SEMI-RELATIVISTIC MULTIPLE-SCATTERING THEORY

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INTRODUCTION

Recently, physical phenomena involving the interaction of spin-orbit coupling and magnetism have received much attention (see Ebert and Schütz (1996) for a review). A fully relativistic treatment of these phenomena was proposed in many cases, but a semi-relativistic approach has some advantages. The usual semi-relativistic calculations are done through the Foldy-Wouthuysen transformation. According to Thaller (Thaller 1992, p.311), this procedure is mathematically unsound and gives complicated expressions for the relativistic corrections. On the other hand, Gesztesy, Grosse and Thaller (1984) have proposed a new semi-relativistic expansion of the Green function for the Dirac equation as a compact and convergent series in $1/c^n$. Their semi-relativistic expansion was carried out up to $1/c^2$ to study magnetic circular dichroism in the x-ray range by Brouder, Alouani and Bennemann (1996).

In this paper, we present another application of the semi-relativistic expansion by evaluating the relativistic corrections to the energy up to $1/c^2$ and $1/c^4$. This gives us explicit correction terms to the usual calculation of anisotropy energy in magnetic systems.

SEMI-RELATIVISTIC EXPANSION OF THE GREEN FUNCTION

The Dirac Hamiltonian for potential V is

$$H = \begin{pmatrix} V(\mathbf{r}) & cD^\dagger \\ cD & V(\mathbf{r}) - 2mc^2 \end{pmatrix},$$

where each matrix element is a 2×2 matrix, V is a 2×2 potential matrix that acts on up and down spins and $D = -i\hbar\sigma \cdot \nabla$ where $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices. Compared to the usual Dirac equation, the energy was shifted by mc^2, so that bound state energies are negative, as for a non-relativistic Hamiltonian. In most cases, D is Hermitian ($D^\dagger = D$). For the simplest cases V is a diagonal matrix, but the formulas are valid when V is non-diagonal, such as in spiral magnetic structures. The Dirac Green function is the 4×4 matrix of operators $G_D(z) = (z - H)^{-1}$.

Gesztesy et al. (1984) proved that

$$G_D = \left[1 - \begin{pmatrix} 0 & \frac{1}{2mc}GD^\dagger(V-z) \\ 0 & \frac{1}{(2mc)^2}[DGD^\dagger + 2m](V-z) \end{pmatrix}\right]^{-1} \begin{pmatrix} G & \frac{1}{2mc}GD^\dagger \\ \frac{1}{2mc}DG & \frac{1}{(2mc)^2}[DGD^\dagger + 2m] \end{pmatrix} \quad (1)$$

where $G = (z - H_{NR})^{-1}$ is the 2×2 Green function corresponding to the 2×2 Hamiltonian $H_{NR} = \frac{1}{2m}D^\dagger D + V = -\frac{\hbar^2\Delta}{2m} + V$. In the case of diagonal V, G is diagonal.

The semi-relativistic expansion is obtained through the identity $(1-T)^{-1} = \sum_n T^n$ in Eq.(1). The result is the convergent series

$$\begin{aligned} G_D &= \begin{pmatrix} G & 0 \\ 0 & 0 \end{pmatrix} + \sum_{n=0}^{\infty} \Big[\frac{1}{(2mc)^{2n+1}} \begin{pmatrix} 0 & GD^\dagger Y^n \\ X^n DG & 0 \end{pmatrix} \\ &+ \frac{1}{(2mc)^{2n+2}} \begin{pmatrix} GD^\dagger(V-z)X^n DG & 0 \\ 0 & [DGD^\dagger + 2m]Y^n \end{pmatrix}\Big] \end{aligned} \quad (2)$$

where $X = [DGD^\dagger + 2m](V-z)$ and $Y = (V-z)[DGD^\dagger + 2m]$. Such an explicit formula cannot be given by the usual semi-relativistic methods.

