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Possible Way To Describe Breit's Interaction in Solids Composed From Heavy Elements

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POSSIBLE WAY TO DESCRIBE BREIT'S INTERACTION IN SOLIDS COMPOSED FROM HEAVY ELEMENTS

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Introduction

The report describes a theoretical procedure which could help evaluate the effect of quantum electrodynamic corrections on the electronic structure of crystals consisting of heavy elements. The procedure uses the effective Breit interaction as correction to traditional

Coulomb interaction between electrons in non-relativistic theory. A number of other simplifying assumptions were made since even such a simplified consideration of quantum electrodynamic effects in crystals is a great challenge. These are as follows.

- Exchange and correlation effects from the nonrelativistic interaction (the Coulomb term) between electrons are described within Density Functional Theory (DFT).
- The Breit correction is on at the phase which involves the calculation of matrix elements between basis functions which define the single-electron spectrum of a crystal. In order to calculate the contribution from the Breit correction, the total wave function of electrons in the crystal is approximated by one Slater determinant consisting of the single-electron DFT-orbitals.
- Only local matrix elements (i.e., the part of the two-electron integral for which both coordinate arguments belong to one and the same muffin-tin sphere) are considered.

I. A GENERAL THEORETICAL PROCEDURE: QED HAMILTONIAN FOR INTERACTING ELECTRONS

It is known that the basic equations of quantum elecrodynamics can be derived with the variational principle if take an operator

$$L = -\frac{1}{2}\frac{\partial A_\mu}{\partial x_\nu}\frac{\partial A_\mu}{\partial x_\nu} - \frac{1}{2}\bar{\psi}(\gamma_\mu\frac{\partial}{\partial x_\mu} + m)\psi - \frac{1}{2}\bar{\psi^c}(\gamma_\mu\frac{\partial}{\partial x_\mu} + m)\psi^c + j_\mu A_\mu \tag{1}$$

for the Lagrange function density and $A_\mu, \psi, \bar{\psi}$, operators of electromagnetic and electron-positron fields ($\bar{\psi}(x) = \psi^+(x)\gamma_4$) as independent variables. Here x_μ is 4-dimensional radius-vector, γ_μ is Diracs matrix, $j_\mu(x)$ is 4-dimensinal electron-positron current density defined by

$$j_\mu(x) = \frac{ie}{2}[\bar{\psi}(x), \gamma_\mu\psi(x)] = \frac{ie}{2}(\bar{\psi}(x)\gamma_\mu\psi(x) - \bar{\psi^c}(x)\gamma_\mu\psi^c(x)), \tag{2}$$

and $\psi^c(x), \bar{\psi^c}$ are charge-conjugated operators of the electron-positron field:

$$\psi^c(x) = C\bar{\psi}(x), \bar{\psi^c}(x) = C^{-1}\psi(x) \tag{3}$$

Noting that

$$\bar{\psi^c}[\gamma_\mu(\frac{\partial}{\partial x_\mu}+ieA_\mu)+m]\psi^c=\psi[\gamma_\mu^T(\frac{\partial}{\partial x_\mu}+ieA_\mu)-m]\bar{\psi}, \tag{4}$$

and varying and rejecting negligible terms in divergence form yield

$$\begin{aligned}\delta L =&\frac{1}{2}\delta A_\mu(\Box A_\mu+j_\mu)+\frac{1}{2}(\Box A_\mu+j_\mu)\delta A_\mu\\ &-\frac{1}{2}\delta\bar{\psi}[\gamma_\mu(\frac{\partial}{\partial x_\mu}-ieA_\mu)+m]\psi+\frac{1}{2}\psi[\gamma_\mu^T(\frac{\overleftarrow{\partial}}{\partial x_\mu}-ieA_\mu)+m]\delta\bar{\psi}\\ &-\frac{1}{2}\delta\psi[\gamma_\mu^T(\frac{\partial}{\partial x_\mu}+ieA_\mu)-m]\bar{\psi}+\frac{1}{2}\bar{\psi}[\gamma_\mu(\frac{\partial}{\partial x_\mu}+ieA_\mu)-m]\delta\psi.\end{aligned} \tag{5}$$

This relation gives equations for the Heisenberg operators of electromagnetic and electron-positron fields:

$$\begin{aligned}\{\gamma_\mu(\frac{\partial}{\partial x_\mu}-ieA_\mu(x))+m\}\psi(x)=0,\\ \{\gamma_\mu^T(\frac{\partial}{\partial x_\mu}+ieA_\mu(x))-m\}\bar{\psi}(x)=0,\\ \Box A_\mu(x)=-j_\mu(x).\end{aligned} \tag{6}$$

Knowing the density of the Lagrange function for quantized fields, we can find the energy-momentum tensor

$$\begin{aligned}T_{\mu\nu}&=L\delta_{\mu\nu}-\frac{\partial L}{\partial\psi,\nu}\psi,\mu-\bar{\psi},\mu\frac{\partial L}{\partial\bar{\psi},\nu}\\ &=\frac{1}{2}\{\frac{\partial A_\sigma}{\partial x_\nu}\frac{\partial A_\sigma}{\partial x_\mu}+\frac{\partial A_\sigma}{\partial x_\mu}\frac{\partial A_\sigma}{\partial x_\nu}-\delta_{\mu\nu}\frac{\partial A_\sigma}{\partial x_\lambda}\frac{\partial A_\sigma}{\partial x_\lambda}\}\\ &+\frac{1}{4}\{\bar{\psi}(\gamma_\nu\frac{\partial\psi}{\partial x_\mu}-\frac{\partial\bar{\psi}}{\partial x_\mu}\gamma_\nu\psi\}+\frac{1}{4}\{\bar{\psi^c}(\gamma_\nu\frac{\partial\psi^c}{\partial x_\mu}-\frac{\partial\bar{\psi}}{\partial x_\mu}\gamma_\nu\psi^c\}\end{aligned} \tag{7}$$

The term $-T_{44}$ in this expression is the energy density operator. Expressing the time derivatives of electron-positron field operators in terms of their spatial derivatives and using the current density definition (2), represent

$$-T_{44}=-T_{44}^0+T_{44}', \tag{8}$$

where

$$T_{44}^0 = \frac{1}{2}\{2\frac{\partial A_\sigma}{\partial x_4}\frac{\partial A_\sigma}{\partial x_4} - \frac{\partial A_\sigma}{\partial x_\lambda}\frac{\partial A_\sigma}{\partial x_\lambda}\}$$
$$+ \frac{1}{4}\bar{\psi}\{\gamma\frac{\overleftarrow{\partial}}{\partial \mathbf{r}} - m\}\psi - \frac{1}{4}\bar{\psi^c}\{\gamma\frac{\partial}{\partial \mathbf{r}} + m\}\psi^c + \frac{1}{4}\bar{\psi^c}\{\gamma\frac{\overleftarrow{\partial}}{\partial \mathbf{r}} - m\}\psi^c, \tag{9}$$

and

$$T'_{44} = j_\mu A_\mu. \tag{10}$$

The Hamiltonian H of the field system is a spatial integral of $-T_{44}$

$$H = -\int T_{44} d^3x = H_0 + H_I, \tag{11}$$

where

$$H_0 = -\int T_{44}^0 d^3x,$$
$$H_I = -\int T'_{44} d^3x = -\int j_\mu A_\mu d^3x. \tag{12}$$

