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Relativistic Scattered-Wave Theory II. Normalization and Symmetrization

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Formalisms for normalization and symmetrization of one-electron Dirac scattered-wave wavefunctions are presented. The normalization integral consists of one-dimensional radial integrals for the spherical regions and an analytic expression for the intersphere region. Symmetrization drastically reduces the size of the secular matrix to be solved. Examples for planar Pb_2Se_2 and tetrahedral Pd_4 are discussed.

I. INTRODUCTION

The formulation of the scattered-wave secular equation based on the one-electron Dirac equation for a polyatomic muffin-tin potential has recently appeared in the literature.[1,2] The resulting relativistic secular equation can be written in the matrix form

$$\mathfrak{M}\mathcal{C} = 0 , \tag{1.1}$$

where the secular matrix $\mathfrak{M}$ and the coefficient vector $\mathcal{C}$ were given by Eqs. (2.20) and (2.18) of Ref. 1. As discussed in Ref. 1, the wavefunction within each atomic sphere and outside the outersphere can be expressed as a partial wave expansion

$$\Psi^\alpha(\mathbf{r}_\alpha) = \sum_Q A_Q^\alpha \begin{bmatrix} g_\kappa^\alpha(r_\alpha)\chi_Q(\hat{r}_\alpha) \\ if_\kappa^\alpha(r_\alpha)\chi_{\overline{Q}}(\hat{r}_\alpha) \end{bmatrix} , \tag{1.2}$$

where $\mathbf{r}_\alpha = \mathbf{r} - \mathbf{R}_\alpha$, and $\mathbf{R}_\alpha$ is the position of the center of the αth sphere. The symbols g_κ^α and f_κ^α represent the Dirac radial functions for the αth sphere and χ_Q is the spin-angular function, where $Q \equiv (\kappa, \mu)$ and $\overline{Q} \equiv (-\kappa, \mu)$ represent the angular momentum quantum numbers.[1] The partial wave coefficients A_Q^α are linearly related to the secular coefficients, i.e., in matrix form

$$\mathcal{C} = \mathcal{B}\mathcal{A} , \tag{1.3}$$

where the matrix $\mathcal{B}$ can be extracted from Eqs. (2.18) of Ref. 1. The intersphere (IS) wavefunction can be calculated from Eq. (1.2) using the surface integral equation[3]

$$\Psi(\mathbf{r}) = -ic \int_{IS} G(\mathbf{r}, \mathbf{r}')\boldsymbol{\alpha} \cdot \hat{n}'\Psi(\mathbf{r}')dS' , \tag{1.4}$$

where G is the free-particle Dirac Green's function (a 4×4 matrix) and $\hat{n}'$ denotes the outward normal from the intersphere region. The vector $\boldsymbol{\alpha}$ is given by

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \tag{1.5}$$

where σ are the Pauli spin matrices.

One can obtain the relativistic one-electron energies and wavefunctions by solving for the zeroes of the determinant of $\mathfrak{M}$ and then the corresponding $\mathcal{C}$. In general, it is not immediately apparent what symmetry properties each of these calculated wavefunctions possesses. In order to distinguish wavefunctions of different symmetries, and more importantly in practical terms to

reduce the computation time involved, we shall "factor out" $\mathfrak{M}$ into smaller "symmetrized" matrices, each of which determines the energies and wavefunctions belonging to a specified representation of the double point group of the given system. Examples of such symmetrized relativistic one-electron energy calculations have been published for the diatomics C_2 and I_2[4] and clusters of PbSe containing up to 12 atoms.[5] The symmetrized wavefunctions thus obtained are generally not normalized. For calculations of charge distributions, dipole moments, and other one-electron properties one has to start from a set of normalized orbitals. Hence, the normalization of wavefunctions is essential in further applications of the relativistic scattered-wave method. In the ensuing two sections derivations for the normalization integrals and the symmetrized secular matrix are presented.

