	0.90350	0.8281
	E_I	0.8077	0.7956	0.8293	0.8173	0.8281
	E_{IV}	10.7747	10.6950	10.9991	10.9982	10.8793
Si	$-\epsilon_I$	0.3057	0.3057	0.6364	0.6381	0.5991
	E_I	0.5755	0.5697	0.6016	0.6015	0.5991
	E_{IV}	7.5821	7.5062	7.6613	7.6421	7.5780
Ge	$-\epsilon_I$	0.2933	0.2909	0.6103	0.6035	0.5796
	E_I	0.5615	0.5557	0.5836	0.5847	0.5796
	E_{IV}	7.7277	7.5966	7.6109	7.6268	7.6259

The basic assumption underlying the pseudopotential concept is the frozen-core approximation [52]. In order to investigate its validity, we have calculated the Kohn–Sham energies for core electrons of atoms in two different valence configurations. Figure 3 depicts the differences in the core energies of atomic Si and Ge, when the valence electrons are in the s^2p^2 or sp^3 configuration. These core energy differences are seen to be systematically smallest in the REXX scheme and largest in the Dirac–Hartree–Fock [53] (DHF) method. Thus, the REXX one-particle energies depend somewhat more weakly on the atomic valence state configuration than the RLDA or Hartree–Fock energies.

The angular momentum components of the scalar relativistic EXX pseudopotential and the corresponding components of the spin–orbit pseudopotential [26] for Ge are depicted in figure 4 and compared to the LDA results. The same cut-off radius $r_c = 1.9$ a_B has been used in both methods and for all angular momentum components. We note that the 4d state that produces the d component of the pseudopotential is bound in the EXX method, in contrast to the situation in the LDA. The more tightly bound core charge in the EXX method screens the nucleus more
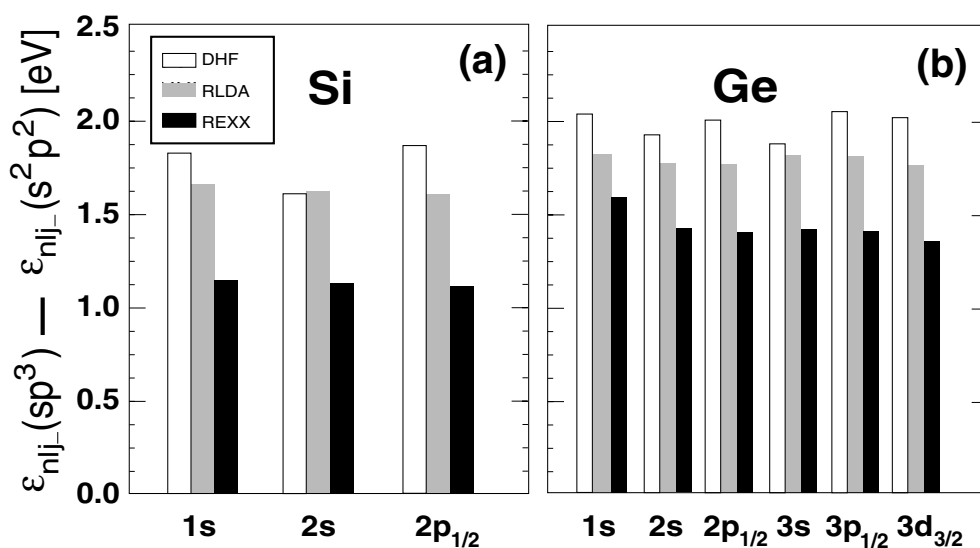
Figure 3. Differences between the core orbital energies in eV, computed in the sp^3 and the s^2p^2 configuration of the valence electrons. The calculations are performed for (a) Si and (b) Ge, within the Dirac–Hartree–Fock (DHF), the relativistic LDA (RLDA), and the present relativistic exact-exchange (REXX) method. The results for the nlj_+ and nlj_- orbital states are identical to within 0.01 eV so only the latter are shown.

effectively and results in a less attractive effective potential for the valence electrons, compared to the LDA. Similar results have been found in the self-interaction-corrected LDA [54].

The difference between the radial logarithmic derivatives of the all-electron wave functions and pseudo-wave functions is another widely used measure for the transferability of a pseudopotential. Figure 5 depicts these differences for several atoms, as calculated within the REXX and RLDA, respectively. Once more, these deviations are seen to be systematically smaller in the REXX, indicating superior transferability. We have checked that this trend depends very weakly on the chosen cut-off radius as well as on the specific position at which the derivatives are computed.

In the pseudopotential calculations that have been performed for figure 5, the semicore 3d states are treated as part of the frozen core. An important difference between the REXX and RLDA calculations is the so-called non-linear core correction (NCC) [55]. We have applied the NCC in the latter case to account for the non-linearity of the LDA exchange and correlation potentials in the core and valence densities. The inclusion of this non-linearity is known to be essential for obtaining transferable LDA pseudopotentials [11, 56]. In the Hartree–Fock method, on the other hand, the density matrix enters the non-local exchange potential linearly which implies the NCC to be strictly zero. While this does not hold for the REXX method, we believe for the following reasons that non-linear core corrections are small in the latter case nevertheless. First of all, we have already seen the REXX pseudopotentials to show better transferability than the LDA pseudopotentials. Secondly, the cohesive properties obtained with the REXX pseudopotentials [11] resemble closely those obtained with the Hartree–Fock pseudopotentials [57]. We have therefore neglected the NCC except in the correlation potential where its effect is marginal.