II. APPROXIMATIONS: INTRODUCTION OF THE BREIT INTERACTION (DIRAC-BREIT)

With the known interaction Hamiltonian we can define a scattering matrix S which contains probability amplitudes of different scattering processes. The effective energy of interaction between two charges (the Breit formula) can be derived through the consideration of the scattering matrix in second order perturbation theory. Using the explicit form of the interaction operator, write the second-order scattering matrix

$$S^{(2)} = -\frac{1}{2}\int T[j_\mu(x) j_\nu(x')] T[A_\mu(x) A_\nu(x')] d^4x d^4x', \tag{13}$$

where T is the time-ordering operator, j_μ is the current density operator and A_μ are 4-potential electromagnetic field operators. Since photons are absent in the initial and final states, the operator $T[A_\mu(x)A_\nu(x')]$ can be replaced by its vacuum mean

$$\langle 0|T[A_\mu(x)A_\nu(x')]|0\rangle = \delta_{\mu\nu}D_c(x-x'). \tag{14}$$

As for contributions from electron currents, they are nonzero from only the terms of the operator $j_\mu(x)j_\nu(x')$, which contain two creation operators and two destruction, all being related to different individual electron states. That is why all the four factors anti-commutate with each other and their pair products commutate. So, T can be omitted and we can write

$$\langle f|S^{(2)}|i\rangle = -\frac{1}{2}\int j_\mu(x)D_c(x-x')j_\mu(x')d^4xd^4x'. \tag{15}$$

Now use the explicit expression of the photon Green's function $D_c(x)$:

$$D_c(x) = \frac{-i}{(2\pi)^4}\int \frac{e^{i\mathbf{k}\mathbf{r}-i\omega t}}{\mathbf{k}^2-\omega^2}d^3kd\omega. \tag{16}$$

Integrating over d^3k gives

$$D_c(x) = \frac{-i}{8\pi^2}\frac{1}{|\mathbf{r}|}\int_{-\infty}^{\infty} e^{-i\omega t+\frac{i}{c}|\omega||\mathbf{r}|}d\omega. \tag{17}$$

Substituting it into (15) yields

$$\langle f|S^{(2)}|i\rangle = \frac{i}{4\pi}\int j_{CA\mu}(\mathbf{r}_1,t)j_{BD\mu}(\mathbf{r}_2,t)\frac{e^{\frac{i}{c}|\omega_{BD}||\mathbf{r_1}-\mathbf{r_2}|}}{|\mathbf{r_1}-\mathbf{r_2}|}d\mathbf{r}_1d\mathbf{r}_2dt, \tag{18}$$

where $\omega_{BD} = \omega_B - \omega_D$.

Now do time integration. Since the states $A, B, ...$ are stationary, $\psi_A(x) = \psi_A(r)e^{-i\omega_A t}$, then

$$j_{CA\mu}(x) = j_{CA\mu}(\mathbf{r})e^{-i\omega_{CA}t}, \tag{19}$$

and

$$\langle f|S^{(2)}|i\rangle = \frac{i}{2}\int j_{CA\mu}(\mathbf{r}_1)\frac{e^{\frac{i}{c}|\omega_{BD}||\mathbf{r_1}-\mathbf{r_2}|}}{|\mathbf{r_1}-\mathbf{r_2}|}j_{DB\mu}(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2. \tag{20}$$

Now go over from the scattering matrix to the matrix of the effective energy of interaction between two charges, V, which is defined by

$$\langle f|S|i\rangle = -2\pi i\langle f|V|i\rangle\delta(\omega_A+\omega_B-\omega_C-\omega_D). \tag{21}$$

According to (18),

$$\langle f|V|i\rangle = -\frac{1}{4\pi}\int j_{CA\mu}(\mathbf{r}_1)j_{DB\mu}(\mathbf{r}_2)\frac{e^{\frac{i}{c}|\omega_{AC}||\mathbf{r}_1-\mathbf{r}_2|}}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2. \tag{22}$$

In (22), we express transient currents in terms of wave functions

$$\langle f|V|i\rangle = \frac{e^2}{4\pi}\int \psi^*_C(\mathbf{r}_1)\psi^*_D(\mathbf{r}_2)\frac{1-\alpha_1\alpha_2}{|\mathbf{r}_1-\mathbf{r}_2|}e^{\frac{i}{c}|\omega_{AC}||\mathbf{r}_1-\mathbf{r}_2|}\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2, \tag{23}$$

where α_1,α_2 are Diracs matrices such that α_1 acts on the function $\psi_A(\mathbf{r}_1)$ and α_2 acts on the function $\psi_B(\mathbf{r}_2)$.

To obtain the effective two-electron interaction Hamiltonian we expand the matrix element in powers v/c up to v^2/c^2.

The expansion of the retardation factor has the form

$$\frac{e^{\frac{i}{c}|\omega_{AC}||\mathbf{r}_1-\mathbf{r}_2|}}{|\mathbf{r}_1-\mathbf{r}_2|} = \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}+i\frac{|\omega_{AC}|}{c}-|\mathbf{r}_1-\mathbf{r}_2|\frac{|\omega_{AC}|^2}{2c^2}. \tag{24}$$

The matrix elements which contain α are equal to v/c by order of magnitude. Therefore in terms which contain $\alpha_1\alpha_2$ we can only leave the first term in expansion (24). After substitution in (22) the second term in (24) will turn zero because the functions ψ_A and ψ_C are orthogonal.

Using now the fact that the ψ_A are solutions of the Dirac equation with frequencies ω_A, we can prove[1] validity of the replacement

$$-|\mathbf{r}_1-\mathbf{r}_2|\frac{|\omega_{AC}|^2}{2c^2}\to\frac{\alpha_1\alpha_2-(\alpha_1\mathbf{n})(\alpha_2\mathbf{n})}{|\mathbf{r}_1-\mathbf{r}_2|}, \tag{25}$$

where

$$\mathbf{n} = \frac{\mathbf{r}_1 - \mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{26}$$

With (25) it is easy to show that the effective two-charge interaction is described by (Breit interaction)

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{e^2}{2}\frac{\alpha_1\alpha_2 + (\alpha_1\mathbf{n})(\alpha_2\mathbf{n})}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{27}$$

In the nonrelativistic limit this expression transforms into[1]

$$\begin{aligned} V(\mathbf{r}) = \frac{e^2}{r} &- \pi\frac{e^2}{m^2c^2}\delta(\mathbf{r}) - \frac{e^2}{4m^2c^2}\frac{1}{r^3}([\mathbf{r}\mathbf{p}_1]\sigma_1 - [\mathbf{r}\mathbf{p}_2]\sigma_2 + 2[\mathbf{r}\mathbf{p}_1]\sigma_2 - 2[\mathbf{r}\mathbf{p}_2])\sigma_1) \\ &- \frac{e^2}{2m^2c^2}(\frac{1}{r}\mathbf{p}_1\mathbf{p}_2 + \frac{1}{r^3}\mathbf{r}(\mathbf{r}\mathbf{p}_1)\mathbf{p}_2) \\ &+ \frac{e^2}{4m^2c^2}(\frac{\sigma_1\sigma_2}{r^3} - \frac{3(\sigma_1\mathbf{r})(\sigma_2\mathbf{r})}{r^5} - \frac{8\pi}{3}\sigma_1\sigma_2\delta(\mathbf{r})), \\ \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \end{aligned} \tag{28}$$

In this expression one can easily see[2] the Darwin interaction (the second term), the spin-orbit + spin-other-orbit interaction (in the first parenthesis), the orbit-orbit interaction (the second parenthesis), the spin-spin (magnetic dipole) interaction (the first two terms in the last parenthesis) and the contact spin-spin interaction (the third term in the last parenthesis).

