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Scalar-relativistic spline augmented plane-wave method using a Douglas Kroll transformation in coordinate representation

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Abstract. A scalar-relativistic Hamiltonian, which contains all relativistic corrections up to second order in the fine structure constant, is derived with coordinate representation of the first order Douglas Kroll transformation. In addition to the correction of second order in the fine structure constant, this Hamiltonian contains the exact relativistic kinetic energy as well as the exact relativistic potential correction up to terms linear in the external potential. Based on this Hamiltonian, we develop a scalar-relativistic extension of the Spline Augmented Plane-Wave method, and show that the matrix elements with the new operator can be evaluated elegantly when using an alternative basis of Spline functions. As a first test we investigate solid silver and gold. By comparing the energies of the core states with the solutions of the radial Dirac equation we find that the stabilization of the *s* levels are slightly overestimated. Even smaller deviations from the Dirac energies are found for higher angular momentum. By comparing the valence band structure with the results for other scalar-relativistic operators, which can be used in a variational context, we find the new operator superior in all aspects: *s*-type bands are reproduced quite well, and again bands which are dominated by higher angular momenta behave even better. On the contrary, the results obtained with simpler scalar-relativistic Hamiltonians are unsatisfactory.

PACS. 71.15.Rf Relativistic effects – 71.15.Ap Plane-wave methods (including augmented plane-wave method)

1 Introduction

The relativistic dynamic of an electron under the influence of an external potential is from first principles described by the Dirac equation for a four component spinor. In crystals early attempts to solve Diracs equation are due to Loucks [1] and Hofmann and Bross [2]. The first self consistent solution was obtained by Christensen and Seraphin [3] with the aid of Slaters augmented plane-wave (APW) method [4]. The work of Christensen and Seraphin was continued later in the framework of the linearized augmented plane-wave (LAPW) scheme by MacDonald *et al.* [5] as well as by Schiekel [6] with the modified augmented plane-wave (MAPW) method. Both latter methods use linear variational techniques. In the meantime, relativistic band structure schemes have been implemented on the basis of various linear and non-linear techniques (see *e.g.* Refs. [7,8]). It may be generally verified, that any numerical treatment of the crystal Dirac equation requires complex arithmetic, even though the crystal has a center of inversion. For this reason the numerical effort for a relativistic band calculation is enlarged by a factor 8^3 with respect to a non relativistic one, in case when all eigensolutions are needed. This enormous increase of computation time is in contradiction to the fact that in solids the positron part of the single-particle spectrum is not relevant, *e.g.* within a self-consistent calculation. The reduction of the four component Dirac problem to a two component theory by eliminating the positron degrees of freedom will reduce the numerical work already by a factor of 8. By further approximations two additional factors of 8 become available: The first one by neglecting the spin degrees of freedom, which is called scalar-relativistic approximation. The second one by reduction to real arithmetic in the case of a center of inversion. The standard technique to accomplish the first reduction is the series of Foldy Wouthuysen (FW) transformations [9] yielding an expansion of the Dirac Hamiltonian into powers of the fine-structure constant γ. Including terms up to second order this operator reads in absence of a magnetic field

$$\mathsf{H}_{\mathrm{FW}} = \vec{\mathsf{p}}^{\,2} - \frac{\gamma^2}{4}\vec{\mathsf{p}}^{\,4} + V(\vec{r}) + \frac{\gamma^2}{8}(\Delta V(\vec{r})) + \frac{\gamma^2}{4}\vec{\boldsymbol{\sigma}}\cdot\left[\mathrm{grad}(V)\times\vec{\mathsf{p}}\right]. \tag{1}$$

(We use Rydberg atomic units, *i.e.* $m_0 = 1/2$, $\hbar = 1$, $e^2 = 2$, and $c = 2/\gamma = 2 \cdot 137.035968$. Length and energies are given in Bohr radii and in Rydberg, respectively.) In (1) the first two terms describe the kinetic energy including the mass velocity term, the second and the third

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term give potential energy including the Darwin term [10], while the last term describes the spin-orbit interaction. Equation (1) is generally accepted since it obeys a structure that is quite close to the Pauli equation. Additionally, the corrections to the Schrödinger equation included in (1) lead to the correct energy shift when first order perturbation theory is applied [11,12]. The energy shifts become wrong, however, in second and higher orders of γ. Also the standard interpretation of the terms in (1) leads to conceptual inconsistencies [13]. Moreover, the analytic behavior of H_{FW} prohibits its use within an all-electron variational framework for the following reasons: First of all, the mass velocity correction $-\gamma^2/4p^4$ to the kinetic energy in (1) is not bounded from below. Consequently, the kinetic energy in (1) becomes negative for $p > 2\gamma^{-1}$. Therefore, when increasing the freedom of an arbitrary Ritz ansatz the eigenvalues always tend towards minus infinity. The critical limit $p > 2\gamma^{-1}$ seems to be relevant for core states only, since the kinetic energies of valence electrons are usually less than $4\gamma^{-2}$ by at least three orders of magnitude. Nevertheless, valence states are effected by the requirement of mutual orthogonality. Secondly, in presence of a Coulomb potential, the Darwin correction to the scalar potential contains contributions $\propto Z\delta(\vec{r})$. This singularity is much weaker than the one of the mass velocity term, but for a complete basis-set the spectrum of the Darwin term is not bounded from below, too. To put it bluntly, the use of (1) in an all-electron variational framework generates almost random numbers, depending only on the freedom of the Ritz ansatz used. Despite theses objections, this operator can successfully be used within the framework of pseudo-potentials. In this case the aforementioned deficiencies of H_{FW} are veiled since the momentum of electrons is restricted to small values and the potential is constructed to be finite at the atomic sites. More recent pseudo-potential calculations, however, incorporate scalar-relativistic effects by the construction of the pseudo-potential instead, and retain the spin-orbit part of (1) only [14]. The problem of negative kinetic energies of (1) was circumvented also in all-electron calculations by Reinisch and Bross [15,16] who developed a quasi-relativistic approximation which uses the first order FW transformation for the valence electrons only while the core electrons are treated with the Dirac equation. With this concept, Reinisch and Bross obtained a very reasonable description of the band structure and of Fermi surface properties [16], as well as of the Compton profile [15] of gold. However, the ground-state total energy showed a strong spurious dependence on the position of the cut between core and valence electrons as well as on the basis-set. A rigorous application of the FW operator to all valence electrons lead to a lattice-constant which was 12.9% too small and to a bulk modulus that was too large by a factor of 5 (Ref. [16]). Without being based on a decoupling procedure so-called scalar-relativistic approximations on the radial part of the Dirac equation were developed independently by Koelling and Harmon [17], by Gollisch and Fritsche [18], and by Takeda [19]. These techniques can, however, not be cast into a linear variational form, since the resulting radial differential equation is not linear in the energy. Therefore, we will give no further discussion of band-schemes based on these techniques here, but discuss this approximation for core states only. Additionally, these scalar-relativistic techniques may contain uncontrolled approximations *e.g.* if the contribution of the small components to the charge density is neglected [19]. Returning to the Dirac equation we note that since the work of Foldy and Wouthuysen mainly two alternative decoupling procedures were suggested: Within a variational framework the scheme of Kurşunoğlu [20] is not very useful since it involves higher time derivatives than the first. The corresponding stationary equation becomes non-liner in the energy. An iterative decoupling procedure for the Dirac Hamiltonian was proposed by Douglas and Kroll (DK) in momentum representation and was applied successfully in a calculation of the fine-structure of Helium [21]. When compared with the FW transformations, the DK transformations have two advantages: First of all, the operators which appear during the transformations can be used in a variational framework. Secondly, they always contain the correct relativistic energy momentum relation after the first step of the transformation, already. The DK transformations, however, are restricted originally to momentum representation, while an all-electron band calculation can be performed sufficiently only in coordinate representation. In the meantime the DK transformations was implemented in quantum chemical calculations of atoms and small molecules by Hess and coworkers (see *e.g.* Refs. [22–26]) together with a basis of Gaussian orbitals. This basis allows to switch easily from coordinate representation to momentum representation. Similar schemes based on the DK transformation in momentum representation have also been applied by other authors [27–35]. Motivated by this success of the DK transformation in momentum representation, we develop a scalar-relativistic band-structure method based on the first-order DK transformation. In contrast to the above-mentioned schemes, the DK transformation is carried out in coordinate representation. This method is implemented in the framework of the spline augmented plane-wave (SAPW) [36,37] method and tested in the case of solid silver and gold. Following this plan, the remainder of the paper is organized as follows: In Section 2 we transfer the technique of Douglas and Kroll to coordinate representation and show how the matrix-elements of the resulting operators can be evaluated using transformed SAPW basis. The results obtained with this technique are presented and discussed in Section 3.