We now turn to applications of the EXX pseudopotentials to solid-state calculations and show that the exact elimination of the unphysical self-interaction significantly improves
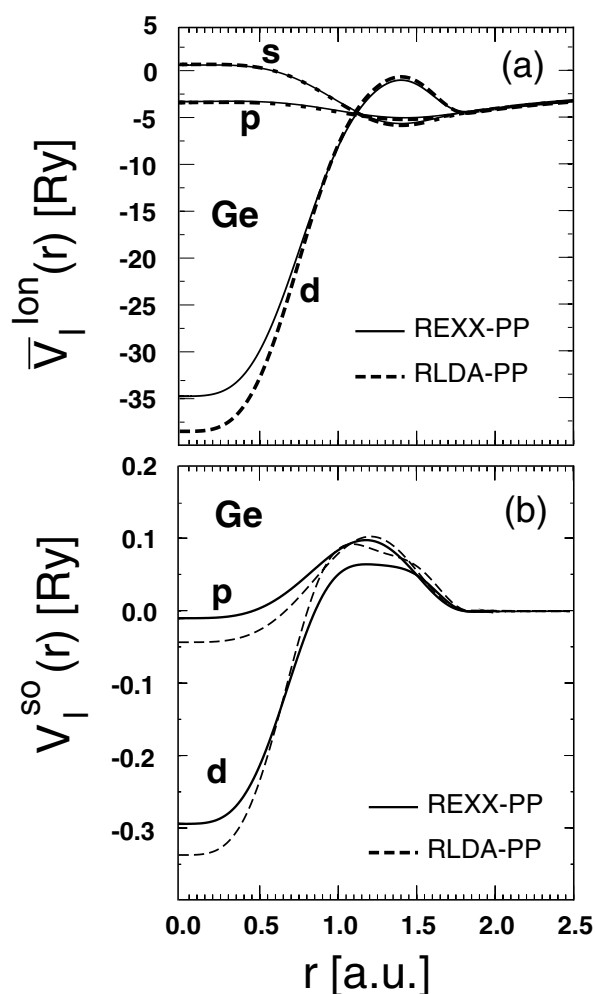
Figure 4. (a) The angular momentum components of the scalar relativistic ionic pseudopotentials and (b) the corresponding components of the spin–orbit pseudopotentials for Ge within the REXX and RLDA methods. The potentials are given in rydbergs and the radial distance r in atomic units. The same cut-off radius $r_c = 1.9$ in atomic units has been used for all angular momentum components in both types of pseudopotential.

electronic spectra for solids as compared to the LDA.