III. LDA(GGA) AS AN APPROXIMATION TO EXCHANGE-CORRELATION ENERGY

As mentioned in Introduction, the exchange-correlation effects related to the Coulomb part (the first term in (27)) are treated here with DFT where LDA (local density approximation) and GGA (generalized gradient approximation) are used most often. A practically convenient approximation for the coupled description of relativistic and magnetic effects within the scope of the electronic density functional was obtained by Pajagopal, Callway, Vosko and Ramana[3–6]. In this approximation, the total energy of a system with electronic density $n(\mathbf{r})$ and magnetization density $m(\mathbf{r})$ is (a periodic system crystal is meant here)

$$E[n,m] = T_s[n] + \int_{\Omega_0} \mathrm{d}r[n(r)V_{ext}(r) + m(r)\cdot B_{ext}(r)] + \int_{\Omega_0}\mathrm{d}\mathbf{r}\int_{\Omega}\mathrm{d}r'\frac{n(r)n(r')}{\mid r-r'\mid}$$

$$+E_{xc}[n,m] + E_{nn}, \qquad (29)$$

where Ω_0 is the volume of the unit cell of the crystal and Ω is the total crystal volume. Energy is calculated per unit cell in atomic units (with energy in Ry). $T_s[n]$ is the kinetic energy of the non-interacting single-particle system, defined by

$$T_s[n] = \sum_k \sum_\lambda \int_{\Omega_0} \mathrm{d}r \Psi^\dagger_\lambda(k,r)\hat{H}_{kin}\Psi_\lambda(k,r)\theta[E_F - E_\lambda(k)], \qquad (30)$$

where the Dirac kinetic energy operator $\hat{H}_{kin}$ (minus electron rest energy) is

$$\hat{H}_{kin} = c\boldsymbol{\alpha}\cdot p + (\beta - I)\frac{c^2}{2}, \qquad (31)$$

c is light velocity ($c = 274.074$ in the system of units being used), p is momentum operator ($\equiv -i\nabla$), $\boldsymbol{\alpha}$ and β are standard Dirac matrices, and I is 4×4 unit matrix. $\Psi_\lambda(k,r)$ stands for the Bloch function with band index λ and wave vector k in the first Brillouin zone (BZ). $E_\lambda(k)$ is band energy and $\theta(x)$ represents unit theta-function which means that all states whose energies are lower than E_F are included in the sum of Eq. (30). The electron density $n(r)$ and the magnetization density $m(r)$ are found using the Bloch function $\Psi_\lambda(k,r)$ as

$$n(r) = \sum_k \sum_\lambda \Psi^\dagger_\lambda(k,r)\Psi_\lambda(k,r)\theta[E_F - E_\lambda(k)], \qquad (32)$$

and

$$m(r) = \sum_k \sum_\lambda \Psi^\dagger_\lambda(k,r)\beta\widetilde{\boldsymbol{\sigma}}\Psi_\lambda(k,r)\theta[E_F - E_\lambda(k)], \qquad (33)$$

respectively. Here $\widetilde{\boldsymbol{\sigma}}$ denotes 4×4 matrices comprised of Pauli matrices $\boldsymbol{\sigma}$:

$$\widetilde{\boldsymbol{\sigma}} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}. \qquad (34)$$

The second term in the right-hand side of (29) is the energy of electron interaction with the external field, where $V_{ext}(r)$ is the external scalar potential(nuclear potential) and $B_{ext}(r)$

is the external magnetic field. The third term is the classic Coulomb energy, E_{xc} is the exchange-correlation energy that is the functional of $n(r)$ and $m(r)$, and E_{nn} is the nuclear repulsion energy.

It should be noted that (29) is already certain simplification of fully relativistic DFT where energy (including the exchange-correlation energy) is the functional of the 4-vector current whose spatial components can be represented by the sum of the orbital electron current (which causes diamagnetic effects) and the spin electron current. Since there are still no satisfactorily validated approximations for the dependence of the exchange-correlation energy functional on orbital current (there is no orbital motion in the uniform electron gas which is usually used for deriving approximations to E_{xc}), it is Eq. (29) that serves as a starting point for numerical techniques at this stage of DFT development. Orbital magnetism does appear in this theory (due to spin-orbit interaction), but its backward (self-consistent) effect on the system is absent. Not accounting for the effects of orbital polarization may result in not exact calculation of orbital magnetic moments.

The application of Hohenberg-Kohn variational principle[7] to the total energy in (29) gives a system of single-particle equations whose self-consistent solution allows us to determine density (r) and magnetization $m(r)$

from (32) and (33):

$$\hat{H}\Psi_\lambda(k,r) = E_\lambda(k)\Psi_\lambda(k,r), \tag{35}$$

where the Dirac spin-polarized Hamiltonian is

$$\hat{H} = \hat{H}_{kin} + V(r) + \beta\widetilde{\boldsymbol{\sigma}} \cdot B(r). \tag{36}$$

The scalar effective potential $V(r)$ resulted from varying (29) is similar to the nonrelativistic case:

$$V(r) = V_{ext}(r) + 2\int_\Omega \mathrm{d}r' \frac{n(r')}{\mid r - r' \mid} + \frac{\delta E_{xc}[n(r), m(r)]}{\delta n(r)}, \tag{37}$$

while the effective magnetic field $B(r)$ is the sum of the external field and the functional derivative E_{xc} with respect to magnetization density:

$$B(r) = B_{ext}(r) + \frac{\delta E_{xc}[n(r), m(r)]}{\delta m(r)}. \tag{38}$$

Kinetic energy (30) can be rewritten in a more convenient form if use (35), orthonormality of $\Psi_\lambda(k,r)$ and definitions of $n(r)$ and $m(r)$:

$$T_s[n] = \sum_k \sum_\lambda E_\lambda(k)\theta[E_F - E_\lambda(k)] - \int_\Omega \mathrm{d}r n(r)V(r) - \int_\Omega \mathrm{d}r m(r)\cdot B(r), \qquad (39)$$

where summation of states implies account for core levels.

Next, in expression (29) for total energy, there are three divergent contributions. They however cancel one another and after some manipulation we obtain

$$E[n,m] = T_s[n] + \frac{1}{2}\int_\Omega \mathrm{d}r n(r)V_C(r) - \frac{1}{2}\sum_a Z_a V'_C(t_a) + \int_\Omega \mathrm{d}r m(r)\cdot B_{ext}(r)$$

$$+E_{xc}[n,m], \qquad (40)$$

where the vectors t_a represent coordinates of atoms in a unit cell, Z_a is nuclear charge on atom a, $V_C(r)$ is the full Coulomb potential and $V'_C(t_a)$ is Coulomb potential on the nucleus without the nucleuss contribution.

Self-consistent solution is obtained through the definition of the initial electron density distribution $n(\mathbf{r})$ (the initial magnetization density $\mathbf{m}(\mathbf{r})$ is taken to be zero) and the magnetic field $\mathbf{B}(\mathbf{r})$. The effective potential is calculated from (37). The next step is to solve (35). With the resulted eigenvalues and eigenfunctions we can calculate Fermi energy and find $n(\mathbf{r})$ and $\mathbf{m}(\mathbf{r})$ from (32) and (33). Then (if self-consistency is not reached yet) we calculate $V(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ from (37) and (38), which completes the self-consistency cycle.

The computational procedure we are considering here is based on the use of (35-38) together with (32-33).

