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# On the separability of relativistic electron propagators

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**Abstract.** In this contribution we examine the separability of relativistic electron propagators. Both, magnetic and non-magnetic systems are studied on the basis of the Kohn-Sham-Dirac equation. We find a Dirac-Green's function in excellent agreement with recent calculations utilizing the left and right-handed solutions to the Dirac equation. Starting from these Dirac-Green's functions we re-derive a rotation matrix formalism that was shown to result in separable scattering matrices in the non-relativistic case. It turns out, that spin-dependent scattering matrices can be formulated which are closely related to their non-relativistic counterparts. These matrices incorporate spin-flip and non spin-flip processes on an equal footing, but are irreducible to sums over composite rotation matrices. The latter result is a major drawback for numerical applications since electron scattering in terms of composite rotations had drawn a lot of attention recently.

**PACS.** 79.60.-i Photoemission and photoelectron spectra – 61.14.Dc Theories of diffraction and scattering

## 1 Introduction

Photoemission is one of the most frequently used tools to identify the chemical composition, atomic geometry, and electronic structure of solids and their surfaces [1]. The emission of electrons from an initial state to some final state due to electron-photon interactions can be formulated according to Fermi's Golden Rule. A key difference between atomic and solid state photoemission is the occurrence of final state scattering of the electronic wavefunctions in the latter case. Delocalized initial states should be calculated within the framework of scattering theory as well. It is therefore customary to factorize the matrix elements appearing in the Golden Rule into purely atomic transition probabilities leading to selection rules and path operators which guide the outgoing electrons through the atomic environment. Within this frame it becomes possible to calculate anisotropy functions that separate atomic from solid state effects. The path operators can be formulated in terms of free particle Green's functions and single site scattering matrices. In numerical applications the advantages of Green's function methods are limited by the number of atoms in the slab (or cluster) and the scattering order to which the calculations should be carried out. One way to overcome these limitations, at least partially, is to express each Green's function in terms of rotation matrices and one-dimensional propagators as suggested by Rehr and Albers [2]. Here, the scattering path of an electron is described by a sum over scattering and termination matrices that depend on composite rotations only. Moreover, each scattering matrix is a sum over solely one angular momentum and therefore the complicated momentum mixing inherent in the exact Green's function method is lifted.

The Rehr-Albers formalism, however, does not explicitly treat electronic spin states and their coupling mechanisms. The inclusion of spin states demands to formulate the theory within the framework of the Dirac theory. Compared to the non-relativistic description of photoemission depicted above, relativistic treatments comprise a number of new features like couplings between the spin and orbital degrees of freedom. During the last decade relativistic theories have been used frequently to relate the structure of surfaces to their magnetic order [3–5]. In addition, such theories are necessary and suitable when discussing circular and magnetic dichroisms as was shown recently by Tong *et al.* [6]. In the majority of cases the emission process itself is formulated within the framework of the Dirac theory while the scattering path of the outgoing electrons is described by the non-relativistic Schrödinger theory. In this contribution explicit expressions for relativistic scattering path operators are extracted and it will be shown that these operators can be reduced to spin-dependent scattering matrices which are fully angular momentum decoupled. We also show, that the Rehr-Albers formalism can not be generalized to the relativistic case since the advantage of utilizing composite rotation matrices is lost. The latter proof can be viewed as a serious shortfall since these composite rotations are essential for deriving

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a numerically fast theory. The situation is even worse in the case of ferromagnetic materials where the procedure breaks down in the beginning.

## 2 Separability of structure constants

Starting from the Golden Rule photoemission intensities can be written as a double sum over all possible scattering paths and final state quantum numbers $L_\mathrm{f} = (l_\mathrm{f}, m_\mathrm{f})$ according to [2]

$$I(\mathbf{k}) \propto \left| \sum_{path} \sum_{L_\mathrm{f}} G_{L_\mathrm{D},L_\mathrm{f}}(\mathbf{R}_i) M_{\mathrm{f,i}} \right|^2 . \quad (1)$$

Therein $M_{\mathrm{f,i}} = \langle \Psi_\mathrm{f} | \Delta | \Psi_\mathrm{i} \rangle$ denotes the transition matrix from an initial to a final state due to an interaction operator $\Delta$, the $G_{L_\mathrm{D},L_\mathrm{f}}(\mathbf{R}_i)$ are matrix elements of Green's functions in an angular momentum and site basis, and $L_\mathrm{D} = (l_\mathrm{D}, m_\mathrm{D})$ is an angular momentum expansion at the point of detection. Our model system may consist of an emitting atom located at $\mathbf{R}_0$, a neighboring atom acting as a scattering center positioned at $\mathbf{R}_1$, and a point of detection $\mathbf{R}_\mathrm{D}$ far away from the atomic ensemble. Within the single scattering approximation the Dyson equation reads

$$G_{L_\mathrm{D},L_\mathrm{f}}(\mathbf{R}_0, \mathbf{R}_1, \mathbf{R}_\mathrm{D}) = G^{(0)}_{L_\mathrm{D},L_\mathrm{f}}(\boldsymbol{\rho}_{\mathrm{D},0}) + \sum_{L_1} G^{(0)}_{L_\mathrm{D},L_1}(\boldsymbol{\rho}_{\mathrm{D},1}) t_{L_1}(\mathbf{R}_1) G^{(0)}_{L_1,L_\mathrm{f}}(\boldsymbol{\rho}_{1,0}). \quad (2)$$