2 General theory

2.1 The Douglas-Kroll transformations and the scalar approximation

The Dirac Hamiltonian for a particle in an external field caused by an electrostatic potential

$$\mathsf{H} = c\vec{\boldsymbol{\alpha}} \cdot \vec{\mathsf{p}} + m_0 c^2 \boldsymbol{\beta} + \mathcal{V}(\vec{r}), \tag{2}$$

($\vec{\boldsymbol{\alpha}}$, $\boldsymbol{\beta}$ and $\mathcal{V}(\vec{r})$ are the Dirac and potential matrices, *i.e.* in standard representation $\mathcal{V}(\vec{r}) = \mathbf{1}\;V(\vec{r})$, and we temporarily included m_0 and c for clarity) is decoupled by a series of unitary transformations which was originally proposed by Douglas and Kroll [21] in momentum representation. Thereby, in contrast to the FW transformations [9] the odd terms, which mix up the large and small components, are removed in all orders of the fine-structure constant γ at each step of a series of unitary transformations. As a result, the DK transformations give an expansion of the even operators into powers of the external electrostatic potential $\mathcal{V}(\vec{r})$ instead of an expansion into powers of fine-structure constant γ. In a preliminary step the kinetic energy and the interaction linear in $\mathcal{V}$ are brought into even form by transforming (2) with the solutions of the free-particle Dirac equation

$$\mathsf{U}_0 = N(\mathsf{p})\left(1+\frac{c(\boldsymbol{\beta}\;\vec{\boldsymbol{\alpha}}\;)\cdot\,\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2}\right), \tag{3}$$

where we have introduced the abbreviations

$$E(\mathsf{p}) = \sqrt{m_0^2c^4 + c^2\mathsf{p}^2} \tag{4}$$

$$N(\mathsf{p}) = \sqrt{\frac{E(\mathsf{p})+m_oc^2}{2E(\mathsf{p})}}. \tag{5}$$

In equations (3-5) and henceforth all functions of the spatial components of the momentum $\vec{\mathsf{p}}$ must be regarded to be operators, *e.g.* $E(\mathsf{p}) = \sqrt{m_0^2c^4 - c^2\Delta}$. After this preliminary transformation the Dirac Hamiltonian becomes

$$\mathsf{H}^{(1)} = \mathsf{U}_0\mathsf{H}\mathsf{U}_0^{-1} = \boldsymbol{\beta}\;E(\mathsf{p}) + \mathsf{V}^{(1)} + \mathsf{R}^{(1)}, \tag{6}$$

where $\mathsf{V}^{(1)}$ and $\mathsf{R}^{(1)}$, respectively, denote the first order even and odd potential operators and are given by

$$\begin{aligned}\mathsf{V}^{(1)} &= N(\mathsf{p})\mathcal{V}(\vec{r})N(\mathsf{p})\\ &\quad + N(\mathsf{p})\frac{c\vec{\boldsymbol{\alpha}}\cdot\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2}\,\mathcal{V}(\vec{r})\,\frac{c\vec{\boldsymbol{\alpha}}\cdot\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2}N(\mathsf{p})\end{aligned} \tag{7}$$

$$\mathsf{R}^{(1)} = N(\mathsf{p})\left(c\boldsymbol{\beta}\;\vec{\boldsymbol{\alpha}}\;\cdot\left[\frac{\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2},\mathcal{V}(\vec{r})\right]\right)N(\mathsf{p}). \tag{8}$$

By expanding the even operator $\mathsf{V}^{(1)}$ into powers of the fine-structure constant one finds up to order γ^2

$$N(\mathsf{p})\mathcal{V}N(\mathsf{p}) = \mathcal{V} - \frac{\gamma^2}{8}\left(\mathsf{p}^2\mathcal{V} + \mathcal{V}\mathsf{p}^2\right) + \ldots \tag{9}$$

and

$$N(\mathsf{p})\frac{c\vec{\boldsymbol{\alpha}}\cdot\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2}\mathcal{V}\frac{c\vec{\boldsymbol{\alpha}}\cdot\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2}N(\mathsf{p}) = \frac{\gamma^2}{4}\left(\vec{\mathsf{p}}\;\mathcal{V}\;\vec{\mathsf{p}} + \vec{\boldsymbol{\Sigma}}\;\cdot[(\vec{\nabla}\mathcal{V})\times\;\vec{\mathsf{p}}]\right) + \ldots \tag{10}$$

($\vec{\boldsymbol{\Sigma}}$ denotes the Dirac spin operator), which both together again give the well known Darwin and spin-orbit terms. We conclude that the even operators $\boldsymbol{\beta}\;E(\mathsf{p})$ and $\mathsf{V}^{(1)}$ in (6) are correct up to powers of γ^2. Therefore, they include all corrections of the second order FW transformation. As it can be seen immediately for the kinetic energy $\boldsymbol{\beta}\;E(\mathsf{p})$ and, as it will become clear from the transformations discussed below for $\mathsf{V}^{(1)}$, both terms are correct to all orders of γ. After this preliminary transformation any nth order odd operator $\mathsf{R}^{(n)}$ is removed by the unitary transformation

$$\mathsf{U}_n = \mathsf{W}_n + \left(1+\mathsf{W}_n^2\right)^{1/2} = 1 + \mathsf{W}_n + \frac{1}{2}\mathsf{W}_n^2 + \ldots\,, \tag{11}$$

with an antihermitian operator W_n. In order remove $\mathsf{R}^{(n)}$, it must fulfill

$$\{\mathsf{W}_n, E(\mathsf{p})\} = \boldsymbol{\beta}\;\;\mathsf{R}^{(n)}, \tag{12}$$

where $\{.,.\}$ denotes the anticommutator. Finally, from (12) it follows that W_n must be odd and of order $\mathcal{V}^n$, too. Explicit expressions for W_1 in momentum representation have been given by Douglas and Kroll [21] and were corrected by Jansen and Hess [24]. After each transformation the Hamiltonian becomes

$$\mathsf{H}^{(n+1)} = \mathsf{U}_n\mathsf{H}^{(n)}\mathsf{U}_n^{-1} = \mathsf{H}^{(n)}_{\text{even}} + \mathsf{V}^{(n+1)} + \mathsf{R}^{(n+1)} + \ldots \tag{13}$$