IV. PRACTICAL ASPECTS OF THE APPROACH IN THE FLAPW METHOD OF BAND STRUCTURE CALCULATION

A. Representation of $n(\mathbf{r}), V(\mathbf{r}), \mathbf{m}(\mathbf{r}), \mathbf{B}(\mathbf{r})$

In the Relativistic Spin-Polarized Full-potential Linearized Augmented Plane Wave (RSPFLAPW) method, like in all others based on APW formalism, space in the unit cell is assumed to consist of the muffin-tin (MT) spheres Ω_a of radius S_a around atoms and the

interstitial region Ω_I. Wave functions are treated through their dual representation (i.e., expansions in spherical harmonics in the muffin-tin spheres and in plane waves in the interstitial region) and it is convenient to use a similar representation for other quantities such as the electron charge density $n(\mathbf{r})$, the effective potential $V(\mathbf{r})$, the magnetization density $\mathbf{m}(\mathbf{r})$ and the magnetic field $\mathbf{B}(\mathbf{r})$. For scalar quantities we then have

$$V(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} & \mathbf{r} \in I \\ \sum_{lm} V_{lm}(r) Y_{lm}(\theta,\varphi) & \mathbf{r} \in MT \end{cases}, \tag{41}$$

and for vector quantities where the representation is valid for each component, we have

$$\mathbf{B}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \mathbf{B}_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} & \mathbf{r} \in I \\ \sum_{lm} \mathbf{B}_{lm}(r) Y_{lm}(\theta,\varphi) & \mathbf{r} \in MT. \end{cases} \tag{42}$$

B. Calculation of electrostatic potential

The effective potential in the Kohn-Sham equations consists of the exchange-correlation part $V_{xc}(\mathbf{r})$ defined by the last term of (37) and the Coulomb part $V_c(\mathbf{r})$ defined by the charge distribution (electrons and nuclei) in the form of the Poisson equation (in the atomic system of units with energy in Ry)

$$\nabla^2 V_c(\mathbf{r}) = -8\pi n(\mathbf{r}). \tag{43}$$

The solution of this equation in real space is far from trivial for crystals. On the other hand, in reciprocal space, the Poisson equation is diagonal which formally allows us to write the solution in a simple form

$$V_c(\mathbf{r}) = 8\pi \sum_{\mathbf{G}} \frac{n_{\mathbf{G}}}{G^2} e^{i\mathbf{G}\mathbf{r}}, \tag{44}$$

where $n_{\mathbf{G}}$ are coefficients in the Fourier expansion of charge density.

However in the LAPW method which is one of the so called full-electron approaches, the density $n(\mathbf{r})$ includes the rapidly varying density of core electrons and the charge of nuclei represented by delta functions. That is why the expansion of the charge density in plane waves in (44) does not converge. So the strongly localized core (and nuclear) density complicates formulation in reciprocal space, while the long-range Coulomb potential

complicates it in real space. The problem was resolved by Hamann[8] and Weinert[9], who developed a hybrid approach. Below described is their solution based on the following observations: (1) The interstitial density is a continuously varying function and the rapidly varying density is in the MT-spheres; (2) The Coulomb potential outside the spheres only depends on the charge outside the spheres and multipoles of the charge inside the spheres; (3) The plane-wave representation of density in the interstitial is unambiguous in the sense that it can be extended with the Fourier expansion of any function inside the spheres without changing the interstitial charge.

The potential is constructed in steps. First we find multipoles of the true charge distribution in each MT-sphere a

$$q_{lm}^{a} = \sqrt{4\pi} \int_{\Omega_a} r^l Y_{lm}(\theta, \varphi) n^a(\mathbf{r}) d\mathbf{r} - \delta_{l,0} Z_a, \tag{45}$$

where Z_a is nuclear charge in the corresponding sphere. Also we determine the multipoles of the plane-wave charge representation extended into the spheres

$$q_{lm}^{a,PW} = \sqrt{4\pi} \int_{\Omega_a} r^l Y_{lm}(\theta, \varphi) \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G}\cdot(\mathbf{r}+\mathbf{a})} d\mathbf{r}. \tag{46}$$

The next step is to construct the so called pseudo-charge which coincides with the interstitial charge distribution and has the same multipoles in the spheres as the true charge distribution. This is accomplished through complementing the plane-wave representation with smooth functions which are zero in the interstitial and have multipoles equal to the difference of the multipoles of (45) and (46). Such a function can be chosen arbitrarily, but what is needed is the ease of its Fourier transform. A good option is

$$\tilde{n}^a(\mathbf{r}) = \sum_{lm} Q_{lm}^a \frac{1}{S_a^{l+3}} \left(\frac{r}{S_a}\right)^l \left(1 - \frac{r^2}{S_a^2}\right)^N Y_{lm}(\mathbf{r}), \tag{47}$$

where S_a is the radius of the MT-sphere of atom a. This function has (N-1) continuous derivatives and its Fourier transform is relatively simple.

AS mentioned above, the coefficients Q_{lm}^a are taken to be such as to reproduce the difference of the true and plane-wave multipoles. Then the Fourier coefficients of (47) are added to the coefficients in the plane-wave expansion of the interstitial charge. The true electrostatic potential in the interstitial is derived from (44). It is now necessary to integrate the

Poisson equation in the spheres. The known interstitial potential on the sphere boundaries is taken for the boundary condition and the Coulomb potential in the spheres is

$$V_{lm}^{MT}(r) = V_{lm}^{PW}(S)\left(\frac{r}{S}\right)^l + \frac{8\pi}{2l+1}\left\{\frac{1}{r^{l+1}}\int_0^r dr' r'^{l+2} n_{lm}(r') + r^l \int_r^S dr' r'^{1-l} n_{lm}(r') - \frac{r^l}{S^{2l+1}}\int_0^S dr' r'^{l+2} n_{lm}(r')\right\} - \frac{2\sqrt{4\pi}Z}{r}\delta_{l,0}, \quad (48)$$

where the last term is contribution from the nuclear potential.

C. Calculation of $V_{xc}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$

$V_{xc}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ are calculated in real space. For each value of the radial variable in the MT-spheres, we calculate density and magnetization (and their gradients for GGA) on a mesh of angular variables. Then we calculate $V_{xc}(\mathbf{r})$ and $\mathbf{B}(\mathbf{r})$ on the same mesh and find their spherical harmonics by integrating with respect to angles. In the interstitial the procedure is similar, but with a 3D structured mesh and Fast Fourier Transform (FFT) which is used for calculating density (magnetization) in each mesh point and then for calculating Fourier coefficients of the exchange-correlation potential and the magnetic field.

D. Basis functions of the RSPFLAPW method

Two types of basis functions are used in our method. The basis functions of the first type are characterized by the relativistic plane waves (Loucks[10]) in the interstitial region:

$$\Phi_A(k+G,s;r)|_{\Omega_i} = \frac{N_{k+G}}{\sqrt{\Omega_0}} \begin{pmatrix} u_s \\ \frac{c\sigma\cdot(k+G)}{c^2+\epsilon^+_{k+G}} u_s \end{pmatrix} \exp[\mathrm{i}(k+G)\cdot r], \tag{49}$$

where G are vectors of the reciprocal lattice, ϵ^+_{k+G} is the positive relativistic energy associated with the wave vector $k+G$, i.e., $2\epsilon^+_{k+G} = -c^2 + c\sqrt{c^2+4(k+G)^2}$, N_{k+G} is a normalization factor, and u_s denotes the spinor function for the spin state $s = \pm\frac{1}{2}$. The basis functions of the second type are zero in Ω_I.