Herein the $L_\mu$ are sets of quantum numbers $L_\mu = (l_\mu, m_\mu)$ and the $\boldsymbol{\rho}_{i+1,i} = k(\mathbf{R}_{i+1} - \mathbf{R}_i)$ are dimensionless bond vectors. The first term, $G^{(0)}_{L_\mathrm{D},L_\mathrm{f}}(\boldsymbol{\rho}_{\mathrm{D},0})$, generates an unscattered wave travelling from the emitting site $\mathbf{R}_0$ towards the detector at point $\mathbf{R}_\mathrm{D}$. The point of detection is positioned at some distance far away from the atomic ensemble and for this the quantum number $L_\mathrm{D}$ is given through the set $(0, 0)$ since this definition leads to plane wave final states. The second term describes single scattering, that is wave propagation from the emitting site $\mathbf{R}_0$ to a scattering center positioned at $\mathbf{R}_1$, conversion of the incoming wave into a scattered wave due to the single site scattering matrix $t_{L_1}(\mathbf{R}_1)$ and finally the propagation of the scattered wave from $\mathbf{R}_1$ towards the detector. The single site scattering matrices are fully determined through the scattering phase shifts and depend parametrically on the position vectors $\mathbf{R}_i$ while functionally they depend on energy.

The definition given above demonstrates, that angular momentum and site expansions of the free particle Green's functions can be understood as propagators leading an outgoing electron from one scattering center to another. Moreover, since these propagators depend on the coordinates of the atomic environment they are sometimes referred to as "structure constants". Such structure constants also appear in theories utilizing scattering path operators [7] and secular equations for Korringa-Kohn-Rostocker determinants [8]. The first step to derive a separable representation of the structure constants consists in applying the Rotation-Translation-Transformation [9] to them. This can be done by writing

$$G^{(0)}_{L,L'}(\boldsymbol{\rho}) = \frac{\mathrm{e}^{\mathrm{i}\rho}}{\rho} \sum_{\mu=-l}^{l} R^l_{m,\mu}(\Omega_\rho^{-1}) g^{|\mu|}_{ll'}(\rho) R^{l'}_{\mu,m'}(\Omega_\rho). \quad (3)$$

The $R^l_{m,\mu}(\Omega_\rho)$ are rotation matrices depending on Euler angles $\Omega_\rho = (\alpha, \beta, \gamma)$ which rotate the coordinate frame. After the rotation the $z$-axis points along some internuclear axis. The dimensionless $z$-axis propagator $g^{|\mu|}_{ll'}(\rho)$ describes the motion of an electron from one atomic center to another. This term depends on the $z$-coordinate only because the $z$-axis of the coordinate frame now parallels the interatomic bond. In the last step the coordinate frame is rotated back to its initial position which is described by $R^l_{m,\mu}(\Omega_\rho^{-1})$ with $\Omega_\rho = (-\gamma, -\beta, -\alpha)$. At this point it is necessary (a) to find an explicit expression for the $g^\mu_{ll'}(\rho)$ and (b) to decouple the angular momenta $l$ and $l'$. One way to proceed is to multiply equation (3) by $R^l_{m,\mu'}(\Omega_\rho)$ from the left and by $R^{l'}_{\mu,m'}(\Omega_\rho^{-1})$ from the right. Then both sides have to be summed over the indices $m$ and $m'$ and the orthogonality of the rotation matrices has to be taken into account. This leads to

$$g^\mu_{ll'}(\rho) = \rho \mathrm{e}^{-i\rho} G^{\mu,\mu}_{ll'}(\rho) \quad (4)$$

with

$$G^{\mu\mu}_{ll'}(\rho) = \sum_{mm'} R^l_{m\mu}(\Omega_\rho) G^{(0)}_{LL'}(\boldsymbol{\rho}) R^{l'}_{\mu m'}(\Omega_\rho^{-1}). \quad (5)$$

It should be emphasized that the $G^{\mu\mu}_{ll'}(\rho)$ are diagonal in $\mu$ which leads to less effort in numerical applications. We now have to find a separable form of equation (4). This second step includes comprehensive analytic work and therefore we only sketch the basics here. A more detailed discussion is given in the original work [2]. Starting from the integral representation of the free particle Green's function Rehr and Albers showed that after some formal manipulations on the integration boundaries and the subsequent application of a special type of transformation the $z$-axis propagators can be written as

$$g^\mu_{ll'}(\rho) = \sum_{\nu=0}^{\tau} \tilde{\gamma}^l_{\mu\nu}(\rho) \gamma^{l'}_{\mu\nu}(\rho) \quad (6)$$

with $\tau = \min(l, l' - \mu)$ and

$$\gamma^l_{\mu\nu}(\rho) = (-1)^\mu N_{l\mu} \frac{z^{\mu+\nu}}{(\mu+\nu)!} \frac{\mathrm{d}^{\mu+\nu}}{\mathrm{d}z^{\mu+\nu}} C_l(z) \quad (7)$$

$$\tilde{\gamma}^l_{\mu\nu}(\rho) = \frac{(2l+1)}{N_{l\mu}} \frac{z^\nu}{\nu!} \frac{\mathrm{d}^\nu}{\mathrm{d}z^\nu} C_l(z). \quad (8)$$