wherein $\mathsf{H}^{(n)}_{\text{even}}$ denotes the even operators of $\mathsf{H}^{(n)}$ up to order $\mathcal{V}^n$. $\mathsf{V}^{(n+1)}$ and $\mathsf{R}^{(n+1)}$ are of order $\mathcal{V}^{n+1}$ and the dots stand for terms of order $\mathcal{V}^{n+2}$ and higher. They are not needed explicitly until the $(n+1)$ st transformation. Especially, $\mathsf{H}^{(n)}_{\text{even}}$ is not modified under the transformation with U_n. Consequently, the operator $\mathsf{H}^{(n)}_{\text{even}}$ is correct to order $\mathcal{V}^n$ and, hence, each $\mathsf{V}^{(j)}$ for $j \leq n$ is correct in all orders of the fine-structure constant. From this point of view $\mathsf{H}^{(1)}_{\text{even}}$, which we are going to use below, contains the most dominant terms, *i.e.* the exact relativistic kinetic energy given by the Klein Gordon like operator

$$\boldsymbol{\beta}\;E(\mathsf{p}) = \begin{pmatrix}\sqrt{m_0^2c^4 - c^2\Delta} & 0\\ 0 & -\sqrt{m_0^2c^4 - c^2\Delta}\end{pmatrix} \tag{14}$$

and the first potential contribution $\mathsf{V}^{(1)}$ which can be rewritten to separate the scalar interaction from the spin-orbit coupling

$$\mathsf{V}^{(1)} = \mathsf{V}^{(1)}_{\text{s}} + \mathsf{V}^{(1)}_{\text{s}-\text{o}} \tag{15}$$

whereby

$$\begin{aligned}\mathsf{V}^{(1)}_{\text{s}} &= N(\mathsf{p})\mathcal{V}(\vec{r})N(\mathsf{p})\\ &\quad + N(\mathsf{p})\frac{c\;\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2}\,\mathcal{V}(\vec{r})\,\frac{c\;\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2}N(\mathsf{p})\end{aligned} \tag{16}$$

$$\begin{aligned}\mathsf{V}^{(1)}_{\text{s}-\text{o}} &= i\vec{\boldsymbol{\Sigma}}\;\cdot\left[N(\mathsf{p})\left(\frac{c\;\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2}\,\mathcal{V}(\vec{r})\right)\right.\\ &\qquad\left.\times\left(\frac{c\;\vec{\mathsf{p}}}{E(\mathsf{p})+m_0c^2}\right)N(\mathsf{p})\right].\end{aligned} \tag{17}$$

In the present formulation the scalar-relativistic Hamiltonian is constructed by adding the kinetic energy to $\mathsf{V}_{\mathrm{s}}^{(1)}$, subtracting the rest energy, and neglecting the small components as well as the spin degrees of freedom. Returning to atomic units we are left with the operator for a scalar wave-function

$$\mathsf{H}_{\mathrm{s}} = \frac{2}{\gamma^2}\left(\sqrt{1-\gamma^2 \mathit{\Delta}} - 1\right) + V_{\mathrm{s}}^{(1)} \tag{18}$$

where $V_{\mathrm{s}}^{(1)}$ is the scalar form of the Dirac operator $\mathsf{V}_{\mathrm{s}}^{(1)}$ which reads in coordinate representation

$$\begin{aligned} V_{\mathrm{s}}^{(1)} = & \sqrt{\frac{\sqrt{1-\gamma^2\mathit{\Delta}}+1}{2\sqrt{1-\gamma^2\mathit{\Delta}}}}\, V(\vec{r})\, \sqrt{\frac{\sqrt{1-\gamma^2\mathit{\Delta}}+1}{2\sqrt{1-\gamma^2\mathit{\Delta}}}} \\ & - \gamma^2 \frac{1}{\sqrt{\sqrt{1-\gamma^2\mathit{\Delta}}+1-\gamma^2\mathit{\Delta}}} \operatorname{tr}(\vec{\boldsymbol{\nabla}}\ V(\vec{r})\vec{\boldsymbol{\nabla}}) \\ & \times \frac{1}{\sqrt{\sqrt{1-\gamma^2\mathit{\Delta}}+1-\gamma^2\mathit{\Delta}}}. \end{aligned} \tag{19}$$

The Hamiltonian (18) is well suited for the use within a band calculation: First of all, its spectrum is bounded from below and the operator can therefore be used within a variational framework. Secondly, it contains the terms linear in V to all orders of the fine-structure constant. Thirdly, like the second order FW transformation, it contains all relativistic corrections to order γ^2 which are diagonal in spin. For an arbitrary basis, however, it will be quite cumbersome to calculate matrix elements, since the square roots containing the Lapacian must be evaluated by their power-expansion. Alternatively, one may transform the entire basis of a Ritz ansatz to be eigenfunctions of p^2 variationally. While the first technique can hardly be carried out because spatial derivatives occur in every order, the second technique requires the calculation of all eigenvalues and eigenvectors of an additional eigenvalue problem. Thereby, the computational effort is increased by a factor of 2, and additional work is to be expected *e.g.* for the calculation of the charge density when the inverse transformation is needed. We avoid the shortcomings of both techniques by the approach described in the next paragraph.

2.2 Evaluation of matrix-elements

Modern band-structure schemes solve the crystal Schrödinger equation with a linear Ritz ansatz. This technique generally requires to calculate the matrix-elements of the Hamiltonian and of the overlap with respect to a certain set of basis functions. Since the Hamiltonian (18) consists of products of sophisticated operator functions of $\vec{\mathsf{p}}$ as well as of $\vec{r}$, a natural basis to evaluate matrix-elements does not exist. Our technique to evaluate matrix-elements with respect to a basis of localized orbitals consists of a general procedure which can be used within all linear derivates of Slaters APW technique and within other linear schemes using a basis of localized orbitals, and of the application of this procedure to the SAPW method.

2.2.1 General procedure

Following an idea of Slater [4], APW-like methods divide the crystal into two regions: First of all into non-overlapping spheres centered at the atomic sites and secondly into the remaining interstitial region. In the latter, the wave function can be approximated by a finite superposition of plane-waves which automatically accounts for Bloch boundary conditions. Within the spheres modern linear versions of the APW methods, such as MAPW, LAPW and SAPW, approximate the wave function by a superposition of radial functions $\mathcal{P}_{nL}$

$$\mathit{\Psi}_{n\vec{k}}(\vec{r}) = \sum_L \sum_{n=1}^{N} A_{nL}\mathcal{P}_{nL}(\vec{r}) \tag{20}$$

with

$$\mathcal{P}_{nL}(\vec{r}) = \mathsf{Y}_L(\widehat{r})\, i^{\ell} P_{n\ell}(r). \tag{21}$$

$\mathsf{Y}_L(\widehat{r})$ denotes a spherical harmonic and $L = (\ell, m)$. In (20) the coefficients A_{nL} are either variational parameters – as in MAPW and SAPW – or determined by matching conditions at the boundary of the spheres – as in LAPW. Also the choice of the $P_{n\ell}(r)$ as well as the range of the sums vary from scheme to scheme. Moreover, Ritz ansätze of the form (20) and (21) are also used by other schemes *e.g.* linear combination of atomic orbitals [7], linear muffin tin orbitals [38] or augmented spherical waves [39]. Within all schemes the matrix elements can be calculated easily in the interstitial region, *e.g.* in APW like methods since plane-waves are pointwhise eigenfunctions of each component of the momentum operator. For this reason, the problem of the calculation of the matrix-elements is an essential one for the localized functions of (20) and (21) only. Furthermore, we distinguish between operators which depend on $\vec{\mathsf{p}} = -i\,\vec{\nabla}$ and operators which depend on $\mathsf{p}^2 = -\mathit{\Delta}$ only. To evaluate the matrix elements with the latter, the basis of the $\{\mathcal{P}_{nL}\}$ is replaced by a set of transformed basis functions $\{\mathcal{T}_{nL}\}$ which are constructed to be eigenfunctions of the non relativistic kinetic energy variationally. *I.e.* they are constructed by solving the generalized hermitian eigenvalue problem

$$\sum_{n'=1}^{N} \left[\langle\mathcal{P}_{nL}| - \mathit{\Delta}|\mathcal{P}_{n'L}\rangle - d_{n''}^2\ \langle\mathcal{P}_{nL}|\mathcal{P}_{n'L}\rangle\right] C_{n',n''}^{(\ell)} = 0, \tag{22}$$

where we used Dirac notation for the matrix elements. The variational eigenfunctions of the non relativistic kinetic energy are then given by

$$\mathcal{T}_{n''L}(\vec{r}) = \sum_{n=1}^{N} C_{n,n''}^{(L)} \mathcal{P}_{nL}(\vec{r}). \tag{23}$$