In the MT-spheres the basis functions of the first type are derived from the solutions of the Dirac equation for the central field with $B = 0$ and for only the spherical component of the effective scalar potential $V^a_0(r)$

$$[\hat{H}_{kin} + V^a_0(r) - \epsilon^a_{il}] \begin{pmatrix} g^a_{il}(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} f^a_{il}(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix} = 0, \tag{50}$$

and from their energy derivatives which are solutions to the equation

$$[\hat{H}_{kin} + V^a_0(r) - \epsilon^a_{il}] \begin{pmatrix} \dot{g}^a_{il}(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} \dot{f}^a_{il}(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix} = \begin{pmatrix} g^a_{il}(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} f^a_{il}(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix}. \tag{51}$$

Here ϵ^a_{il} are energy parameters that must be defined self-consistently; $\Omega_{i;l;\mu}(\theta,\varphi)$ are spin-angle functions; l is the quantum number of the orbital moment; i defines the total moment j as $j = l + i$ ($i = \pm\frac{1}{2}$, not confuse with imaginary unit i), μ is the z-projection of the total moment. The relativistic quantum number κ is related to l and i as

$$\begin{aligned} \kappa &= l, & i &= -\tfrac{1}{2} \\ \kappa &= -l-1, & i &= \tfrac{1}{2}. \end{aligned}$$

The spin-angle functions are derived using the sum of moments:

$$\Omega_{i;l;\mu}(\theta,\varphi) = \sum_{s=\pm\frac{1}{2}} C^{l\mu}_{is} Y_{l;\mu-s}(\theta,\varphi) u_s, \tag{52}$$

where $Y_{l;\mu-s}(\theta,\varphi)$ are spherical harmonics[11] and $C_{is}^{l;\mu}$ are Clebsch-Gordan coefficients that are convenient to express with the parameter $u_{l\mu}=\mu/(l+1/2)$:

$$C^{l;\mu}=\begin{pmatrix} C^{l;\mu}_{-\frac{1}{2}-\frac{1}{2}} & C^{l;\mu}_{-\frac{1}{2}\frac{1}{2}} \\ C^{l;\mu}_{\frac{1}{2}-\frac{1}{2}} & C^{l;\mu}_{\frac{1}{2}\frac{1}{2}} \end{pmatrix}=\frac{1}{\sqrt{2}}\begin{pmatrix} \sqrt{1+u_{l\mu}} & -\sqrt{1-u_{l\mu}} \\ \sqrt{1-u_{l\mu}} & \sqrt{1+u_{l\mu}} \end{pmatrix}. \tag{53}$$

The spin-angle functions are orthonormalized:

$$\int \Omega^{\dagger}_{i;l;\mu}(\theta,\varphi)\Omega_{i';l';\mu'}(\theta,\varphi)\sin\theta \mathrm{d}\theta\mathrm{d}\varphi=\delta_{ii'}\delta_{ll'}\delta_{\mu\mu'}. \tag{54}$$

The radial functions $g^a_{il}(r)\ \ f^a_{il}(r)$ are solutions to the following system of coupled differential equations:

$$\frac{\mathrm{d}(rg^a_{il})}{\mathrm{d}r}=-\frac{\kappa}{r}(rg^a_{il})+\frac{c^2+\epsilon^a_{il}-V^a_0}{c^2}(rf^a_{il}) \tag{55}$$

$$\frac{\mathrm{d}(rf^a_{il})}{\mathrm{d}r}=\frac{\kappa}{r}(rf^a_{il})-(\epsilon^a_{il}-V^a_0)(rg^a_{il}). \tag{56}$$

For the energy derivatives of the radial functions, we must solve the system

$$\frac{\mathrm{d}(r\dot{g^a_{il}})}{\mathrm{d}r}=-\frac{\kappa}{r}(r\dot{g^a_{il}})+\frac{c^2+\epsilon^a_{il}-V^a_0}{c^2}(r\dot{f^a_{il}})+\frac{1}{c^2}(rf^a_{il}) \tag{57}$$

$$\frac{\mathrm{d}(r\dot{f^a_{il}})}{\mathrm{d}r}=\frac{\kappa}{r}(r\dot{f^a_{il}})-(\epsilon^a_{il}-V^a_0)(r\dot{g^a_{il}})-(rg^a_{il}). \tag{58}$$

It is convenient to use the normalized radial functions

$$\langle g^2\rangle+\langle f^2\rangle/c^2=1, \tag{59}$$

which means that the radial solution and its energy derivative are orthogonal:

$$\langle g|\dot{g}\rangle+\langle f|\dot{f}\rangle/c^2=0. \tag{60}$$

From the solution of (50) and (51), it is convenient to make two linear combinations $R_1^{ail\mu}(r)$ and $R_2^{ail\mu}(r)$[12]

$$R_1^{ail\mu}(r)=p_1^{ail}\begin{pmatrix} g^a_{il}(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c}f^a_{il}(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix}+q_1^{ail}\begin{pmatrix} \dot{g}^a_{il}(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c}\dot{f}^a_{il}(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix}, \tag{61}$$

and

$$R_2^{ail\mu}(r) = p_2^{ail} \begin{pmatrix} g_{il}^a(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} f_{il}^a(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix} + q_2^{ail} \begin{pmatrix} \dot{g}_{il}^a(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} \dot{f}_{il}^a(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix}, \tag{62}$$

such that the following relations hold on the boundaries of the MT-spheres:

$$R_1^{ail\mu}(S_a) = \begin{pmatrix} 1 & \Omega_{i;l;\mu}(\theta,\varphi) \\ 0 & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix}, \tag{63}$$

and

$$R_2^{ail\mu}(S_a) = \begin{pmatrix} 0 & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} \cdot 1 & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix}. \tag{64}$$

Now we can write the basis functions of the first type inside the MT-spheres as linear combinations of $R_1^{ail\mu}(r)$ and $R_2^{ail\mu}(r)$:

$$\Phi_A(k+G,s,r)|_{\Omega_a} = \sum_{il\mu} [y_1^{ail\mu}(k+G,s) R_1^{ail\mu}(r) + y_2^{ail\mu}(k+G,s) R_2^{ail\mu}(r)]. \tag{65}$$

Properties of (63) and (64) and the requirement that the large and small components of functions defined in (49) and (65) be continuous on the boundaries of the muffin-tin spheres for all quantum numbers (i,l,μ) $l \leqslant l_{max}$ allow us to determine the coefficients $y_1^{ail\mu}(k+G,s)$ and $y_2^{ail\mu}(k+G,s)$:

$$\begin{aligned} y_1^{ail\mu}(k+G,s) &= \frac{4\pi}{\sqrt{\Omega}} \mathrm{i}^l \mathrm{e}^{\mathrm{i}(k+G)t_a} N_{k+G} C_{is}^{l\mu} j_l(\mid k+G \mid S_a) Y_{l\mu-s}^*(\widehat{k+G}) \\ y_2^{ail\mu}(k+G,s) &= \frac{4\pi}{\sqrt{\Omega}} \mathrm{i}^{l-2i} \mathrm{e}^{\mathrm{i}(k+G)t_a} N_{k+G} C_{is}^{l\mu} \frac{c^2 \mid k+G \mid}{c^2 + \epsilon_{k+G}^+} \\ &\qquad \times j_{l+2i}(\mid k+G \mid S_a) Y_{l\mu-s}^*(\widehat{k+G}). \end{aligned} \tag{66}$$

The basis functions of the second type are local functions[12] which are defined similarly to what was proposed by Singh[13] for nonrelativistic formalism. They are nonzero only inside the MT-spheres and can be used to increase the variational freedom of valence states, and they help describe semicore states equally with the valence states. The local orbitals are constructed beginning with the solution of (50) and (51) for appropriately chosen energy

parameters ϵ_n^a where n is a set of quantum numbers unambiguously defining each local orbital. Then the second energy derivative from the solution of (50) is added, creating the linear combination R_3^{an}

$$R_3^{an}(r) = p_3^{an} \begin{pmatrix} g_{il}^a(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} f_{il}^a(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix} + q_3^{an} \begin{pmatrix} \dot{g}_{il}^a(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} \dot{f}_{il}^a(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix} + \begin{pmatrix} \ddot{g}_{il}^a(r) & \Omega_{i;l;\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} \ddot{f}_{il}^a(r) & \Omega_{-i;l+2i;\mu}(\theta,\varphi) \end{pmatrix}, \tag{67}$$

whose large and small components tend to zero on the sphere boundary. The second derivatives are solutions to