II. NORMALIZATION

After the secular equation has been solved, we obtain a set of unnormalized eigenfunctions of the one-electron Dirac Hamiltonian. In the atomic and outer regions, denoted by S, the normalization of the wavefunctions is trivial. The contribution of S to the normalization integral can be written using Eq. (1.2) as a sum of one-dimensional radial integrals, i.e.,

$$\int_S \Psi^{\alpha\dagger}\Psi^\alpha d^3r = \sum_Q |A_Q^\alpha|^2 \int_{r_1}^{r_2} r^2[(g_\kappa^\alpha)^2 + (f_\kappa^\alpha)^2]dr , \tag{2.1}$$

where $r_1 = 0$ and $r_2 = b_\alpha$ for an atomic sphere with radius b_α, and $r_1 = b_0$ and $r_2 = \infty$ for the outer sphere. These radial integrals are easy to compute numerically. However, normalization of the wavefunction in the intersphere region is quite nontrivial, since the intersphere wavefunction consists of multicenter expansions. Nevertheless, the normalization integral can be explicitly evaluated using the surface integrals (1.4) as in the nonrelativistic case.[6] This process is rather cumbersome; therefore, an alternative approach is outlined below.

The intersphere normalization integral for the nth orbital can be written as

$$I_0 = \int_{IS} \Psi_n^\dagger\Psi_n d^3r . \tag{2.2}$$

From the Dirac equation $H\Psi_n = W_n\Psi_n$ and the Hellmann–Feynman theorem one obtains

$$\frac{\partial W_n}{\partial \overline{V}} = \int \Psi_n^\dagger \frac{\partial H}{\partial \overline{V}} \Psi_n d^3r = \int_{IS} \Psi_n^\dagger \Psi_n d^3r = I_0 , \qquad (2.3)$$

where $\overline{V}$ is the constant intersphere potential. Equation (2.3) could be used to calculate the intersphere normalization integral numerically. But as in the nonrelativistic case,[7] this is both a time-consuming and computationally unreliable process.

One can rewrite the secular equation (1.1) for a general energy W as

$$\mathfrak{M}(W, \overline{V}) \, \mathfrak{e}(W, \overline{V}) = \lambda(W, \overline{V}) \, \mathfrak{e}(W, \overline{V}) , \qquad (2.4)$$

where λ is a scalar. For energies $W = W_n$ one gets $\lambda = 0$. It follows that

$$\frac{\partial W_n}{\partial \overline{V}} = -\left(\frac{\partial \lambda}{\partial \overline{V}} \Big/ \frac{\partial \lambda}{\partial W} \right)_{W=W_n} . \qquad (2.5)$$

Using the Hermiticity of $\mathfrak{M}$ and straightforward matrix manipulations with Eq. (2.4) we arrive at the relation

$$\frac{\partial \lambda}{\partial W} = \frac{\mathfrak{e}^\dagger \dfrac{\partial \mathfrak{M}}{\partial W} \mathfrak{e}}{\mathfrak{e}^\dagger \mathfrak{e}} , \qquad (2.6)$$

and a similar one for $\partial \lambda / \partial \overline{V}$. Combining Eqs. (2.3), (2.5), and (2.6) we obtain

$$I_0 = - \frac{\mathfrak{e}^\dagger \dfrac{\partial \mathfrak{M}}{\partial \overline{V}} \mathfrak{e}}{\mathfrak{e}^\dagger \dfrac{\partial \mathfrak{M}}{\partial W} \mathfrak{e}} \Bigg|_{W=W_n} . \qquad (2.7)$$