Here, $z = 1/i\rho$ and the polynomials $C_l(z)$ satisfy the recurrence relation

$$\frac{\mathrm{d}^m}{\mathrm{d}z^m} \{ C_{l+1} = C_{l-1} - (2l+1) z C_l \} \quad (9)$$

together with the initial conditions $C_0(z) = 1$ and $C_1(z) = 1 - z$.

It is now straightforward to insert these $z$-axis propagators into equation (3) yielding to

$$G^{(0)}_{LL'}(\boldsymbol{\rho}) = \frac{\mathrm{e}^{\mathrm{i}\rho}}{\rho} \sum_{\mu=-l}^{l} \sum_{\nu=0}^{\tau} R^{l}_{m\mu}(\Omega_\rho^{-1}) \tilde{\gamma}^{l}_{\mu\nu}(\rho) \gamma^{l'}_{\mu\nu}(\rho) R^{l'}_{\mu m'}(\Omega_\rho) \tag{10}$$

$$\stackrel{\mathrm{def}}{=} \frac{\mathrm{e}^{\mathrm{i}\rho}}{\rho} \sum_{\lambda} \tilde{\Gamma}^{L}_{\lambda}(\boldsymbol{\rho}) \Gamma^{L'}_{\lambda}(\boldsymbol{\rho}). \tag{11}$$

Thus, we have finally reached the desired decoupled form of the structure constants. Equation (10) became prominent for numerical applications [11] during the past years because if substituted into the Dyson equation (2) it can be separated according to

$$G_{L_\mathrm{D},L_\mathrm{f}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_1, \mathbf{R}_0) = M_{L_\mathrm{D},L_\mathrm{f}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_0) + N_{L_\mathrm{D},L_\mathrm{f}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_1, \mathbf{R}_0) \tag{12}$$

with

$$M_{L_\mathrm{D},L_\mathrm{f}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_0) = \frac{\mathrm{e}^{\mathrm{i}\rho_{\mathrm{D},0}}}{\rho_{\mathrm{D},0}} \sum_{\lambda} \tilde{\Gamma}^{L_\mathrm{D}}_{\lambda}(\boldsymbol{\rho}_{\mathrm{D},0}) \Gamma^{L_\mathrm{f}}_{\lambda}(\boldsymbol{\rho}_{\mathrm{D},0}) \tag{13}$$

$$N_{L_\mathrm{D},L_\mathrm{f}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_1, \mathbf{R}_0) = \frac{\mathrm{e}^{\mathrm{i}\rho_{\mathrm{D},1}}}{\rho_{\mathrm{D},1}} \frac{\mathrm{e}^{\mathrm{i}\rho_{1,0}}}{\rho_{1,0}} \sum_{L_1} \sum_{\lambda,\lambda'} \tilde{\Gamma}^{L_\mathrm{D}}_{\lambda}(\boldsymbol{\rho}_{\mathrm{D},1}) \times \Gamma^{L_1}_{\lambda}(\boldsymbol{\rho}_{\mathrm{D},1}) t_{l_1}(\mathbf{R}_1) \tilde{\Gamma}^{L_1}_{\lambda'}(\boldsymbol{\rho}_{1,0}) \Gamma^{L_\mathrm{f}}_{\lambda'}(\boldsymbol{\rho}_{1,0}). \tag{14}$$

Now we re-arrange the $N_{L_\mathrm{D},L_\mathrm{f}}$ term and sum over $L_1$ first. Then we define the functions

$$F_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) = \sum_{L_1} \Gamma^{L_1}_{\lambda}(\boldsymbol{\rho}_{\mathrm{D},1}) t_{l_1}(\mathbf{R}_1) \tilde{\Gamma}^{L_1}_{\lambda'}(\boldsymbol{\rho}_{1,0}) \tag{15}$$

and

$$T^{L_\mathrm{D},L_0}_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) = \tilde{\Gamma}^{L_\mathrm{D}}_{\lambda}(\boldsymbol{\rho}_{\mathrm{D},1}) \Gamma^{L_\mathrm{f}}_{\lambda'}(\boldsymbol{\rho}_{1,0}) \tag{16}$$

where the latter one can be viewed as a termination function since it incorporates the quantum numbers of the initial and final states. With these definitions equation (12) reads

$$G_{L_\mathrm{D},L_\mathrm{f}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_1, \mathbf{R}_0) = \frac{\mathrm{e}^{\mathrm{i}\rho_{\mathrm{D},0}}}{\rho_{\mathrm{D},0}} \sum_{\lambda} T^{L_\mathrm{D},L_\mathrm{f}}_{\lambda,\lambda}(\boldsymbol{\rho}_{\mathrm{D},0}) + \frac{\mathrm{e}^{\mathrm{i}\rho_{\mathrm{D},1}}}{\rho_{\mathrm{D},1}} \frac{\mathrm{e}^{\mathrm{i}\rho_{1,0}}}{\rho_{1,0}} \sum_{\lambda,\lambda'} T^{L_\mathrm{D},L_\mathrm{f}}_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) F_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}). \tag{17}$$