Using this new basis set the Ritz ansatz for the wave functions within the spheres (20) is replaced by

$$\mathit{\Psi}_{n\vec{k}}(\vec{r}) = \sum_L \sum_{n=1}^{N} \widetilde{A}_{nL}\mathcal{T}_{nL}(\vec{r}), \tag{24}$$

whereby the expansion coefficients in (24) and (20) are related *via*

$$\widetilde{A}_{nL} = \sum_{n'=1}^{N} C^{(\ell)}_{n'n} A_{n'L} \tag{25}$$

and a corresponding inverse relation. By construction, this transformation possesses the following analytic properties. (i) As solutions of a linear, hermitian eigenvalue problem, the $\mathcal{T}_{nL}$ are mutually orthogonal and span the same function space as the original orbitals. (ii) Since $-\Delta$ is invariant under rotations, the transformation can be carried out for each L separately and the $C^{(\ell)}_{n'n}$ do not depend on m. For this reason, the computational effort for the construction of the $\mathcal{T}_{nL}$ can be neglected when compared with the effort for the entire band calculation. (iii) Since $-\Delta$ is a positive operator the eigenvalues d_n^2 are greater than zero. (iv) within the new basis, matrix elements of arbitrary operator functions f of Δ can be evaluated easily

$$\langle \mathcal{T}_{nL} | f(\Delta) | \mathcal{T}_{n'L'} \rangle = f(-d^2_{n\ell})\, \delta_{L,L'} \delta_{n,n'}. \tag{26}$$

To evaluate finally the matrix elements containing ∇_j $j = 1,2,3$ we note that these operators occur only quadratically in the Hamiltonian (18). The matrix elements can thus be guaranteed to become hermitian by acting with the leftmost and rightmost of the ∇_j operators on bra and ket respectively. The final integration can then be done using the expansion of the $\mathcal{T}_{nL}$ into spherical harmonics (21). Explicit formulas depend on the scheme used.

2.2.2 Application to the SAPW method

We use the linear Ritz ansatz of the Spline Augmented Plane-Wave (SAPW) method [36,37] that consists of plane-waves as well as of localized spline orbitals

$$\langle \vec{r} | n\vec{k} \rangle_{\mathrm{SAPW}} = \sum_j A_j \langle \vec{r} | \vec{q}_j \rangle \tag{27}$$
$$+ \sum_L^{\ell \le \lambda} \sum_{n=1}^{N(\ell)} A_{Ln} \langle \vec{r} | B; Ln \rangle$$
$$\langle \vec{r} | \vec{q}_j \rangle = e^{i \vec{q}_j \cdot \vec{r}} \tag{28}$$
$$\langle \vec{r} | B; Ln \rangle = Y_L(\hat{r})\, (ir)^\ell\, B_{n\ell}(r). \tag{29}$$

Herein $\vec{q}_j = \vec{k} + \vec{G}_j$, $\vec{G}_j$ is a reciprocal lattice vector, the A's denote variational parameters, and the radial functions $B_{n\ell}$ are the normalized B-splines defined on a radial grid of N points in reference [36]. The $B_{n\ell}$ are restricted to the non-overlapping atomic spheres centered at the nuclei and vanish including their first derivatives at the boundary of the spheres. Therefore, (27) has continuous first derivative everywhere by definition. Thus, the SAPW method provides a linear discretation of the radial part of the wave-functions, which can be refined systematically by increasing the number of points in the radial grid to obtain any accuracy wanted. For this reason, the SAPW scheme was shown to be well suited to deal with a potential of general shape as well as for the calculation of response functions. For details we refer to references [36,37,40]. Since the plane-waves in (28) are eigenfunctions of the momentum operator the matrix-elements $\langle \vec{q}_j | \mathsf{H}_{\mathrm{s}} | \vec{q}_n \rangle$ can be evaluated easily. The matrix elements with the Spline functions are evaluated with the technique described above: We construct a new basis of spline orbitals $|T; sL\rangle$

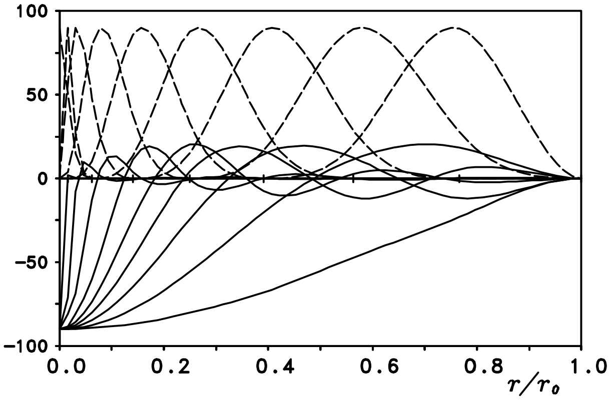

Fig. 1. The radial part of the spline orbitals as defined by (30) (solid curves) and of the localized spline orbitals (broken curves), both for $N = 9$ and $\ell = 1$. For convenience a factor r^ℓ was taken out and the functions were normalized to fit the scale. The bars on the zero line indicate the points of the quadratic grid used.

$$|T; sL\rangle = \sum_{n=1}^{N(\ell)} C^{(\ell)}_{n,n'} |B, sL\rangle \tag{30}$$

using the eigenvectors of (22). In addition to the general properties discussed above, the coefficients $C^{(\ell)}_{n,n'}$ as well as the parameters d for fixed N become universal constants when we use the scaling properties of integrals of B-Splines with the radius of the atomic spheres [37]. They can be calculated once and for all in advance and define a new orthonormal basis of spline orbitals. The radial part of these orbitals is compared with the localized B-splines of the original ansatz (29) in Figure 1. While the original functions were always positive and had a restricted support, the new spline functions are generally extended over the entire sphere and show an oscillating behavior. The resulting node structure is responsible for their orthogonality. To evaluate the matrix-elements with H_s, we must be aware of the fact that the $|T;\, Ls\rangle$ are not eigenfunctions of $-\Delta$ pointwhise, but that we have

$$\langle T; L's' | T; Ls \rangle = \delta_{L',L}\, \delta_{s',s} \tag{31}$$
$$\langle T; L's' | -\Delta | T; Ls \rangle = \delta_{L',L}\, \delta_{s',s}\, d^2_{\ell s}. \tag{32}$$