Equation (2.7) represents the contribution of the *normalized* charge from the intersphere region. In order to normalize the wavefunctions we have to relate this normalized charge to the unnormalized charge that we calculate from the solution of the secular equation. This can be accomplished by recognizing the fact that

$$\frac{\overline{I}_0}{I_0} = \frac{\overline{I}_\alpha}{I_\alpha} , \qquad (2.8)$$

where (~) denotes unnormalized charges. The *unnormalized* charge in the αth atomic sphere $\overline{I}_\alpha$ is given by Eq. (2.1). Being analogous to I_0 in Eq. (2.7), the normalized charge I_α is given by

$$I_\alpha = - \frac{\mathfrak{e}^\dagger \dfrac{\partial \mathfrak{M}}{\partial \overline{V}_\alpha} \mathfrak{e}}{\mathfrak{e}^\dagger \dfrac{\partial \mathfrak{M}}{\partial W} \mathfrak{e}} \Bigg|_{W=W_n} , \qquad (2.9)$$

where $\overline{V}_\alpha$ is an arbitrary constant potential added inside the αth sphere. The remaining task is to determine $\overline{I}_\alpha / I_\alpha$. We start with Eq. (2.1), and use the property[8]

$$\int_0^b r^2 (g^2 + f^2) \, dr = -(bg)^2 \frac{\partial}{\partial W} \left(\frac{cf}{g} \right) . \qquad (2.10)$$

Then, with the explicit expressions of $\mathfrak{M}$ and $\mathfrak{e}$ given in Eq. (2.18) of Ref. 1 and some algebraic manipulations, we finally obtain

$$\overline{I}_0 = \begin{cases} \dfrac{W}{c^2 k E} \mathfrak{e}^\dagger \dfrac{\partial \mathfrak{M}}{\partial k} \mathfrak{e} \Big|_{W=W_n} & \text{for } E = W - \dfrac{c^2}{2} > 0 , \\[3mm] -\dfrac{W}{c^2 \gamma |E|} \mathfrak{e}^\dagger \dfrac{\partial \mathfrak{M}}{\partial \gamma} \mathfrak{e} \Big|_{W=W_n} , & \text{for } E < 0 , \end{cases} \qquad (2.11)$$

where energies are measured with respect to $\overline{V}$. The parameters k and γ are given by

$$k = \begin{cases} \left(E + \dfrac{E^2}{c^2} \right)^{1/2} , & \text{for } E > 0 , \\[3mm] i\gamma = i \left(|E| - \dfrac{E^2}{c^2} \right)^{1/2} , & \text{for } E < 0 . \end{cases} \qquad (2.12)$$

Thus, Eqs. (2.11) provide us with analytical expressions for evaluating normalization integrals in the intersphere region. With this result and the atomic and outer regions charges computed numerically using Eq. (2.1) the normalization procedure is complete.

III. SYMMETRIZATION

Our approach for the symmetrization of the relativistic scattered-wave secular equations follows that for the *nonrelativistic* case reported by Diamond.[9] Since the relativistic four-component wavefunction Ψ^α in sphere α [Eq. (1.2)] is expanded in terms of half-integral angular momentum $(j\mu)$ eigenfunctions, the symmetrized wavefunctions must transform as the extra irreducible representations (irrep) of the double molecular point group of the given cluster.[10] In fact, under a rotation R the half-integral angular momentum eigenfunctions or spin–angular functions $\chi_{\kappa\mu}$ (or $\chi_{jl\mu}$) transform as[11]

$$O_R \chi_{jl\mu}(\hat{r}) = \sum_{\mu'} (-)^{l\pi_R} D^j_{\mu'\mu}(R) \chi_{jl\mu'}(\hat{r}) , \qquad (3.1)$$

where D^j is the rotation matrix representation and π_R is zero (one) for proper (improper) rotations. If we define the upper components of Ψ^α as

$$\phi^\sigma_{jl\mu}(\mathbf{r}_\alpha) = g^\alpha_\kappa(r_\alpha) \chi_{jl\mu}(\hat{r}_\alpha) , \qquad (3.2)$$

with σ denoting an equivalent set of N atoms, we obtain from Eq. (3.1)