Inspecting the inner nature of the $F_{\lambda,\lambda'}$ we find

$$F_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) = \sum_{L_1} t_{l_1}(\mathbf{R}_1) \gamma^{l_1}_{\mu\nu}(\rho_{\mathrm{D},1}) R^{l_1}_{\mu m_1}(\Omega_{\rho_{\mathrm{D},1}}) \times R^{l_1}_{\mu' m_1}(\Omega^{-1}_{\rho_{1,0}}) \tilde{\gamma}^{l_1}_{\mu'\nu'}(\rho_{1,0}) \tag{18}$$

$$= \sum_{l_1} t_{l_1}(\mathbf{R}_1) \gamma^{l_1}_{\mu\nu}(\rho_{\mathrm{D},1}) R^{l_1}_{\mu\mu'}(\Omega_{\rho_{\mathrm{D},1}\rho_{1,0}}) \times \tilde{\gamma}^{l_1}_{\mu'\nu'}(\rho_{1,0}). \tag{19}$$

In this form the functions $F_{\lambda,\lambda'}$ only depend on the composite rotation matrices $R^{l_1}_{\mu\mu'}$ and for that a backrotation is not necessary. This elimination of backrotations drastically reduces the complexity of the formalism. From rotation matrix theory we also know that each such matrix can be factored as

$$R^{l_1}_{\mu\mu'}(\Omega_{\rho_{\mathrm{D},1}\rho_{1,0}}) = \mathrm{e}^{\mathrm{i}\tilde{\alpha}\mu} d^{l_1}_{\mu\mu'}(\tilde{\beta}) \mathrm{e}^{\mathrm{i}\tilde{\gamma}\mu'} \tag{20}$$

and this in turn allows us to write

$$F_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) = \mathrm{e}^{i\tilde{\alpha}\mu} f^{\tilde{\beta}}_{\lambda,\lambda'}(\rho_{\mathrm{D},1}, \rho_{1,0}) \mathrm{e}^{i\tilde{\gamma}\mu'} \tag{21}$$

with scattering factors $f_{\lambda,\lambda'}$ depending on bond lengths and scattering angles $\tilde{\beta}$ only and given through

$$f^{\tilde{\beta}}_{\lambda,\lambda'}(\rho_{\mathrm{D},1}, \rho_{1,0}) = \sum_{l_1} t_{l_1}(\mathbf{R}_1) \gamma^{l_1}_{\mu\nu}(\rho_{\mathrm{D},1}) d^{l_1}_{\mu\mu'}(\tilde{\beta}) \tilde{\gamma}^{l_1}_{\mu'\nu'}(\rho_{1,0}). \tag{22}$$

Moreover, by including multiple scattering, and therefore additional $F_{\lambda,\lambda'}$ terms, it can be shown that the scattering path depends on the additive angles $\omega_i = \tilde{\gamma}_i + \tilde{\alpha}_{i+1}$.

## 3 Relativistic formulation

There are two possible reasons to develop a relativistic formulation of electron emission and scattering. The first is related to kinematic effects like contractions and expansions of orbitals [10] caused by core electrons with Fermi momentum comparable to $mc$. Electronic orbitals less localized at the nuclei show a response contraction (or expansion) that may lead to bond length modifications in molecules. The second reason is linked to the inclusion of spin degrees of freedom in the description of emission and scattering processes. Spin-polarized photoemission is influenced by two different mechanisms. First, there is spin-orbit interaction between polarized electrons endowed with some magnetic moment and a scattering potential which is not necessarily spin polarized. Second, there is quantum mechanical exchange interaction between the magnetic moments of the electrons and the substrate. The inclusion of both effects can however be a cumbersome task. Therefore most of the early calculations were carried out within a hybrid formalism in which either spin-orbit or exchange interactions are excluded [13]. Later on, these lacks of completeness were removed by solving the 4-component Dirac equation rather than some scalar-relativistic approximation to it [4].