Hence, the overlap with the plane waves $\langle \vec{q}_j | T; Ls \rangle$ does not vanish. By straightforward calculation one finds for the matrix-elements of the kinetic energy [41]

$$\langle T; L's'|\frac{2}{\gamma^2}\left(\sqrt{1-\gamma^2\Delta}-1\right)|T;Ls\rangle = \frac{2}{\gamma^2}\left(\sqrt{1+\gamma^2 d_{\ell s}^2}-1\right)\delta_{L',L}\delta_{s',s} \quad (33)$$

$$\langle \vec{q}_j|\frac{2}{\gamma^2}\left(\sqrt{1-\gamma^2\Delta}-1\right)|T;Ls\rangle = \frac{2}{\gamma^2}\left(\sqrt{1+\gamma^2 q_j^2}-1\right)\langle \vec{q}_j|T;Ls\rangle \quad (34)$$

and of the potential energy

$$\begin{aligned}\langle T; L', s'|V_s^{(1)}|T;Ls\rangle = {}& \langle T; L', s'|V|T;Ls\rangle \\ & \times g(\gamma d_{\ell',s'})\, g(\gamma d_{\ell,s}) \\ & + \gamma^2\langle T; L', s'|\mathrm{tr}\left(\vec{\mathsf{p}}\ V\ \vec{\mathsf{p}}\right)|T;Ls\rangle \\ & \times h(\gamma d_{\ell',s'})\, h(\gamma d_{\ell,s}) \quad (35)\\ \langle \vec{q}_j|V_s^{(1)}|T;Ls\rangle = {}& \langle \vec{q}_j|V|T;Ls\rangle\, g(\gamma q_j)\, g(\gamma d_{\ell,s}) \\ & + \gamma^2\langle \vec{q}_j|\mathrm{tr}\left(\vec{\mathsf{p}}\ V\ \vec{\mathsf{p}}\right)|T;Ls\rangle \\ & \times h(\gamma q_j)\, h(\gamma d_{\ell,s}). \quad (36)\end{aligned}$$

Thereby, the correction factors g and h depend only on the eigenvalues d associated with the orbitals (or on the length of the propagation vectors of the plane-waves). They are given by

$$g(x) = \sqrt{\frac{\sqrt{1+x^2}+1}{2\sqrt{1+x^2}}} \quad (37)$$

$$h(x) = \frac{1}{\sqrt{2(\sqrt{1+x^2}+1+x^2)}}\cdot \quad (38)$$

The matrix-elements of the overlap and the potential are calculated with the techniques described previously in reference [36]. The necessity to calculate $\vec{\mathsf{p}}\ V\ \vec{\mathsf{p}}$ explicitly, with the procedure discussed above, is a new feature of the DK transformation in coordinate representation. Thereby, the computational effort for the entire band calculation is enlarged by roughly 10%. Explicit formulas for the matrix-elements of the traces of $\vec{\mathsf{p}}\ V\ \vec{\mathsf{p}}$ for the SAPW ansatz are given in the appendix. In contrast to what one would have expected from (18) and (19) the final form of the matrix-elements (33-36) turns out to be rather simple when the transformation (30) is used.

3 Results

Along the lines of the derivation in the previous section, three scalar-relativistic Hamiltonians can be used in a variational band calculations. Firstly, all scalar terms of the first-order DK transformation (DK1) lead to the operator (18). While it is not possible to find valuable approximations on the kinetic energy by expanding it into powers of γ, such approximations can indeed be obtained for the relativistic potential correction. The most simple of them is just replacing $V_s^{(1)}$ by the non-relativistic potential V which leads to the Klein-Gordon equation (KG). Thirdly, a more sophisticated approximation is to be obtained by including the corrections to the potential up to order γ^2. This leads to the KG equation supplemented by the Darwin term (KGD). While the first method is rigorously justified by the derivation in Section 2 the two latter approaches are temptingly simple, although the KGD approach suffers from the singular $\delta(\vec{r})$ contributions. Both require no additional computational effort when compared with a non-relativistic calculation. To test the usefulness of these three scalar-relativistic approximations we performed the following band calculations for silver and gold: First of all, the self-consistent one particle potential was determined by a non-relativistic (NON) calculation using the scheme outlined in reference [37]. Thereby, the local correlation potential of Gunnarsson and Lundqvist [42] was used. The other calculations were performed with the three aforementioned scalar-relativistic operators keeping the potential fixed. In addition we calculated the the relativistic energy shift in first-order perturbation theory (PT1), using the FW operator. In all calculations we used about 60(90) plane-waves according to the condition $q_j^2 \le [\frac{2\pi}{a}]^2 \cdot 15.0(19.1)$ and 129(65) s-, 65(33) p-, 33(33) d-, 17(0) f-spline function defined on a Moruzzi-type grid [43] for gold(silver). In addition we compare the results for the core states obtained with the approximate Hamiltonians with their counterparts calculated by means of the scalar-relativistic radial differential equations (SRRDE) by Koelling and Harmon [17]

$$g'_\ell = 2m_0c\left(1-\frac{V-E}{2m_0c^2}\right)\phi_\ell \quad (39)$$

$$\phi'_\ell = -\frac{2}{r}\phi_\ell + \left[\frac{\ell(\ell+1)}{2m_0cr^2\left(1-\frac{V-E}{2m_0c^2}\right)} + \frac{1}{c}(V-E)\right]g_\ell.$$

Here g_ℓ and ϕ_ℓ denote the radial parts of the small and the large components of the Dirac equation, respectively. Similar expressions have been derived by other authors [18,19]. These SRRDE can be shown [17–19] to reproduce the exact energies and wave-functions of the Dirac equation for s-states while they are an approximation for states with $\ell > 0$. Since equations (39) are apparently non-linear with respect to the energy E, no (energy-independent) Hamiltonian belongs to them, and, therefore, they may not be used in a fully-linear variational band-calculation. However we like to mention, that they are widely used within linearized, energy-window (see *e.g.* [38]) schemes, which we do not address here.

3.1 Core states

The most crucial hurdle in any approximation on the relativistic eigensolutions is the description of the core states since they influence all higher levels by the requirement

Table 1. Energy levels of the core states for silver for the different Hamiltonians. We compare the exact relativistic energies obtained by solving the radial Dirac equation with the corresponding non-relativistic energies and with results calculated with the SAPW method using the Klein-Gordon (KG), the Klein-Gordon plus Darwin (KGD), the first-order Douglas-Kroll (DK1) Hamiltonian, and first-order perturbation theory (PT1). The last column displays the energies obtained by solving the scalar-relativistic radial differential equations (SRRDE).

operator	exact	non	KG	KGD	DK1	PT1	SRRDE
method	integration	SAPW	SAPW	SAPW	SAPW		integration
$1s\,\frac{1}{2}$	−1865.07	−1798.14	−2096.87	−2093.76	−1889.62	−1866.54	−1865.07
$2s\,\frac{1}{2}$	−273.932	−257.203	−298.883	−298.676	−276.433	−273.465	−273.932
$2\overline{p}$	−246.554	−239.306	−246.125	−247.049	−246.392	−246.893	−246.222
$3s\,\frac{1}{2}$	−48.4135	−44.8329	−53.0979	−53.0633	−48.8802	−48.2884	−48.2169
$3\overline{p}$	−39.2851	−37.6101	−39.2080	−39.3741	−39.2568	−39.3239	−39.2477
$3\overline{d}$	−24.6038	−24.2122	−24.5934	−24.6824	−24.6061	−24.6757	−24.6055
$4s\,\frac{1}{2}$	−4.6217	−3.9119	−5.5329	−5.5250	−4.7131	−4.5911	−4.6217
$4\overline{p}$	−1.9334	−1.6289	−1.9156	−1.9478	−1.9164	−1.9320	−1.9327

Table 2. Energies of the core states of gold for the different Hamiltonians. The SAPW value of the $4f$-orbital was corrected empirically by subtracting 0.0483 Ryd. The notations are explained in Table 1.