$$O_R \phi^\sigma_{jl\mu}(\mathbf{r}_\alpha) = \sum_{\alpha'\mu'} \Delta^{(j)\alpha'\alpha}_{\mu'\mu}(R) \phi^\sigma_{jl\mu'}(\mathbf{r}_{\alpha'}) , \qquad (3.3)$$

where $\Delta^{(j)}$ is the direct matrix product

$$\Delta^{(j)}(R) = \overline{\delta}(R) \otimes \mathfrak{D}^j_l(R) , \qquad (3.4)$$

with $\mathfrak{D}^j_l \equiv D^j(-)^{l\pi_R}$ and the $N \times N$ matrix

$$\overline{\delta}(R)_{\alpha'\alpha} = \begin{cases} 1, & \text{when } R\mathbf{R}_\alpha = \mathbf{R}_{\alpha'} , \\ 0, & \text{otherwise} . \end{cases} \qquad (3.5)$$

Note that the atoms α and α' belong to the same equivalent set. The representation $\Delta^{(j)}$ is generally reducible and is expressible as a direct sum of the irreps of the group, i.e.,

$$\Delta^{(j)} = n_1^j \Gamma^1 \oplus n_2^j \Gamma^2 \oplus \cdots \oplus n_\nu^j \Gamma^\nu \oplus \cdots , \qquad (3.6)$$

where n_ν^j is the number of times the irrep Γ^ν is contained in $\Delta^{(j)}$. This multiplicity can be evaluated using Eqs. (3.4) and (3.5) and elementary group theory to yield

$$n_\nu^j = \frac{1}{g} \sum_R \text{Tr}[\Gamma^\nu(R)]^* \, \text{Tr}[\overline{\delta}(R)] \, \text{Tr}[\mathfrak{D}^j_l(R)] , \qquad (3.7)$$

where g is the order of the group and Tr denotes the trace of a square matrix.

We have now laid the groundwork for the projection of double group basis functions transforming as the nth row of the νth irrep, in terms of which the symmetrized wavefunctions are expanded. The tool is the projection operator $\mathcal{P}^{\nu}_{\eta\eta}$ defined by

$$\mathcal{P}^{\nu}_{\eta\eta} = \frac{l_{\nu}}{g} \sum_{R} \Gamma^{\nu}(R)^{*}_{\eta\eta} O_{R} , \qquad (3.8)$$

where l_{ν} is the dimension of the irrep. For a given κ (or jl), and a given σ, by applying $\mathcal{P}^{\nu}_{\eta\eta}$ to every $\phi^{\sigma}_{jl\mu}$ with the help of Eq. (3.3), and orthonormalizing the resulting functions, we obtain n_{ν}^{j} orthonormal basis functions F with quantum numbers jl. Each of these basis functions transforms as the ηth row of the νth irrep under the operations of the double molecular point group on the σth equivalent set of atoms. In particular, we have

$$F^{\sigma}_{\nu\eta\kappa n} = \sum_{\alpha'\mu'} S^{\nu\eta\alpha}_{\kappa n\mu'} \phi^{\sigma}_{\kappa\mu'}(\mathbf{r}_{\alpha'}) , \qquad (3.9a)$$

or in matrix form

$$\mathcal{F} = \mathcal{L}\Phi , \qquad (3.9b)$$

where $n = 1, \ldots, n_{\nu}^{j}$ and the matrix $\mathcal{L}$ is unitary in $\alpha\mu$. The projection of bases from the lower components of Ψ^{α} is completely analogous and the symmetrized wavefunctions in the spherical regions can be written as

$$\overline{\Psi}_{\nu\eta} = \sum_{\kappa n\sigma} \overline{A}^{\sigma}_{\nu\eta\kappa n} \begin{pmatrix} {}^{U}F^{\sigma}_{\nu\eta\kappa n} \\ {}^{L}F^{\sigma}_{\nu\eta\kappa n} \end{pmatrix} , \qquad (3.10)$$

where $U(L)$ denotes upper (lower) components. With the irrep indices $\nu\eta$ suppressed Eq. (3.10) can be rewritten as