In the following we examine the applicability Rehr-Albers procedure to magnetic and non-magnetic systems. As in Section 2 we concentrate on the electron propagators. Recently, Ankudinov and Rehr also extended the Rehr-Albers formalism to the relativistic case [14]. Their calculations focussed on the emission matrix and had left the propagators in their non-relativistic form. Complementary, our work discusses the separability of the propagators in the relativistic case. We start from

the Kohn-Sham-Dirac Hamiltonian [15,16] in the absence of a magnetic field [17]

$$\mathcal{H}_{\rm D}\Psi_n = (\boldsymbol{\alpha}\mathbf{p} + \beta + V_{\rm eff}[n(\mathbf{r})]\mathbf{1}_{4\times4})\,\Psi_n = \epsilon_n\Psi_n \qquad (23)$$

with $\mathbf{p} = -i\,\nabla$ being the electron momentum and $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ as well as $\beta$ denote standard Dirac matrices. The effective potential $V_{\rm eff}$ is a functional of the electronic number density $n(\mathbf{r})$ and is chosen to be spherically symmetric and bounded by non-overlapping spheres. It contains the interactions between the electronic system and the nuclei through a Coulomb potential $V_{\rm ext}[n]$, the interactions between the electrons themselves through a Hartree potential $V_H[n]$, and an exchange-correlation potential $V_{\rm xc}[n]$ that accounts for exclusion principles and correlated motion within the many-electron system. The latter one has to be approximated and within the local density approximation (LDA) it can be written as

$$V_{\rm xc} \approx \epsilon_x \left\{1 + n\left(\frac{\delta\Phi_{\rm DF}(n)}{\delta n} + \frac{\delta\Phi_{\rm T}(n)}{\delta n}\right)\right\} + n\frac{\delta\epsilon_x}{\delta n}\left(\Phi_{\rm DF}(n) + \Phi_{\rm T}(n)\right) + \epsilon_{\rm c} + \frac{\delta\epsilon_{\rm c}}{\delta n} \qquad (24)$$

where $\Phi_{\rm DF}(n)$ and $\Phi_{\rm T}(n)$ are Dirac-Fock and Transverse corrections, respectively. They can be found in a work by MacDonald and Vosko [18]. Finally, the $\epsilon_n^2 = k_n^2 + 1$ represent single particle energies. A relativistic generalisation of the theory presented in Section 2 requires the derivation of single-site $t$-matrices and structure constants from the Kohn-Sham-Dirac Hamiltonian (23). The $t$-matrices can be obtained from solutions inside and outside the potential spheres by matching their values and slopes continuously at the sphere boundaries. Inside each sphere the solutions are expanded according to [19]

$$\Psi_n^{\rm in}(\mathbf{r}) = \sum_{\kappa,m_j} \frac{1}{r}\begin{bmatrix} f_\kappa(r)\ \chi_\kappa^{m_j}(\mathbf{r}) \\ ig_\kappa(r)\ \chi_{-\kappa}^{m_j}(\mathbf{r})\end{bmatrix} \qquad (25)$$

wherein $\kappa = \{\pm1, \pm2, \pm3,\ \cdots\}$ and the quantum numbers $m_j$ take the values $\{-j,\ -j+1,\ \cdots,\ j-1,\ j\}$ provided $j = |\kappa| - \frac{1}{2}$ is satisfied. The $\chi$'s are spin-angular functions defined by Clebsch-Gordon coefficients $\mathcal{C}$ and Pauli Spinors $\chi^{m_s}$

$$\chi_\kappa^{m_j} = \sum_{m_s=\uparrow,\downarrow} \mathcal{C}(l\,\frac{1}{2}\,j; m_j - m_s, m_s) Y_l^{m_j-m_s}(\hat{\mathbf{r}})\chi^{m_s} \qquad (26)$$

$$\chi_{-\kappa}^{m_j} = \sum_{m_s=\uparrow,\downarrow} \mathcal{C}(\bar{l}\,\frac{1}{2}\,j; m_j - m_s, m_s) Y_{\bar{l}}^{m_j-m_s}(\hat{\mathbf{r}})\chi^{m_s} \qquad (27)$$

with quantum numbers $l$ and $\bar{l}$ given through

$$l = \begin{cases} \kappa & \text{for} \quad \kappa > 0 \\ -\kappa - 1 & \text{for} \quad \kappa < 0 \end{cases} \qquad (28)$$

and

$$\bar{l} = \begin{cases} \kappa - 1 & \text{for} \quad \kappa > 0 \\ -\kappa & \text{for} \quad \kappa < 0. \end{cases} \qquad (29)$$

Outside the spheres the wave function is represented by the scattered wave form

$$\Psi_n^{\rm out}(\mathbf{r}) = \sum_{\kappa m_j} a_{\kappa m_j}^n \left\{J_\kappa^{m_j}(\mathbf{r}) + t_\kappa^n(\epsilon_n) H_\kappa^{m_j}(\mathbf{r})\right\} \qquad (30)$$

with $J_\kappa^{m_j}(\mathbf{r})$ and $H_\kappa^{m_j}(\mathbf{r})$ being Bessel and Hankel spinors with upper (u) and lower (l) components defined through $\left(S_\kappa = \frac{\kappa}{|\kappa|}\right)$

$$J_\kappa^{m_j}(\mathbf{r}) = \begin{bmatrix} J_{\kappa,m_j}^u(\mathbf{r}) \\ J_{\kappa,m_j}^l(\mathbf{r})\end{bmatrix} = \begin{bmatrix} j_l(k_n r)\chi_\kappa^{m_j}(\hat{r}) \\ \frac{ik_nS_\kappa}{\epsilon_n+1} j_{\bar{l}}(k_n r)\chi_{-\kappa}^{m_j}(\hat{r})\end{bmatrix} \qquad (31)$$