$$[\hat{H}_{kin} + V_0^a(r) - \epsilon_n^a] \begin{pmatrix} \ddot{g}_n^a(r) & \Omega_n^\mu(\theta,\varphi) \\ \frac{\mathrm{i}}{c} \ddot{f}_n^a(r) & \Omega_{-n\mu}(\theta,\varphi) \end{pmatrix} = 2 \begin{pmatrix} \dot{g}_n^a(r) & \Omega_{n\mu}(\theta,\varphi) \\ \frac{\mathrm{i}}{c} \dot{f}_n^a(r) & \Omega_{-n\mu}(\theta,\varphi) \end{pmatrix}, \tag{68}$$

and the corresponding radial components are determined through integration of the equations

$$\frac{\mathrm{d}(r\ddot{g}_n^a)}{\mathrm{d}r} = -\frac{\kappa}{r}(r\ddot{g}_n^a) + \frac{c^2 + \epsilon_n^a - V_0^a}{c^2}(r\ddot{f}_n^a) + \frac{2}{c^2}(r\dot{f}_n^a) \tag{69}$$

$$\frac{\mathrm{d}(r\ddot{f}_n^a)}{\mathrm{d}r} = \frac{\kappa}{r}(r\ddot{f}_n^a) - (\epsilon_n^a - V_0^a)(r\ddot{g}_n^a) - 2(r\dot{g}_n^a). \tag{70}$$

Now the Bloch sums of the functions R_3^{an}

$$\Phi_B^{an}(k,r) = \sum_R \mathrm{e}^{\mathrm{i}k(t_a+R)} R_3^{an}(r_a), \tag{71}$$

are used as the basis functions of the second type. Here R are lattice vectors and r_a is the radius vector measured from the center of atom a: $r_a = r - t_a$.

Now we can write the solution of the Dirac-Kohn-Sham equations (35) as a linear combination of the basis functions of types 1 and 2:

$$\Psi_\lambda(k,r) = \sum_{Gs} A_\lambda^{Gs}(k)\Phi_A(k+G,s;r) + \sum_{an} B_\lambda^{an}(k)\Phi_B^{an}(k;r). \tag{72}$$

The coefficients $A_\lambda^{Gs}(k)$ and $B_\lambda^{an}(k)$ are determined variationally.

E. Matrix elements of the one-electron Hamiltonian and the overlapping matrix in the RSPFLAPW method

The variational problem which emerges from the Dirac equation for a crystal (35) with (72) reduces to the generalized eigenvalue and eigenfunction problem[12]

$$\begin{bmatrix} H_{AA} & H_{BA}^{\dagger} \\ H_{BA} & H_{BB} \end{bmatrix} \begin{vmatrix} A \\ B \end{vmatrix} = E \begin{bmatrix} O_{AA} & O_{BA}^{\dagger} \\ O_{BA} & O_{BB} \end{bmatrix} \begin{vmatrix} A \\ B \end{vmatrix}, \tag{73}$$

where indices are omitted for short. The matrix elements O and H (Overlapping and Hamiltonian, respectively) can be split into interstitial and MT components, and for the Hamiltonian, the latter can be split into spherical (kinetic energy and the $l = 0$ scalar potential) and non-spherical terms (including the contribution from the magnetic field).

1. The interstitial contribution to H and O

The interstitial contribution only exists from the functions of the first type. It is calculated from the definition of basis functions in the interstitial region (49) and the properties of Pauli matrices. After some manipulation we obtain the following.

The overlapping integral is

$$O_{AA}^{Gs;G's'}(k)|_{\Omega_I} = \frac{N_{k+G}N_{k+G'}}{\Omega_0} \int_{\Omega_I} \mathrm{e}^{\mathrm{i}(\mathbf{G}'-\mathbf{G})r} \mathrm{d}r \left\{ \delta_{ss'} + \frac{c^2}{(c^2+\epsilon_{k+G}^{+})(c^2+\epsilon_{k+G'}^{+})} \right.$$
$$\left. \times \left[(k+G)\cdot(k+G')\delta_{ss'} + \mathrm{i}[(k+G)\times(k+G')]\cdot < u_s|\boldsymbol{\sigma}|u_{s'} > \right] \right\}. \tag{74}$$

Matrix elements of the kinetic energy operator are

$$(H_{kin})_{AA}^{Gs;G's'}(k)|_{\Omega_I} = \epsilon_{k+G'}^{+} O_{AA}^{Gs;G's'}(k)|_{\Omega_I}. \tag{75}$$

Matrix elements of the scalar potential are

$$V_{AA}^{Gs;G's'}(k)|_{\Omega_I} = \frac{N_{k+G}N_{k+G'}}{\Omega_0} \int_{\Omega_I} V(r)\mathrm{e}^{\mathrm{i}(\mathbf{G}'-\mathbf{G})r} \mathrm{d}r \{ \delta_{ss'} + \frac{c^2}{(c^2+\epsilon_{k+G}^{+})(c^2+\epsilon_{k+G'}^{+})}$$
$$\times \left[(k+G)\cdot(k+G')\delta_{ss'} + \mathrm{i}[(k+G)\times(k+G')]\cdot < u_s|\boldsymbol{\sigma}|u_{s'} > \right] \}. \tag{76}$$

Matrix elements of the magnetic field are

$$B_{AA}^{Gs;G's'}(k)|_{\Omega_I} = \frac{N_{k+G}N_{k+G'}}{\Omega_0}\int_{\Omega_I} B(r)\mathrm{e}^{\mathrm{i}(\mathbf{G}'-\mathbf{G})r}\mathrm{d}r\{n_B\cdot < u_s|\boldsymbol{\sigma}|u_{s'} > -\frac{c^2}{(c^2+\epsilon_{k+G}^+)(c^2+\epsilon_{k+G'}^+)}[(n_B\cdot(k+G))((k+G')\cdot < u_s|\boldsymbol{\sigma}|u_{s'} >) +(n_B\cdot(k+G'))((k+G)\cdot < u_s|\boldsymbol{\sigma}|u_{s'} >) -((k+G)\cdot(k+G'))(n_B\cdot < u_s|\boldsymbol{\sigma}|u_{s'} >) -\mathrm{i}n_B\cdot[(k+G)\times(k+G')]\delta_{ss'}]\}, \quad (77)$$

where the vector n_B shows the direction of the magnetic field.

2. The contribution of overlapping and the spherical part of the Hamiltonian in the MT-spheres to the matrix elements

The matrices of the overlapping integrals and the spherical Hamiltonian in the MT-spheres are diagonal in $(il\mu)$. Using (65) and (71) yields

$$(H_{MT}-EO)_{AA}^{Gs;G's'}(k)|_{MT} = \sum_a\sum_{il\mu} \{y_1^{*ail\mu}(k+G,s)y_1^{ail\mu}(k+G',s')\int_{\Omega_a} R_1^{\dagger ail\mu}(r)[H_{kin}+V_0-E]R_1^{ail\mu}(r)\mathrm{d}r +y_1^{*ail\mu}(k+G,s)y_2^{ail\mu}(k+G',s')\int_{\Omega_a} R_1^{\dagger ail\mu}(r)[H_{kin}+V_0-E]R_2^{ail\mu}(r)\mathrm{d}r +y_2^{*ail\mu}(k+G,s)y_1^{ail\mu}(k+G',s')\int_{\Omega_a} R_2^{\dagger ail\mu}(r)[H_{kin}+V_0-E]R_1^{ail\mu}(r)\mathrm{d}r +y_2^{*ail\mu}(k+G,s)y_2^{ail\mu}(k+G',s')\int_{\Omega_a} R_2^{\dagger ail\mu}(r)[H_{kin}+V_0-E]R_2^{ail\mu}(r)\mathrm{d}r\}, \quad (78)$$

$$(H_{MT}-EO)_{BA}^{an;G's'}(k)|_{MT} = \sum_{i'l'\mu'} \{y_1^{ai'l'\mu'}(k+G',s')\int_{\Omega_a} R_3^{\dagger an}(r)[H_{kin}+V_0-E]R_1^{ai'l'\mu'}(r)\mathrm{d}r +y_2^{ai'l'\mu'}(k+G',s')\int_{\Omega_a} R_3^{\dagger an}(r)[H_{kin}+V_0-E]R_2^{ai'l'\mu'}(r)\mathrm{d}r\}, \quad (79)$$

$$(H_{MT}-EO)_{BB}^{a,nn'}|_{MT} = \int_{\Omega_a} R_3^{\dagger an}(r)[H_{kin}+V_0-E]R_3^{an'}(r)\mathrm{d}r. \quad (80)$$