$$\overline{\Psi} = \sum_{\sigma\alpha_{\sigma}Q} \hat{A}^{\alpha\sigma}_{Q} \begin{pmatrix} {}^{U}\phi^{\alpha\sigma}_{Q} \\ {}^{L}\phi^{\alpha\sigma}_{Q} \end{pmatrix} , \qquad (3.11)$$

where

$$\hat{A} = \sum_{n} \overline{A} S \qquad (3.12)$$

and α_{σ} is the αth atom in the σth equivalent set. It is immediately apparent that the symmetrized wavefunction expressed in Eq. (3.11) has the same form as the unsymmetrized one given by Eq. (1.2). Hence, a similar secular equation results, the only difference being the secular coefficients, where c is replaced by $\hat{c}$. In

TABLE I. Basis functions for Pb$_2$Se$_2$.

Group D_{2h}	κ	No. bases in extra irreps	
		E_g	E_u
Outer sphere	-1	1	0
	1	0	1
	-2	0	2
	2	2	0
Pb spheres	-1	1	1
	1	1	1
	-2	2	2
Se spheres	-1	1	1
	1	1	1
	-2	2	2

TABLE II. Basis functions for Pd$_4$.

Group T_d	κ	No. bases in extra irreps		
		E_2	E_3	Q
Outer sphere	-1	1	0	0
	1	0	1	0
	-2	0	0	1
	2	0	0	1
	-3	0	1	1
	3	1	0	1
	-4	1	1	1
	4	1	1	1
	-5	1	0	2
Pd spheres	-1	1	1	1
	1	1	1	1
	-2	1	1	3
	2	1	1	3
	-3	2	2	4

view of Eq. (1.3), $\hat{c}$ and $\hat{a}$ are related in the same way as c and a. If we rearrange the secular equations in terms of $\hat{c}$ [analog of $\hat{a}$ in Eq. (3.12)], and use the unitarity of $\mathcal{L}$, the final symmetrized secular equation becomes

$$\overline{\mathfrak{M}}\,\overline{c} = 0 , \qquad (3.13)$$

where

$$\overline{\mathfrak{M}} = \mathcal{L}^{\dagger}\mathfrak{M}\mathcal{L} . \qquad (3.14)$$

Given the double group operations, the irrep matrices, and the geometry of the system the matrices $\mathcal{L}$ can be generated for any given κ. The symmetrized matrix $\overline{\mathfrak{M}}$ has indices κn instead of $\alpha\kappa\mu$ for the unsymmetrized $\mathfrak{M}$. Thus, the procedures specified above result in a secular matrix of greatly reduced size.

We shall illustrate our point by considering the following two examples. The first is the planar tetratomic molecule Pb$_2$Se$_2$,[12] which has D_{2h} symmetry. If in determining the valence levels we choose $\kappa = -1, 1, -2, 2$ for the outer sphere, and $\kappa = -1, 1, -2$ for the atomic spheres, the dimension of the unsymmetrized secular determinant is 44. But from Table I the symmetrized secular matrix for each of the two two-dimensional extra irreps E_g and E_u is only 11×11.

Next we consider the tetrahedral cluster Pd$_4$.[13] If the bases are truncated at $l = 4$ for the outer sphere, and $l = 2$ for the atomic spheres, the unsymmetrized relativistic secular matrix is 122×122. However, as one can deduce from Table II, the dimensions of the secular matrices for the two-dimensional irreps E_2 and E_3 and the four-dimensional irrep Q are 11, 10, and 20, respectively.

IV. SUMMARY

We have developed formalisms for which normalization and symmetrization of one-electron Dirac scattered-wave wavefunctions can be easily implemented. The normalized wavefunctions will enable us to carry out self-consistent-field calculations and compute one-electron properties. The symmetrization procedure re-

sults in drastically reduced secular matrices as illustrated by the examples.

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