$$H_\kappa^{m_j}(\mathbf{r}) = \begin{bmatrix} H_{\kappa,m_j}^u(\mathbf{r}) \\ H_{\kappa,m_j}^l(\mathbf{r})\end{bmatrix} = ik_n(\epsilon_n+1)\begin{bmatrix} h_l(k_n r)\chi_\kappa^{m_j}(\hat{r}) \\ \frac{ik_nS_\kappa}{\epsilon_n+1} h_{\bar{l}}(k_n r)\chi_{-\kappa}^{m_j}(\hat{r})\end{bmatrix}. \qquad (32)$$

The details about the procedure are the same as in the non-relativistic case and have been derived elsewhere [20]. Here, it is important that the t-matrices in (30) solely depend on the quantum number $\kappa$. The formulation of a free particle Green's function is a problem that is slightly different from the non-relativistic case. The essential point is that the Green's function has to be constructed by dyadic products of free particle eigenstates rather than by scalar products as in the Kohn-Sham theory. Such dyadic products are defined through $\mathbf{A}\otimes\mathbf{B} = \mathbf{C} \equiv A_i \otimes B_j = C_{ij}$ where $\mathbf{A}$ and $\mathbf{B}$ are arbitrary tensors of rank one and the resultant $\mathbf{C}$ is of rank two. Therefore, the relativistic Green's Function can be written as

$$G_0(\mathbf{r},\mathbf{r}') = \sum_{\kappa,m_j}\left\{H_\kappa^{m_j}(\mathbf{r}) \otimes J_\kappa^{m_j+}(\mathbf{r}')\Theta(r-r') + J_\kappa^{m_j}(\mathbf{r}) \otimes H_\kappa^{m_j+}(\mathbf{r}')\Theta(r'-r)\right\} \qquad (33)$$

where the $\Theta(r-r')$ are usual step functions. This Green's function differs from that derived by Rose [19] since it is not possible to obtain the Green's function for $r < r'$ from that for $r' < r$ by simply interchanging $r$ and $r'$. This result has also been found by Tamura [21] who studied the relativistic Green's function in terms of the left and right handed solutions to the Dirac equation. Evaluating the dyadic products gives exactly the same elements of the $2\times2$ Green's matrix as derived by Tamura [22].

The last step in our calculation consists in deriving a multipolar expansion for $G_0$. In straightforward generalization of the non-relativistic results [23] we write

$$G_0(\mathbf{r}_m,\mathbf{r}'_n) = \sum_{\kappa m_j}\sum_{\kappa' m'_j} G_{\kappa',m'_j}^{\kappa,m_j}(\boldsymbol{\rho}_{mn}) \times\left\{J_\kappa^{m_j}(-\mathbf{r}) \otimes J_{\kappa'}^{m'_j}(\mathbf{r}')\Theta_{r>r'} + J_\kappa^{m_j}(\mathbf{r}) \otimes J_{\kappa'}^{m'_j}(-\mathbf{r}')\Theta_{r<r'}\right\} \qquad (34)$$

with cell centered coordinates $\mathbf{r}_i = \mathbf{r} - \mathbf{R}_i$ and bond vectors $\boldsymbol{\rho}_{mn} = k(\mathbf{R}_m - \mathbf{R}_n)$. Additionally, the relativistic structure constants can be obtained from their non-relativistic counterparts by means of the Onodera-Okazaki

relation [24]

$$G^{\kappa,m_j}_{\kappa',m'_j}(\boldsymbol{\rho}_{mn}) = \sum_{m_s=\uparrow,\downarrow} C^{\kappa,m_j}_{m_s,m_j-m_s} G^{l',m'_j-m_s}_{l,m_j-m_s}(\boldsymbol{\rho}_{mn}) C^{\kappa',m'_j}_{m_s,m'_j-m_s} \tag{35}$$

with $C^{k,l}_{i,j}$ denoting Clebsch-Gordon coefficients. This relation is essentially useful for separating the relativistic structure constants since it allows us to use the results obtained in the last section. A re-derivation of the relation has also been presented by Wang *et al.* [25]. Then the structure constants can be written as

$$G^{\kappa,m_j}_{\kappa',m'_j}(\boldsymbol{\rho}_{mn}) = \frac{\mathrm{e}^{\mathrm{i}\cdot\rho}}{\rho} \sum_{\lambda} \sum_{m_s=\uparrow,\downarrow} C^{\kappa,m_j}_{m_s,m_j-m_s} \tilde{\Gamma}^{l,m_j-m_s}_{\lambda}(\boldsymbol{\rho}_{mn}) \times \Gamma^{l',m'_j-m_s}_{\lambda}(\boldsymbol{\rho}_{mn}) C^{\kappa',m'_j}_{m_s,m'_j-m_s} \tag{36}$$