operator	exact	non	KG	KGD	DK1	PT1	SRRDE
method	integration	SAPW	SAPW	SAPW	SAPW		integration
$1s\,\frac{1}{2}$	−5980.65	−5363.97	−9098.46	−8848.64	−6265.74	−5908.23	−5980.65
$2s\,\frac{1}{2}$	−1062.70	−892.705	−1463.00	−1429.40	−1095.88	−1034.43	−1062.70
$2\overline{p}$	−931.775	−858.378	−922.661	−928.515	−926.628	−924.362	−922.240
$3s\,\frac{1}{2}$	−250.571	−206.550	−338.173	−331.010	−257.920	−243.232	−250.571
$3\overline{p}$	−211.639	−190.317	−209.683	−211.024	−210.584	−209.459	−209.533
$3\overline{d}$	−165.626	−159.921	−165.414	−166.191	−165.556	−165.985	−165.532
$4s\,\frac{1}{2}$	−52.6246	−41.0061	−75.1885	−73.3356	−54.5004	−50.5430	−52.6246
$4\overline{p}$	−39.5495	−34.0064	−39.0623	−39.3893	−39.2818	−38.9083	−39.0226
$4\overline{d}$	−22.6191	−21.1094	−22.5707	−22.7359	−22.6014	−22.6633	−22.5972
$5s\,\frac{1}{2}$	−5.4179	−3.0507	−10.1921	−9.7896	−5.8031	−4.9419	−5.4179
$4\overline{f}$	−4.1568	−3.8228	−4.1429	−4.2126	−4.1553	−4.2024	−4.1549

of orthogonality. To set up benchmarks for the energies of the core levels we solved the radial Dirac equation for the core states for the spherically symmetric part of the one particle potential. To compare these energies with the results of a scalar-relativistic calculation it is necessary use the mean energy of Dirac states defined as the weighted average

$$E_{n,\overline{\ell}} = \frac{\ell\; E_{n\ell,\ell-\frac{1}{2}} + (\ell+1)\; E_{n\ell,\ell+\frac{1}{2}}}{2\ell+1}. \tag{40}$$

A similar integration procedure was used in case of SRRDE. The core levels with the SAPW method were obtained by setting the number of plane-waves in the ansatz (27) equal to zero and excluding the non-spherical parts of the one particle potential. Therefore, by construction, the value of these radial function is zero outside the atomic spheres. This is well justified for the core levels in silver as well as for the s, p, and d-states in gold. The $4f$-levels of gold, however, are significantly different from zero also in the interstitial region. The difference in energy between the exact solution of the radial Schrödinger equation and the solution confined to the atomic spheres turned out to be 0.0483 Ryd. In order to compare the values from the SAPW calculations with the solution of the radial Dirac equation, we subtracted this value in advance, thereby assuming that it is independent from the Hamiltonian used. The results for the core levels in silver and gold are shown in Tables 1 and 2, respectively. Table 1 shows that in the case of silver the best scalar-relativistic technique is DK1. Except for the $1s$-state the difference to the corresponding eigenvalues of the Dirac equation are far less than 1%. Oppositely, the KG approach generally overestimates the relativistic corrections and consequently underestimates the energies of the low core states by about 10%. At first sight it seems quite surprising, that the latter cannot significantly be improved by including the Darwin term. A more detailed analysis [41] shows that, because of the $\delta(\vec{r})$

contributions, the KGD eigenvalues do not converge with increasing number of basis functions. The basis-set used here was chosen to give a balance between a good description of the localization 1s-state and the overshooting tendency of the $\delta(\vec{r})$ contributions. Finally, the results obtained with PT1 are quite good: For p- and d-states they turns out to be almost as good as the DK results, while PT1 gives even better energies for the s-states. Finally, the energies obtained with the SRRDE are, as it is expected, exact for all s-states while the underestimate the relativistic effects for p-states slightly more than DK1. The 3$\overline{d}$-state is described very reasonably by SRRDE. There is, however, no substantial difference between the exact result, DK1, and SRRDE for this state. These results are not very surprising since relativistic corrections are small in silver. Therefore, the quality of the PT1 results reveals the fact that the energy-shifts are given by expectation values of the FW operator which are proportional to γ^2. When compared with this, any variational treatment is handicapped by the fact that the states are modified, too. Thereby, higher orders of γ are included implicitly, which are no longer described correctly by H_{FW} or the Darwin term. This is illustrated by the fact, that a variational treatment of the FW operator does not even lead to a ground state. While silver is an example for a material with rather weak relativistic effects gold provides a severe test for any relativistic calculation. In Table 2 we observe that, apart from s-states which are exact within SRRDE, again DK1 gives the best scalar-relativistic results. In contrast to silver the DK1 results are now closer to the exact values for most of the levels than the estimates of PT1. Moreover one discovers the following trend: While DK1 generally overestimates the relativistic energy shifts for s-states slightly, it underestimates p, d, and f-states shifts, whereby the error becomes smaller with increasing angular momentum. Interestingly, this trend is not found in the results obtained by PT1 which overestimates the energy-shifts for higher p, d, and f-states systematically. This demonstrates, that the DK1 Hamiltonian contains corrections beyond the order of γ^2, too, which become important in the case of gold but could be neglected in the case of silver. When compared with SRRDE, the energies obtained within DK1 are superior for all p- d- and f-states, while, oppositely, SRRDE is exact for s-states by construction. Remarkably, SRRDE leads to an energy for the 2$\overline{p}$-state, which is even worse than its counterpart obtained with first-order perturbation theory. In contrast to silver we find now that neither the KG nor the KGD approach give an at least sufficient description of the deep core levels. For the 1 s -state in gold the relativistic energy-shift is overestimated by almost an order of magnitude with the KG operator. For the higher p, d, and f-levels KGD leads to eigenvalues which are roughly as good as PT1, but which are obtained with a variational procedure. However, s-states are still described very poor. These failures of the KG and KGD Hamiltonians arise from the fact that only s-states have non-vanishing value at the atomic sites. They are, therefore, to a large extent influenced by the relativistic correction of the potential. Neglecting it by using the KG Hamiltonian underestimates the energies drastically. Moreover, by comparing KGD and DK1 we learn that the Darwin term can hardly describe this phenomenon while $V_s^{(1)}$ works quite well. Nevertheless, to describe the s-states with the same accuracy as the p-, d-, and f-states higher orders of DK transformations seem to be necessary. This is, however, a demanding task and can only be the subject to further work.

Table 3. Valence band energies of silver. The notations are explained in Table 1.

	non	DK1	KGD	KG
Γ_1	1.7605	1.6908	1.6267	1.6260
$\Gamma_{25'}$	1.9078	1.8657	1.8590	1.8668
Γ_{12}	1.9793	1.9329	1.9256	1.9342
L_1	1.8088	1.7671	1.7502	1.7553
L_3	1.9067	1.8650	1.8583	1.8667
L_3	2.0342	1.9847	1.9769	1.9860
L_1	2.2641	2.2311	2.2292	2.2320
$L_{2'}$	2.5687	2.4702	2.3909	2.3936

Table 4. Valence band energies of gold. The notations are explained in Table 1.

	non	DK1	KGD	KG
Γ_1	2.3558	2.0956	1.7718	1.7376
$\Gamma_{25'}$	2.5139	2.3734	2.3613	2.3762
Γ_{12}	2.6214	2.4629	2.4494	2.4660
L_1	2.3806	2.2324	2.0706	2.0458
L_3	2.5120	2.3732	2.3612	2.3760
L_3	2.7055	2.5334	2.5188	2.5367
L_1	2.8961	2.7725	2.5718	2.5583
$L_{2'}$	3.3065	2.9286	2.7706	2.8015

3.2 Valence bands

To judge the quality of the energies of the valence bands obtained within the several scalar-relativistic approximations, we first compare the absolute values of the band energies at Γ and L in Tables 3 and 4 for silver and gold, respectively.