The most demanding expression (78) can be simplified through explicit summation over moment projections with use of (66) for y_1 and y_2 and the identity (proved from the explicit expressions for Clebsch-Gordan coefficients (53) and the theorem of spherical harmonic summation)

$$\sum_{\mu} C_{is}^{l\mu} C_{is'}^{l\mu} Y_{l\mu-s}(\widehat{\mathbf{k}+\mathbf{G}}) Y_{l\mu-s'}^{*}(\widehat{\mathbf{k}+\mathbf{G}'}) = \frac{|\kappa|}{4\pi} P_l(\mathbf{k}+\widehat{\mathbf{G};\mathbf{k}}+\mathbf{G}')\delta_{ss'} + \frac{iS_\kappa}{4\pi} P_l'(\mathbf{k}+\widehat{\mathbf{G};\mathbf{k}}+\mathbf{G}') \frac{[(\mathbf{k}+\mathbf{G})\times(\mathbf{k}+\mathbf{G}')]\cdot\langle s|\sigma|s'\rangle}{|\mathbf{k}+\mathbf{G}|\cdot|\mathbf{k}+\mathbf{G}'|}, \tag{81}$$

where the relativistic quantum number $\kappa = l(l+1) - j(j+1) - 1/4$ and S_κ is the sign of κ. After some manipulation we obtain

$$\begin{aligned}
(H_{MT} - EO)_{AA}^{Gs;G's'}(k)|_{MT} = \sum_a \frac{4\pi}{\Omega} e^{i(\mathbf{G}'-\mathbf{G})\mathbf{a}} N_{k+G} N_{k+G'} \sum_{il} \Big[& |\kappa| P_l(\mathbf{k}+\widehat{\mathbf{G};\mathbf{k}}+\mathbf{G}')\delta_{ss'} \\
& + iS_\kappa P_l'(\mathbf{k}+\widehat{\mathbf{G};\mathbf{k}}+\mathbf{G}') \frac{[(\mathbf{k}+\mathbf{G})\times(\mathbf{k}+\mathbf{G}')]\cdot\langle s|\sigma|s'\rangle}{|\mathbf{k}+\mathbf{G}|\cdot|\mathbf{k}+\mathbf{G}'|} \Big] \\
\times \Big\{ j_l(|\mathbf{k}+\mathbf{G}|S_a) j_l(|\mathbf{k}+\mathbf{G}'|S_a) & \int_{\Omega_a} R_1^{\dagger ail\mu}(r)[H_{kin}+V_0-E]\, R_1^{ail\mu}(r)\mathrm{d}r \\
& + \frac{S_a^2 c^2 |\mathbf{k}+\mathbf{G}'|}{2(c^2+E_{k+G'}^{+})} i^{2i-1} j_l(|\mathbf{k}+\mathbf{G}|S_a) j_{l+2i}(|\mathbf{k}+\mathbf{G}'|S_a) \\
& \times \int_{\Omega_a} R_1^{\dagger ail\mu}(r)[H_{kin}+V_0-E] R_2^{ail\mu}(r)\mathrm{d}r \\
& + \frac{S_a^2 c^2 |\mathbf{k}+\mathbf{G}|}{2(c^2+E_{k+G}^{+})} (-i)^{2i-1} j_{l+2i}(|\mathbf{k}+\mathbf{G}|S_a) j_l(|\mathbf{k}+\mathbf{G}'|S_a) \\
& \times \int_{\Omega_a} R_2^{\dagger ail\mu}(r)[H_{kin}+V_0-E] R_1^{ail\mu}(r)\mathrm{d}r \\
& + \frac{S_a^4 c^4 |\mathbf{k}+\mathbf{G}|\cdot|\mathbf{k}+\mathbf{G}'|}{4(c^2+E_{k+G}^{+})(c^2+E_{k+G'}^{+})} j_{l+2i}(|\mathbf{k}+\mathbf{G}|S_a) j_{l+2i}(|\mathbf{k}+\mathbf{G}'|S_a) \\
& \times \int_{\Omega_a} R_2^{\dagger ail\mu}(r)[H_{kin}+V_0-E] R_2^{ail\mu}(r)\mathrm{d}r \Big\}.
\end{aligned} \tag{82}$$

Here summation over total moment projections is absent. The radial integrals are calculated analytically from (50, 51, 61, 62, 59, 60).

3. The contribution of the non-spherical potential and the magnetic field in the MT-spheres to the matrix elements

The non-spherical contributions of the effective potential and the contributions of magnetic field to Hamiltonian elements are calculated as

$$H_{AA}^{Gs;G's'}(k)|_{NMT} = \sum_{a} \sum_{il\mu;i'l'\mu'} \{y_1^{*ail\mu}(k+G,s) y_1^{ai'l'\mu'}(k+G',s') \int_{\Omega_a} R_1^{\dagger ail\mu}(r) \hat{H}_{NMT} R_1^{ai'l'\mu'}(r) \mathrm{d}r + y_1^{*ail\mu}(k+G,s) y_2^{ai'l'\mu'}(k+G',s') \int_{\Omega_a} R_1^{\dagger ail\mu}(r) \hat{H}_{NMT} R_2^{ai'l'\mu'}(r) \mathrm{d}r + y_2^{*ail\mu}(k+G,s) y_1^{ai'l'\mu'}(k+G',s') \int_{\Omega_a} R_2^{\dagger ail\mu}(r) \hat{H}_{NMT} R_1^{ai'l'\mu'}(r) \mathrm{d}r + y_2^{*ail\mu}(k+G,s) y_2^{ai'l'\mu'}(k+G',s') \int_{\Omega_a} R_2^{\dagger ail\mu}(r) \hat{H}_{NMT} R_2^{ai'l'\mu'}(r) \mathrm{d}r\}, \quad (83)$$

$$H_{BA}^{an;G's'}(k)|_{NMT} = \sum_{i'l'\mu'} \{y_1^{ai'l'\mu'}(k+G',s') \int_{\Omega_a} R_3^{\dagger an}(r) \hat{H}_{NMT} R_1^{ai'l'\mu'}(r) \mathrm{d}r + y_2^{ai'l'\mu'}(k+G',s') \int_{\Omega_a} R_3^{\dagger an}(r) \hat{H}_{NMT} R_2^{ai'l'\mu'}(r) \mathrm{d}r\}, \quad (84)$$

$$H_{BB}^{a,nn'}|_{NMT} = \int_{\Omega_a} R_3^{\dagger an}(r) \hat{H}_{NMT} R_3^{an'}(r) \mathrm{d}r. \quad (85)$$

Here non-spherical scalar potential and magnetic field integrals are calculated with the representation

$$H_{NMT}(r) = \sum_{l\neq 0 m} V_{lm}(r) Y_{lm}(\widehat{r}) + \sum_{lm} B_{lm}(r) Y_{lm}(\widehat{r}), \quad (86)$$

definitions (61, 62, 67) and identity (52).