In some cases, one is not interested in the Green function but in the Hamiltonian. Grigore, Nenciu and Purice (1989) and Thaller (1992, p.184) gave a formula for the relativistic corrections to the non relativistic eigenstates of energy E_0. The following discussion is a bit abstract, but it will be illustrated by examples in the next two sections. Equation (2) is rewritten as

$$G_D(z) = \sum_{n=0}^{\infty} \kappa^n G_n(z), \quad (3)$$

with $\kappa = 1/(2mc)$. Define the projector $P(\kappa)$ and its semi-relativistic expansion by

$$P(\kappa) = \frac{1}{2\pi i}\oint_\Gamma G_D(z)dz = \sum_{n=0}^{\infty} \kappa^n P_n, \text{ with } P_n = \frac{1}{2\pi i}\oint_\Gamma G_n(z)dz, \quad (4)$$

where Γ is a positively oriented contour in the complex plane that isolates the non-relativistic energy E_0 from the other energies of the spectrum. Define also the 4×4 non-relativistic projector $P_0 = P(0)$. The projector $P(\kappa)$ projects onto the eigenstates with relativistic energies E included in contour Γ. In the subspace spanned by the relativistic eigenstates with energies included in Γ, the Hamitonian is given by

$$P(\kappa)HP(\kappa) = \frac{1}{2\pi i}\oint_\Gamma zG_D(z)dz,$$

This formula can be used directly, but to compare with more standard perturbation theory, we can use, for instance, the unitary operator (Kato 1980, p.99)

$$U(\kappa) = [1 - (P(\kappa) - P_0)^2]^{-1/2}[1 - P_0 - P(\kappa) + 2P(\kappa)P_0] \quad (5)$$

that can be used to express the relativistic eigenstates in terms of the non-relativistic ones, because of the interwinning property $U(\kappa)P_0 = P(\kappa)U(\kappa)$. The relativistic corrections to the eigenstates of energy E_0 can be obtained by diagonalising the effective Hamiltonian

$$\tilde{H}(\kappa) = E_0P_0 + \frac{1}{2\pi i}P_0U(\kappa)^{-1}\oint_\Gamma (z - E_0)G_D(z)dzU(\kappa)P_0 \equiv E_0P_0 + \sum_{n=0}^{\infty}\kappa^n\tilde{H}_n. \quad (6)$$

It is useful to define the intermediate terms

$$\frac{1}{2\pi i}\oint_\Gamma (z-E_0)G_D(z)dz=\sum_{n=0}^{\infty}\kappa^n K_n,\ \mathrm{with}\ K_n=\frac{1}{2\pi i}\oint_\Gamma (z-E_0)G_n(z)dz, \tag{7}$$

So that $\tilde{H}_n$ can be expressed in terms of P_m and K_m. In the next two sections, we shall carry out this expansion up to κ^2 and κ^4.

SECOND-ORDER $1/c$ EXPANSION

This type of calculation being somewhat unfamiliar, a simple example will be presented in detail. To calculate $\tilde{H}(\kappa)$, we expand $U(\kappa)P_0$ in terms of P_n in Eq.(6) and multiply by the proper K_n in Eq.(6).

Calculation of $\tilde{H}_0$ and $\tilde{H}_1$

We start by showing that K_0 and K_1 are zero, so that expansion (3) starts with κ^2. K_0 and K_1 are the integrals over Γ of G_0 and G_1. From Eq.(2) we have

$$G_0=\begin{pmatrix} G & 0\\ 0 & 0\end{pmatrix}\quad G_1=\begin{pmatrix} 0 & GD^\dagger\\ DG & 0\end{pmatrix}. \tag{8}$$

Using the usual expression for the Green function, we have

$$G(z)=\sum_{m\alpha}\frac{|\psi_m^\alpha\rangle\langle\psi_m^\alpha|}{z-E_m}=\sum_m\frac{p_m}{z-E_m}, \tag{9}$$

where $p_m=\sum_\alpha|\psi_m^\alpha\rangle\langle\psi_m^\alpha|$ is the projector onto the (eventually degenerate) eigenstates $|\psi_m^\alpha\rangle$ with energy E_m of the non relativistic Hamiltonian H_{NR}. $|\psi_m^\alpha\rangle$ is a two-component spinor. The projector property $p_m p_n=\delta_{mn}p_n$ will be often used. From Eq.(9) we find

$$\frac{1}{2\pi i}\oint_\Gamma (z-E_0)G(z)dz=\sum_m p_m\frac{1}{2\pi i}\oint_\Gamma\frac{(z-E_0)dz}{z-E_m}.$$

According to the Cauchy theorem, the integral is zero if $E_m\neq E_0$, because the singularity E_m is not inside Γ, and it is zero when $E_m=E_0$ because the singularity of the denominator is compensated by the numerator. Therefore, K_0 and K_1 are zero.