and by introducing the shorthand notations

$$\tilde{U}^{\kappa,m_j}_{\lambda}(\boldsymbol{\rho}_{mn}, m_s) = C^{\kappa,m_j}_{m_s,m_j-m_s} \tilde{\Gamma}^{l,m_j-m_s}_{\lambda}(\boldsymbol{\rho}_{mn}) \tag{37}$$

$$U^{\kappa',m'_j}_{\lambda}(\boldsymbol{\rho}_{mn}, m_s) = \Gamma^{l',m'_j-m_s}_{\lambda}(\boldsymbol{\rho}_{mn}) C^{\kappa',m'_j}_{m_s,m'_j-m_s} \tag{38}$$

they reduce to the compact form

$$G^{\kappa,m_j}_{\kappa',m'_j}(\boldsymbol{\rho}_{mn}) = \frac{\mathrm{e}^{\mathrm{i}\cdot\rho}}{\rho} \sum_{\lambda} \sum_{m_s=\uparrow,\downarrow} \tilde{U}^{\kappa,m_j}_{\lambda}(\boldsymbol{\rho}_{mn}, m_s) \times U^{\kappa',m'_j}_{\lambda}(\boldsymbol{\rho}_{mn}, m_s). \tag{39}$$

This equation yields the same result as the one published by Fujikawa and Yimagawa [26], although we used an alternative route to derive it. It should be mentioned that due to the explicit appearance of spin states equation (39) is especially useful when discussing spin-flip scattering. In the next step we have to reveal in which way the scattering amplitudes are influenced by equation (39). The relativistic scattering path for the atomic system described in Section 2 is given by

$$\begin{aligned} G^{\kappa_\mathrm{D},m_{j\mathrm{D}}}_{\kappa_\mathrm{f},m_{j\mathrm{f}}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_1, \mathbf{R}_0) &= G^{\kappa_\mathrm{D},m_{j\mathrm{D}}}_{\kappa_\mathrm{f},m_{j\mathrm{f}}}(\boldsymbol{\rho}_{\mathrm{D},0}) \\ &\quad + \sum_{\kappa_1 m_{j1}} G^{\kappa_\mathrm{D},m_{j\mathrm{D}}}_{\kappa_1,m_{j1}}(\boldsymbol{\rho}_{\mathrm{D},1}) \\ &\quad \times t_{\kappa_1}(\mathbf{R}_1) G^{\kappa_1,m_{j1}}_{\kappa_\mathrm{f},m_{j\mathrm{f}}}(\boldsymbol{\rho}_{1,0}) \qquad (40) \\ &= M^{\kappa_\mathrm{D},m_{j\mathrm{D}}}_{\kappa_\mathrm{f},m_{j\mathrm{f}}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_0) \\ &\quad + N^{\kappa_\mathrm{D},m_{j\mathrm{D}}}_{\kappa_\mathrm{f},m_{j\mathrm{f}}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_1, \mathbf{R}_0) \qquad (41) \end{aligned}$$

and in complete analogy to Section 2 we obtain for the direct and single scattered Green's Function

$$M^{\kappa_\mathrm{D},m_{j\mathrm{D}}}_{\kappa_\mathrm{f},m_{j\mathrm{f}}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_0) = \frac{\mathrm{e}^{\mathrm{i}\rho_{\mathrm{D},0}}}{\rho_{\mathrm{D},0}} \sum_{\lambda} \sum_{m_s} \mathbf{T}^{m_s,m_s}_{\lambda,\lambda}(\boldsymbol{\rho}_{\mathrm{D},0}) \tag{42}$$

$$N^{\kappa_\mathrm{D},m_{j\mathrm{D}}}_{\kappa_\mathrm{f},m_{j\mathrm{f}}}(\mathbf{R}_\mathrm{D}, \mathbf{R}_1, \mathbf{R}_0) = \frac{\mathrm{e}^{\mathrm{i}\rho_{\mathrm{D},1}}}{\rho_{\mathrm{D},1}} \frac{\mathrm{e}^{\mathrm{i}\rho_{\mathrm{D},0}}}{\rho_{\mathrm{D},0}} \times \sum_{\lambda,\lambda'} \sum_{m_s,m'_s} \mathbf{T}^{m_s,m'_s}_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) F^{m_s,m'_s}_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) \tag{43}$$

where we have used the notation

$$\begin{aligned} \mathbf{T}^{m_s,m'_s}_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) &= \left(T^{\kappa_\mathrm{D},m_{j\mathrm{D}}}_{\kappa_\mathrm{f},m_{j\mathrm{f}}}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0})\right)^{m_s,m'_s}_{\lambda,\lambda'} \qquad (44) \\ &= \tilde{U}^{\kappa_\mathrm{D},m_{j\mathrm{D}}}_{\lambda}(\boldsymbol{\rho}_{\mathrm{D},1}, m_s) \\ &\quad \times U^{\kappa_\mathrm{f},m_{j\mathrm{f}}}_{\lambda'}(\boldsymbol{\rho}_{1,0}, m'_s) \qquad (45) \end{aligned}$$

together with

$$F^{m_s,m'_s}_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) = \sum_{\kappa_1,m_{j1}} U^{\kappa_1,m_{j1}}_{\lambda}(\boldsymbol{\rho}_{\mathrm{D},1}, m_s) t_{\kappa_1}(\mathbf{R}_1) \times \tilde{U}^{\kappa_1,m_{j1}}_{\lambda'}(\boldsymbol{\rho}_{1,0}, m'_s). \tag{46}$$