It has been established that the failure of the LDA to predict an indirect band gap of bulk diamond-structure Ge is related to the relative overbinding of the 4s states with respect to the 4p states in atomic Ge [58,59]. The low energy of the 4s states favours a direct band gap at the centre of the Brillouin zone as is consistently found in LDA calculations (see figure 6) [54,59]. In the EXX method, on the other hand, we find the orbital energy difference $E(4s) - E(4p)$ in atomic Ge to be 150 meV smaller than in the LDA, which amounts to a corresponding rise of the more localized 4s state. When we now perform a EXX pseudopotential plane-wave calculation for bulk Ge, following the method of reference [11], we obtain the correct energetic ordering of the lowest energy gaps in bulk Ge, independently of whether we use the LDA or EXX functional for the valence exchange potential in the solid (see figure 6). A similar result
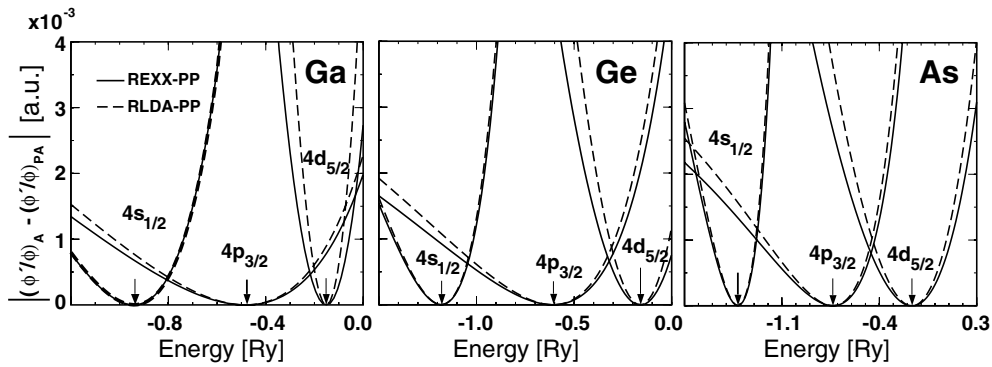
Figure 5. Deviations between pseudo-atomic (PA) and all-electron radial logarithmic derivatives (A) in atomic units, as calculated in the REXX and RLDA methods for the atoms Ga, Ge, and As. The arrows mark the energies in rydbergs of the all-electron REXX orbital states. For better comparison, the RLDA curves for each orbital lj have been shifted horizontally in such a way that they coincide with the REXX curves at the marked energies. The same pseudopotential cut-off radius r_c (equal to 2.2, 1.9, and 2.2 for Ga, Ge, and As, respectively) has been used for all angular momentum components. The radial logarithmic derivatives are computed at $r = 2.4$ atomic units.
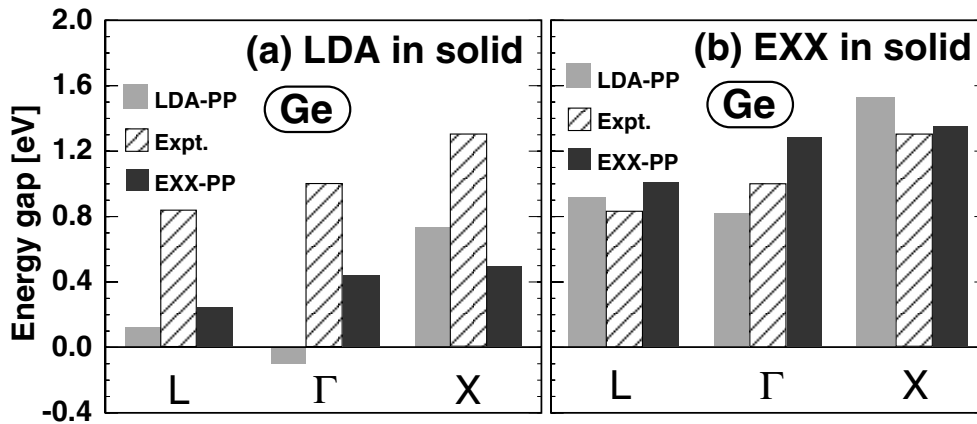

Figure 6. (a) Energy gaps in eV at the high-symmetry $\vec{k}$-points L, Γ, and X in bulk Ge, as calculated with the LDA and EXX pseudopotentials and compared to experimental values taken from reference [62]. In (a), the LDA is used for the valence electrons in solids. In (b), the EXX density functional for the valence electrons in the solid is employed.

has recently been found on the basis of self-interaction-corrected LDA pseudopotentials [54]. These findings confirm that band gaps depend crucially on an accurate modelling of the atomic core potentials [58].

As a further stringent test, we have computed EXX pseudopotentials for a series of elements with filled d shells which have been treated as valence states. On the basis of these EXX pseudopotentials, we have calculated the electronic structure of zinc-blende ZnO, ZnS, ZnSe, and CdSe employing the plane-wave method and treating the valence electrons in the solid within the LDA [60]. If the LDA is used both for the construction of the ionic pseudopotentials as well as for the valence electrons in the solid, the discrepancy between the theoretical and experimental centre of gravity of the d bands is 2.4, 2.6, 2.6, 2.6 eV for

ZnO, ZnS, ZnSe, and CdSe, respectively. If, by contrast, the EXX ionic pseudopotentials are combined with an LDA treatment of the valence electrons, the discrepancy between theory and experiment diminishes by approximately 70%. Specifically, the remaining difference between the predicted and measured average position of the d bands amounts to 0.6, 1.6, 0.7, 0.8 eV for the same sequence of materials. These results are consistent with analogous trends in the atomic eigenvalues. In neutral atomic Zn, for example, the REXX and RLDA calculations yield energies of -15.47 eV and -10.30 eV, respectively, for the $3d_{5/2}$ orbital.

We expect further improvements if the EXX method is used consistently for all electrons, in accord with what we have found previously for other semiconductors [11].

5. Conclusions

We have presented a method for constructing norm-conserving pseudopotentials within the relativistic exact-exchange Kohn–Sham scheme. A generalized averaging has been employed for open-shell atoms. Most importantly, we have developed a rigorous 'unscreening' method for calculating ionic pseudopotentials that does not require the knowledge of the explicit dependence of the exchange or correlation functional on the valence electron density. In contrast to LDA, the EXX Kohn–Sham potential possesses the correct asymptotic limit and consequently yields bound unoccupied orbitals in atoms. Thus, all angular momentum components of the EXX pseudopotential, irrespective of their occupancy in the neutral atom, can be treated on an equal footing. We have been able to demonstrate that the ionic REXX pseudopotentials are only weakly dependent on the valence configuration and therefore show a better transferability than their LDA counterparts. Since the EXX method eliminates the self-repulsion between electrons, it corrects some typical LDA errors. We have found systematic improvements for bulk Ge and some II–VI semiconductors with filled d bands by employing EXX pseudopotentials, even if the valence electrons are still modelled by the LDA method.

Acknowledgments

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