Expansion (6) requires the calculation of $U(\kappa)P_0$ to zero-th order: $U(\kappa)P_0\simeq P_0$. Using Eqs.(4) and (8), P_0 is obtained from

$$\frac{1}{2\pi i}\oint_\Gamma G(z)dz=\sum_m p_m\frac{1}{2\pi i}\oint_\Gamma\frac{dz}{z-E_m}=p_0\quad\mathrm{so\ that}\quad P_0=\begin{pmatrix} p_0 & 0\\ 0 & 0\end{pmatrix}.$$

This shows that P_0 is indeed the projector onto the non-relativistic eigenstates of energy E_0. In conclusion, $\tilde{H}_0=P_0K_0P_0$ and $\tilde{H}_1=P_0K_1P_0+P_0P_1K_0P_0+P_0K_0P_1P_0$, are zero in Eq.(6).

Calculation of $\tilde{H}_2$

To calculate $\tilde{H}(\kappa)$ up to order κ^2, we need only the expansion of $U(\kappa)P_0$ up to order 0 (i.e. P_0) and the term K_2 coming from G_2

$$G_2(z)=\begin{pmatrix} GD^\dagger(V-z)DG & 0\\ 0 & DGD^\dagger+2m\end{pmatrix}. \tag{10}$$

From the previous calculation, the only nonzero matrix element of K_2 is

$$\frac{1}{2\pi i}\oint_\Gamma (z-E_0)GD^\dagger(V-z)DGdz = \sum_{m,n} p_m \frac{1}{2\pi i}\oint_\Gamma \frac{(z-E_0)D^\dagger(V-z)Ddz}{(z-E_m)(z-E_n)} p_n.$$

By the residue theorem, the integral is $D^\dagger(V-E_0)D$ when $m=n=0$ and zero otherwise. Finally, the first relativistic correction to the energies and eigenstates corresponding to the non-relativistic energy E_0 is given by $\tilde{H}(\kappa) \simeq E_0 p_0 + 1/(2mc)^2 p_0 D^\dagger(V-E_0)Dp_0$. In other words, the relativistic corrections are obtained by diagonalising the perturbation matrix

$$\frac{1}{(2mc)^2}\langle\psi_0^\alpha|D^\dagger(V-E_0)D|\psi_0^\beta\rangle = \frac{\hbar^2}{(2mc)^2}\langle\sigma\cdot\nabla\psi_0^\alpha|(V-E_0)|\sigma\cdot\nabla\psi_0^\beta\rangle. \qquad (11)$$

This result is remarkably simple as compared to the usual methods. For a spin-polarised potential V, Kraft, Oppeneer, Antonov and Eschrig (1995) used the elimination method and found the κ^2 corrections as a sum of 9 terms, which is equivalent to our Eq.(11). They notice that three terms of their sum have a known physical meaning (spin-orbit, Darwin and mass-velocity corrections), but "the other terms have no special name".

In the realistic case where the potential is spin-dependent, the "spin-orbit" method is in trouble (should the spin-orbit parameter be calculated with the up or the down spin potential?). The present formalism allows for the use of spin-dependent potential and wavefunctions.

FOURTH-ORDER $1/c$ EXPANSION

The calculation of the magnetic anisotropy of non-cubic materials requires an expansion up to $1/c^4$. Except in the case of fully relativistic calculations, the expansion is never carried out consistently and only the spin-orbit perturbation is calculated to second order (or to infinite order), without taking account of the other terms of the $1/c^4$ expansion. In this section, we shall follow Gesztesy et al. (1984) and Grigore et al. (1989) to calculate the terms $\tilde{H}_3$ and $\tilde{H}_4$. $\tilde{H}_3$ will be found zero and $\tilde{H}_4$ will give us terms that must be added to the second order spin-orbit calculation to obtain a consistent semi-relativistic expansion.