We have thus found a relativistic formulation that seems to be equivalent to the non-relativistic result (15). The obvious difference consists in the explicit appearance of the electronic spin states within the termination and scattering matrices. Therefore, the description of the scattering path contains spin-flip and non spin-flip processes on an equal footing and allows to analyze spin dependent effects that arise due to the interaction between the scattering potential and the scattered electrons.

However, the remarkable lacuna of equation (46) will become clear if we try to formulate the scattering matrices $F_{\lambda,\lambda'}$ in terms of just one composite rotation matrix. Starting from (46), choosing the definitions (37) and finally adapting (10) we get

$$F^{m_s,m'_s}_{\lambda,\lambda'}(\boldsymbol{\rho}_{\mathrm{D},1}, \boldsymbol{\rho}_{1,0}) = \sum_{\kappa_1} t_{\kappa_1}(\mathbf{R}_1) \gamma^{l_1}_{\mu\nu}(\boldsymbol{\rho}_{\mathrm{D}1}) \tilde{\gamma}^{l_1}_{\nu'\mu'}(\boldsymbol{\rho}_{10}) \times Q^{\kappa_1,m_s,m'_s}_{\nu\nu'}(\Omega_{\rho_{\mathrm{D}1}}, \Omega_{\rho_{10}}) \tag{47}$$

with

$$Q^{\kappa_1,m_s,m'_s}_{\nu\nu'}(\Omega_{\rho_{\mathrm{D}1}}, \Omega_{\rho_{10}}) = \sum_{m_{j1}} C^{\kappa_1,m_{j1}}_{m_s,m_{j1}-m_s} R^{l_1}_{\nu,m_{j1}-m_s}(\Omega_{\rho_{\mathrm{D}1}}) \times R^{l_1}_{m_{j1}-m'_s,\nu'}(\Omega^{-1}_{\rho_{10}}) C^{\kappa_1,m_{j1}}_{m'_s,m_{j1}-m'_s}. \tag{48}$$

The latter equation is the relativistic analogue to (18) and thus requires a formulation in terms of composite rotations. Unfortunately, the appearance of Clebsch-Gordon coefficients is a circumstance under which the rotation matrices can not be united and therefore (47) is not strictly comparable to (18). Moreover, in the case of spin-flip processes, that is $m_s \neq m'_s$, the rotation matrices themselves prevent a unification. Therefore one may conclude that the separable approach to electron scattering introduced by Rehr and Albers can not be generalized rigorously to theories based on the Dirac equation. In addition, the same result is true for ferromagnetically ordered solids. In this case the scattering potentials are derivable from Spin-DFT [27] or from the more involved Current-DFT [28]. Then the starting point is the Kohn-Sham-Dirac Hamiltonian

$$\begin{aligned} \mathcal{H}_\mathrm{D}\Psi_n = \{&\boldsymbol{\alpha}\mathbf{p} + \boldsymbol{\beta}\left(1 + \boldsymbol{\sigma}\mathbf{B}_{\mathrm{eff}}[n(\mathbf{r}), \boldsymbol{m}(\mathbf{r})]\right) \\ &+ V_{\mathrm{eff}}[n(\mathbf{r}), \boldsymbol{m}(\mathbf{r})]\mathbf{1}_{4\times4}\}\Psi_n = \epsilon_n\Psi_n. \end{aligned} \tag{49}$$

The presence of a magnetic field breaks the spherical symmetry of the problem and demands to calculate t-matrices depending on the quantum numbers $\kappa$ and $m_j$ rather than on $\kappa$ only. The application of the Rehr-Albers formalism to ferromagnets therefore breaks down already in the beginning, since one is not allowed to separate the t-matrices from the summation over $m_{j1}$ quantum numbers.

## 4 Conclusion

We tried to derive separable relativistic electron propagators. The calculations showed that angular momentum decoupling is possible by introducing spin dependent propagators that are related to a free particle Green's Function satisfying the Kohn-Sham-Dirac equation. Our investigation indicates that these Green's Functions are slightly different from that obtained by Rose. They do − on the other hand − agree well with the calculations by Tamura. In the case of non-magnetic materials the appearance of Clebsch-Gordon coefficients and the off-diagonal nature of the rotation matrices in spin space enables us to introduce composite rotation matrices. For ferromagnetic materials there is an additional hindrance due to the $m_{j1}$ dependence of the single site scattering matrices. This fact is especially deplorable since the application of the Rehr-Albers formalism to layered magnetic materials could be a potentially fertile field of research. The only way to conserve the numerical advantages of separable propagators seems to calculate the non-relativistic $G_{LL'}$ in a separate step and then inserting them into the Onodera-Okazaki relation.

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