In case of silver we find that s-type bands (Γ_1 and $L_{2'}$) are stabilized with respect to the other bands. This effect is larger in case of the KGD and KG than in the DK1 calculation. As we have learned from the analysis of the core levels in the last paragraph, the s-stabilization is overestimated in the KG and KGD calculations. Thereby, the differences between the exact energies and the KG, KGD, or DK1 estimates decrease by at least one order of magnitude when going from one shell to the next. Extrapolating this result to the valence bands we conclude that the KG and KGD values for s-type states have errors as

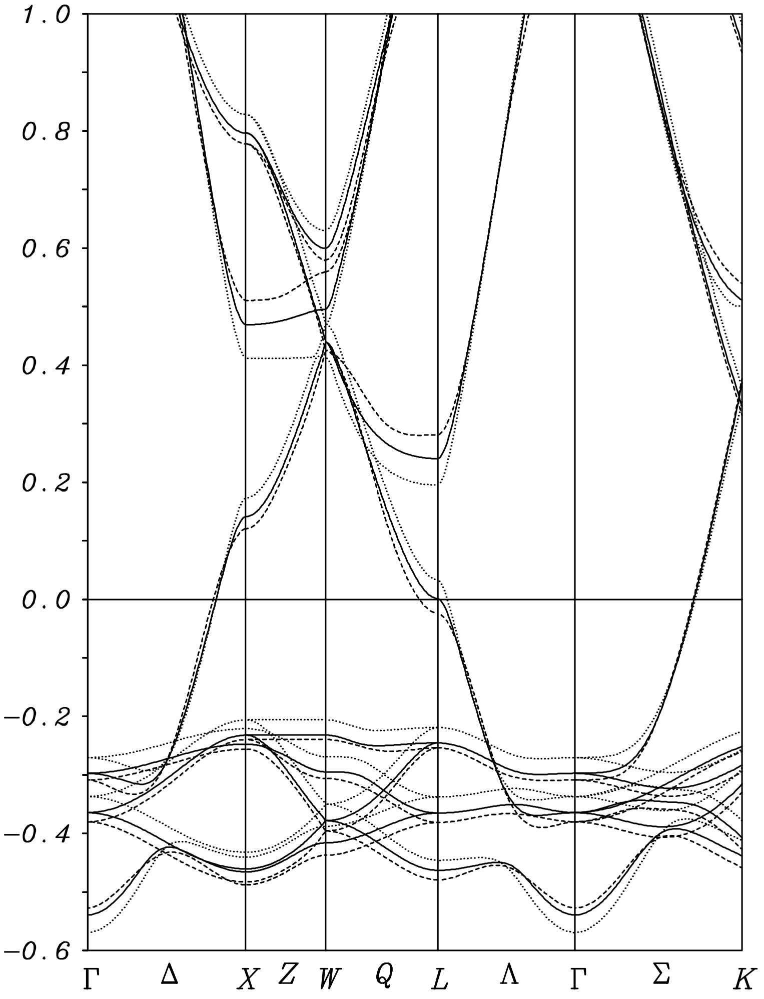

Fig. 2. Valence band structure of silver with the DK1 operator (solid lines), the KGD operator (dotted lines), and non-relativistic (broken lines) with respect to the Fermi energy.

large as 0.1 Ryd. This is almost the order of the energy shift. In contrast, the DK1 results for s-type states are accurate within about some 0.01 Ryd. The situation looks much better in case of the d -type bands: Since already the energies of the $3d$-states of silver were reproduced within 0.003 Ryd for the DK1 calculation the error in the d-type bands should be in the order of some 0.1 mRyd and thus has the same magnitude as the intrinsic error. In case of gold the relativistic energy-shifts of the valence bands are larger by roughly one order of magnitude. Again the d-type bands are described more precisely than the s-bands: By extrapolating the errors of the core states we find errors for the s- and d-type bands of about 0.1 Ryd and about 0.04 Ryd, respectively. The KG and KGD approaches overestimate the relativistic stabilization of the s-type states by about 0.3 Ryd and 0.6 Ryd, respectively, for gold and are now larger than the relativistic energy shifts themselves. We conclude that, for heavy elements, a reasonable description of the relativistic valence band structure by a scalar-relativistic operator can be obtained only with the DK1 Hamiltonian. On the contrary, KG and KGD overestimate the stabilization of the s-bands drastically. Only for intermediate elements, such as silver, the simple KG and KGD approaches work satisfactorily.

To support this conclusion Figures 2 and 3 show the band structure of silver and gold, respectively, but – in contrast to the discussion above – with respect to the Fermi level. Since the Fermi level in the noble metals lies between the d- and s-bands, it reacts sensitively on the stabilization effects discussed above. For this reason the Fermi energy E_{F} was lowered by 0.058 Ryd and by 0.424 Ryd in the case of silver and gold, respectively, for the DK1 calculations when compared with NON. For the KGD Hamiltonian this effect was even more pronounced. While silver (see Fig. 2) shows only moderate relativistic modification of the band energies still some conclusions can be drawn with respect to the optical properties. The essential feature of silver is the interband absorption edge at which stems from transitions near L and X. It is underestimated systematically in a non relativistic calculation. At X KGD and NON posses almost the same transition frequency while it is enlarged by almost 10 mRyd for the DK1 operator. At L the L_1 level is shifted above the Fermi level for the KGD Hamiltonian and intersects

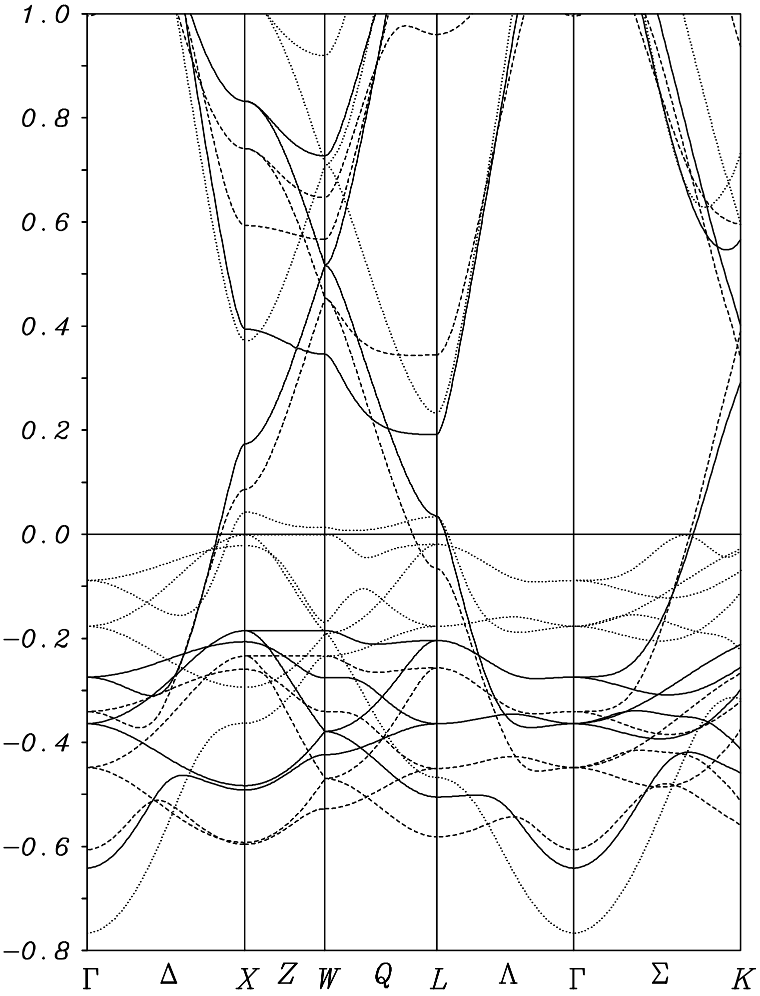

Fig. 3. Valence band structure of gold with the DK1 operator (solid lines), the KGD operator (dotted lines), and non-relativistic (broken lines) with respect to the Fermi energy.