To obtain $\tilde{H}(\kappa)$ up to the fourth-order term, we need to expand $U(\kappa)P_0$ up to second order in Eq.(5): $U(\kappa)P_0 \simeq P_0 + \kappa P_1 P_0 + \kappa^2(P_2P_0 + (1/2)P_1^2P_0)$. With the methods of the previous paragraph, we can show that

$$\begin{aligned} P_1 &= \begin{pmatrix} 0 & p_0D^\dagger \\ Dp_0 & 0 \end{pmatrix} \qquad K_2 = \begin{pmatrix} p_0D^\dagger(V-E_0)Dp_0 & 0 \\ 0 & 0 \end{pmatrix} \\ K_3 &= \begin{pmatrix} 0 & p_0D^\dagger(V-E_0)Dp_0D^\dagger \\ Dp_0D^\dagger(V-E_0)Dp_0 & 0 \end{pmatrix}. \end{aligned}$$

The third-order term is $\tilde{H}_3 = P_0K_3P_0 + P_0P_1K_2P_0 + P_0K_2P_1P_0$. All the terms of the sum are zero, so that $\tilde{H}_3 = 0$ (more generally, $\tilde{H}_n = 0$ for odd n).

For the fourth-order term, we need P_2, which requires the evaluation of

$$I = \frac{1}{2\pi i}\oint_\Gamma GD^\dagger(V-z)DGdz = \sum_{m,n} p_m \frac{1}{2\pi i}\oint_\Gamma \frac{D^\dagger(V-z)Ddz}{(z-E_m)(z-E_n)} p_n,$$

that we split into a sum over $n \neq m$ and a sum over $n = m$. The partial fraction decomposition

$$\begin{aligned} \frac{x-z}{(z-E_m)(z-E_n)} &= \frac{x-E_m}{(E_m-E_n)(z-E_m)} + \frac{x-E_n}{(E_n-E_m)(z-E_n)} \\ \frac{x-z}{(z-E_n)^2} &= \frac{x-E_n}{(z-E_n)^2} - \frac{1}{(z-E_n)} \end{aligned}$$

and the residue theorem yield

$$\begin{aligned} I &= \sum_{n\neq 0} p_0 D^\dagger (V-E_0) D \frac{p_n}{(E_0-E_n)} + \sum_{m\neq 0} \frac{p_m}{(E_0-E_m)} D^\dagger (V-E_0) D p_0 - p_0 D^\dagger D p_0 \\ &= p_0 D^\dagger (V-E_0) D G^\perp(E_0) + G^\perp(E_0) D^\dagger (V-E_0) D p_0 - p_0 D^\dagger D p_0, \end{aligned}$$

where $G^\perp(E_0) = \sum_{n\neq 0} p_n/(E_0-E_n)$ is the perpendicular Green function, often used in perturbation theory and that has the important property $p_0 G^\perp(E_0) = G^\perp(E_0) p_0 = 0$. The fourth order terms are given by the hamiltonian matrix $\tilde{H}_4 = P_0 K_4 P_0 + P_0 P_1 K_3 P_0 + P_0 K_3 P_1 P_0 + P_0 P_1 K_2 P_1 P_0 + P_0 P_2 K_2 P_0 + P_0 K_2 P_2 P_0 + (1/2) P_0 K_2 P_1^2 P_0 + (1/2) P_0 P_1^2 K_2 P_0$. Let us call $Z = p_0 D^\dagger D p_0 D^\dagger (V-E_0) D p_0 + p_0 D^\dagger (V-E_0) D p_0 D^\dagger D p_0$ the sum of the second and third terms. The usual method yields that the fourth term is zero, the sum of the fifth and sixth terms is $-Z$ and the sum of the seventh and eighth terms is $Z/2$. Moreover, the first term is $P_0 K_4 P_0 = p_0 D^\dagger (V-E_0) D G^\perp(E_0) D^\dagger (V-E_0) D p_0 + 2m p_0 D^\dagger (V-E_0)^2 D p_0 - Z$. The final result is