In what the splitting of the matrix elements into spherical (Section IV E 2) and non-spherical contributions is advantageous is that in expression (83) whose calculation requires considerable time, summation over l can only be done for physically significant l (usually to $l = 2$ or 3), while in the easier-to-calculate formulas from Section IV E 2, the required continuity of basis functions for the correct treatment of the kinetic energy operator results in the maximal $l \geq 8$.

F. Correction to matrix elements with allowance for Breit interaction

Since we calculate the effects of the Breit interaction by representing the total electron wave function of the system as one Slater determinant, the contribution to the total energy will be

$$E_{tot}^{Br} = \frac{1}{2}\sum_{jj'}\{\langle\psi_j^*(\mathbf{r})\psi_{j'}^*(\mathbf{r}')B(\mathbf{r},\mathbf{r}')\psi_j(\mathbf{r})\psi_{j'}(\mathbf{r}')\rangle - \langle\psi_j^*(\mathbf{r})\psi_{j'}^*(\mathbf{r}')B(\mathbf{r},\mathbf{r}')\psi_{j'}(\mathbf{r})\psi_j(\mathbf{r}')\rangle\}, \quad (87)$$

where the indices j, j' run over core states and valence levels, and the operator $B(\mathbf{r},\mathbf{r}')$ is the second term in (27).

Varying the valence orbitals and using the expansion of the valence wave functions (72) and representations of basis functions (65,71) gives the following contributions to the matrix elements (the same notation as in IV E)

$$\begin{aligned} H_{AA}^{Gs;G's'}(k)|_{Br} = &\sum_a\sum_j\sum_{il\mu;i'l'\mu'}\sum_{k,k'=1,2} y_k^{*ail\mu}(k+G,s)y_{k'}^{ai'l'\mu'}(k+G',s') \\ &\{\int_{\Omega_a} R_k^{\dagger ail\mu}(r')\langle\psi_j^*(\mathbf{r})B(\mathbf{r},\mathbf{r}')\psi_j(\mathbf{r})\rangle R_{k'}^{ai'l'\mu'}(r')\mathrm{d}r' \\ &-\int_{\Omega_a} R_k^{\dagger ail\mu}(r')\langle\psi_j^*(\mathbf{r})B(\mathbf{r},\mathbf{r}')R_{k'}^{ai'l'\mu'}(r')\rangle\psi_j(\mathbf{r})\mathrm{d}r'\}, \end{aligned} \quad (88)$$

$$\begin{aligned} H_{BA}^{an;G's'}(k)|_{Br} = &\sum_j\sum_{i'l'\mu'}\sum_{k'=1,2} y_{k'}^{ai'l'\mu'}(k+G',s') \\ &\{\int_{\Omega_a} R_3^{\dagger an}(r')\langle\psi_j^*(\mathbf{r})B(\mathbf{r},\mathbf{r}')\psi_j(\mathbf{r})\rangle R_{k'}^{ai'l'\mu'}(r')\mathrm{d}r' \\ &-\int_{\Omega_a} R_3^{\dagger an}(r')\langle\psi_j^*(\mathbf{r})B(\mathbf{r},\mathbf{r}')R_{k'}^{ai'l'\mu'}(r')\rangle\psi_j(\mathbf{r})\mathrm{d}r'\}, \end{aligned} \quad (89)$$

$$\begin{aligned} H_{BB}^{a,nn'}|_{Br} = &\sum_j \\ &\{\int_{\Omega_a} R_3^{\dagger an}(r')\langle\psi_j^*(\mathbf{r})B(\mathbf{r},\mathbf{r}')\psi_j(\mathbf{r})\rangle R_3^{an'}(r')\mathrm{d}r' \\ &-\int_{\Omega_a} R_3^{\dagger an}(r')\langle\psi_j^*(\mathbf{r})B(\mathbf{r},\mathbf{r}')R_3^{an'}(r')\rangle\psi_j(\mathbf{r})\mathrm{d}r'\}, \end{aligned} \quad (90)$$

Write the operator $B(\mathbf{r},\mathbf{r}')$ in component-wise form

$$B(\mathbf{r},\mathbf{r}')=\sum_{\beta\gamma}\alpha_{\beta,r}\alpha_{\gamma,r'}[-\frac{\delta_{\beta\gamma}}{|\mathbf{r}-\mathbf{r}'|}-\frac{(r-r')_\beta(r-r')_\gamma}{|\mathbf{r}-\mathbf{r}'|^3}], \tag{91}$$

and represent it in the orthonormal basis of all possible products of the large and small components of radial functions (similarly to what was done for the non-relativistic case in[14] where the product basis was used for the implementation of the GW method):

$$B(\mathbf{r},\mathbf{r}')=\sum_{\beta\gamma}\alpha_{\beta,r}\alpha_{\gamma,r'}\sum_{LL'}\sum_{tt'}\Pi_{tL}(\mathbf{r})M^{\beta\gamma}_{tL,t'L'}\Pi_{t'L'}(\mathbf{r}'), \tag{92}$$

where

$$\Pi_{tL}(\mathbf{r})=\Pi_{tL}(r)Y_L(\hat{\mathbf{r}}) \tag{93}$$

and

$$M^{\beta\gamma}_{tL,t'L'}=\int\int\Pi_{tL}(\mathbf{r})[-\frac{\delta_{\beta\gamma}}{|\mathbf{r}-\mathbf{r}'|}-\frac{(r-r')_\beta(r-r')_\gamma}{|\mathbf{r}-\mathbf{r}'|^3}]\Pi_{t'L'}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{94}$$

Not difficult, but rather lengthy details in the calculation of $M^{\beta\gamma}_{tL,t'L'}$ will be presented in the next report along with data of the code structure.

With the product basis the expressions in the braces of (88,89,90) are reduced to sums of the products of integrals of three functions, which can be calculated with standard methods.

$$\begin{aligned}
&\int_{\Omega_a}R_k^{\dagger\,ail\mu}(r')\langle\psi_j^*(\mathbf{r})B(\mathbf{r},\mathbf{r}')\psi_j(\mathbf{r})\rangle R_{k'}^{ai'l'\mu'}(r')\mathrm{d}r'\\
&\qquad-\int_{\Omega_a}R_k^{\dagger\,ail\mu}(r')\langle\psi_j^*(\mathbf{r})B(\mathbf{r},\mathbf{r}')R_{k'}^{ai'l'\mu'}(r')\rangle\psi_j(\mathbf{r})\mathrm{d}r'\\
&=\sum_{\beta\gamma}\sum_{LL'}\sum_{tt'}\{\int d\mathbf{r}'R_k^{\dagger\,ail\mu}(r')\alpha_{\gamma,r'}R_{k'}^{ai'l'\mu'}(r')\Pi^a_{t'L'}(\mathbf{r}')M^{a,\beta\gamma}_{tL,t'L'}\\
&\qquad\qquad\times<\psi_j^*(\mathbf{r})\alpha_{\beta,r}\psi_j(\mathbf{r})\Pi_{tL}(\mathbf{r})>\\
&\qquad-\int d\mathbf{r}'R_k^{\dagger\,ail\mu}(r')\alpha_{\gamma,r'}\psi_j(\mathbf{r})\Pi^a_{t'L'}(\mathbf{r}')M^{a,\beta\gamma}_{tL,t'L'}\\
&\qquad\qquad\times<\psi_j^*(\mathbf{r})\alpha_{\beta,r}R_{k'}^{ai'l'\mu'}(r')\Pi_{tL}(\mathbf{r})>\},
\end{aligned} \tag{95}$$

Quite similar formulas are true for expressions in (89) and (90).

Conclusion and future plans

The report described a general theoretical procedure which would be used for evaluating the effect of the Breit interaction on the electronic structure of some f-electron elements. Calculated results and details of the computer code will be presented in the next quarterly report.

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