for the DK1 Hamiltonian and the probability for transitions vanishes here. However, this should no be taken too serious, since we compare energy levels obtained with the same non relativistic potential. As we found during first self-consistent calculations the L_1 level becomes occupied again in case of DK1. In the conduction bands DK1 predicts only moderate stabilizations of s-type bands while for KGD the topology of the conduction bands is modified along Z. In case of gold (see Fig. 3), the energy shifts are much larger: The KGD calculation modifies the band structure completely and introduces a indirect band gap in the conduction band between about 0.02 and 0.22 Ryd. Thereby the Fermi level is lowered, such that the d-type bands *e.g.* at $\Gamma_{25'}$ and Γ_{12} lie only slightly below E_{F}. The low Fermi level disguises that Γ_1 which we find now at -0.771 Ryd below E_{F} has much to low energy. These predictions disagree with even the most elementary experimental features of gold *e.g.* with its read color. In contrast to KGD, DK1 shows, when compared with the non-relativistic calculation, a stabilization of the s-type with respect to the d-type bands which does not modify the metallic character of gold: In the valence bands s-type states are lowered by about 0.2 Ryd while the energy of d-type bands is increased by almost 0.5 Ryd. The latter effect is caused by the difference in the Fermi level. These results support our statement, that a variational treatment of scalar-relativistic effects in band theory for heavy elements needs at least the first order Douglas Kroll DK1 operator.

4 Conclusions

The DK1 operator includes the exact kinetic energy as well as a modified form of the potential correction. Both terms avoid the singularities of the mass-velocity term and of the Darwin term. With this step we established a linear Hamiltonian to be used in any variational framework in coordinate representation. The scalar relativistic SAPW scheme provides linear method which includes all relativistic corrections in order γ^2 but also important parts of higher orders. Therefore, its results for heavy metals go significantly beyond perturbation theory. A detailed comparison with experimental data can, however, only be performed with self-consistent data which is subject of our further work.

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Appendix: Matrix-elements of the trace operators

The matrix-elements of $\mathrm{tr}(\vec{\mathsf{p}}\ V\ \vec{\mathsf{p}})$ can be trivially be evaluated only in the case when the orbitals in bra and ket are plane-waves. Then one gets

$$\langle \vec{k}_j|\mathrm{tr}(\vec{\mathsf{p}}\ V\ \vec{\mathsf{p}})|\vec{k}_m\rangle = \vec{k}_j \cdot \vec{k}_m\, V(\vec{G}_j - \vec{G}_m). \tag{A.1}$$

In the cases with at least one spline orbital we use

$$\begin{aligned}\langle \vec{r}|\ \vec{\mathsf{p}}\ |T;sL\rangle = {}& \partial_r\left(r^\ell T_{s\ell}(r)\right)\cdot i^{\ell-1}\vec{r}^{\,\mathrm{o}}\, Y_L(\vec{r}^{\,\mathrm{o}})\\ &+ r^{\ell-1}T_{s\ell}(r)\cdot i^{\ell-1} r\vec{\nabla} Y_L(\vec{r}^{\,\mathrm{o}}).\end{aligned} \tag{A.2}$$

Since $\vec{r}^{\,\mathrm{o}}\ Y_L(\vec{r}^{\,\mathrm{o}})$ and $r\vec{\nabla}Y_L(\vec{r}^{\,\mathrm{o}})$ are functions of the unit vector $\vec{r}^{\,o}$ only, they can again be expanded into real valued spherical harmonics. By straightforward manipulation we put (A.2) into the form

$$\langle \vec{r}|\ \vec{\mathsf{p}}\ |T;sL\rangle = \sum_{L'} (ir)^{\ell'}\, \vec{F}_{s,L',L}(r)\, Y_{L'}(\vec{r}^{\,o}) \tag{A.3}$$

whereby

$$\begin{aligned}\vec{F}_{s,L',L}(r) = \frac{1}{r^{\ell'}}\Big(&\partial_r\left(r^\ell T_{s\ell}(r)\right)\cdot \vec{C}_{L'L}\\ &+ r^{\ell-1}T_{s\ell}(r)\cdot \vec{D}_{L'L}\Big)\end{aligned} \tag{A.4}$$

with the matrix elements of the unit vector $\vec{C}_{L'L} = i^{\ell-\ell'-1}\langle L'|\ \vec{r}^{\,\mathrm{o}}\ |L\rangle$ and the unit gradient $\vec{D}_{L'L} = i^{\ell-\ell'-1}\langle L'|r\vec{\nabla}|L\rangle$. Both of them can be evaluated easily with Wigner Eckart’s theorem. Furthermore, they obey the dipole selection rule $\ell' = \ell \pm 1$. Therefore, the sum in (A.3) contains only a few terms. Moreover, since $\vec{D}_{L'L}$ vanishes for $\ell = 0$ and $T_{s\ell}$ is a cubic spline, $\vec{F}_{s,L',L}$ is finite at the origin even if $\ell = 0$ and $\ell' = 1$. Using (A.4) we find

$$\begin{aligned}\langle \vec{k}_j|\mathrm{tr}(\vec{\mathsf{p}}\, V\, \vec{\mathsf{p}})|T;sL\rangle = {}& \frac{1}{\Omega}\sum_{L_1,L_2,L_3} i^{\ell_1-\ell_2} Y_{L_2}(\vec{k}_j^{\,\mathrm{o}})\\ &\times \int_0^{r_o} j_{\ell_2}(k_j r)\, Z_{L_3}(r)\, \vec{k}_j \cdot \vec{F}_{s,L_1,L}(r)\, r^{\ell_1+1}\,\mathrm{d}r\end{aligned} \tag{A.5}$$

(j_ℓ denotes the spherical Bessel function and Ω is the volume of the unit cell) and

$$\begin{aligned}\langle T;s_1L_1|\mathrm{tr}(\vec{\mathsf{p}}\, V\, \vec{\mathsf{p}})|T;s_2L_2\rangle = {}& \frac{1}{\Omega}\sum_{L_3,L_4,L_5} \frac{\langle L_3|L_4|L_5\rangle}{i^{(\ell_2-\ell_5)}}\\ &\times \int_0^{r_0} Z_{L_4}(r)\, \vec{F}^{\,*}_{s_1,L_1,L_3}(r)\cdot \vec{F}_{s_2,L_2,L_5}(r)\, r^{\ell_3+\ell_4+1}\,\mathrm{d}r.\end{aligned} \tag{A.6}$$

Thereby, we made use of the fact that V is diagonal in coordinate representation and can, within the atomic spheres, be written as

$$\langle \vec{r}|V|\vec{r}\,'\rangle = \delta(\vec{r} - \vec{r}\,')\,\frac{1}{r}\sum_L Y_L(\vec{r}^{\,\mathrm{o}})\, Z_L(r). \tag{A.7}$$

To do the radial integrations in (A.5) and (A.6) we use the fact that $\vec{F}_{s,L',L}$ is a polynomial spline with continuous first derivative. The effective charge $Z_L(r)$ is represented by a cubic spline, too. Then, together with the power expansion of the spherical Bessel functions the integrations can be carried out analytically. The formulae are lengthy but quite simple and are omitted here. Finally, we wish to remark that for every finite shape-approximation on the effective potential in the atomic spheres in (A.7) all sums over angular momenta in (A.5) and (A.6) become restricted to a finite range. This is caused either by the ansatz together with the dipole selection rule or by the triangle relation for the Gaunt coefficients $\langle L_1|L_3|L_2\rangle$ which vanish unless $|\ell_1 - \ell_2| \le \ell_3 \le \ell_1 + \ell_2$.

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