$$\begin{aligned} \tilde{H}_4 &= p_0 D^\dagger (V-E_0) D G^\perp(E_0) D^\dagger (V-E_0) D p_0 + 2m p_0 D^\dagger (V-E_0)^2 D p_0 \\ &- (1/2) p_0 D^\dagger D p_0 D^\dagger (V-E_0) D p_0 - (1/2) p_0 D^\dagger (V-E_0) D p_0 D^\dagger D p_0. \end{aligned} \tag{12}$$

For a non-degenerate energy level, this result is identical to the one of Gesztesy et al. (1984), because $D^\dagger D p_0 = 2m[H_{NR} p_0 - V p_0] = -2m(V-E_0) p_0$.

For comparison with the usual second-order perturbation in the spin-orbit coupling, we assume that the first order calculation has taken all first-order effects into account as in Eq.(11). The second-order perturbation due to the interaction operator W is given by

$$E \simeq E_0 + \langle \psi_0 | W | \psi_0 \rangle + \sum_{n\neq 0} \frac{|\langle \psi_n | W | \psi_0 \rangle|^2}{E_0 - E_n} = E_0 + \langle \psi_0 | W | \psi_0 \rangle + \langle \psi_0 | W^\dagger G^\perp(E_0) W | \psi_0 \rangle.$$

Since the first order corrections are represented by the operator $W = D^\dagger (V-E_0) D$, the first term of $\tilde{H}_4$ is the second-order perturbation for W and the additional terms that must be taken into account to carry out a consistent calculation up to $1/c^4$ are

$$\begin{aligned} &\frac{2m}{(2mc)^4} \langle D\psi_0^\alpha | (V-E_0)^2 | D\psi_0^\beta \rangle - \frac{1}{2(2mc)^4} \sum_\gamma \langle D\psi_0^\alpha | D\psi_0^\gamma \rangle \langle D\psi_0^\gamma | (V-E_0) | D\psi_0^\beta \rangle - \\ &\frac{1}{2(2mc)^4} \sum_\gamma \langle D\psi_0^\alpha | (V-E_0) | D\psi_0^\gamma \rangle \langle D\psi_0^\gamma | D\psi_0^\beta \rangle \end{aligned} \tag{13}$$

Again, the economy of the method is remarkable. Equation (12) is valid whether energy E_0 is degenerate or non degenerate. For a non-degenerate level, the last two terms are identical and $\tilde{H}_4$ is the sum of three terms. The equivalent expression obtained by Morrison and Moss (1980) by the Foldy-Wouthuysen method is a sum of eleven terms for a non-magnetic Coulomb potential (for a magnetic one, this number would be at least doubled). Moreover, many of their terms are infinite and "delta function recipies" must be used to find a consistent sum. This is in contrast with the present formula, which is valid even for potentials with Coulomb-type singularities.

CONCLUSION

The purpose of this paper was to explain the new semi-relativistic expansion and to show how it can be used to carry our explicit calculations in physical cases. The results are simple, finite and useful, for instance to calculate the magnetic anisotropy of non-cubic systems. For cubic materials, the expansion must be carried out up to $\tilde{H}_8$. The power of the present method comes also from its versatility. It can be used to calculate properties of materials with spiral magnetic structure. It can also be extended straightforwardly to current- and spin-density-functional theory (CSDFT). Hjelm, Trygg, Eriksson, Johansson and Wills (1995) and Ebert and Battocletti (1996) have suggested that a correct estimation of orbital magnetisation requires the CSDFT developed by Vignale and Rasolt (1988). The present formalism can be transposed easily to CSDFT. The only change is that D becomes $\sigma \cdot (-i\hbar\nabla - q\mathbf{A})$ instead of $-i\hbar\sigma \cdot \nabla$ where $\mathbf{A}$ is the self-consistent vector potential. Moreover, several non-relativistic energies can be taken into account together in the perturbation by including them into a common contour Γ.

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