

Relativistic scattered-wave theory*

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A scattered-wave formalism based on the one-electron Dirac equation for a muffin-tin potential is presented. It is shown that the resulting relativistic secular equations reduce to their nonrelativistic counterparts in the infinite-rest-energy limit.

I. INTRODUCTION

The application of the multiple scattering or scattered-wave technique to determine the electronic structure of polyatomic molecules was originally proposed by Slater¹ and subsequently developed by Johnson.² This approach has been coupled with the $X\alpha$ statistical approximation for the exchange correlation.³ The resulting self-consistent-field- $X\alpha$ -scattered-wave (SCF- $X\alpha$ -SW) method has been applied with considerable success to various organic and inorganic molecules.⁴ The formalism has also been adapted to the problem of localized states in solids.⁵ The SCF- $X\alpha$ -SW method has proved unique in that it combines accuracy with practicality in terms of the necessary computational effort.

The first application of the method to a case where relativistic effects are important was reported by Pratt,⁶ in the calculation of the electronic states associated with vacancies in PbTe. The formalism was modified to include mass-velocity and Darwin corrections to the energy, neglecting the spin-orbit interaction in order to eliminate the need for the introduction of spin-angular functions in the description of the wave functions. Thus the modification does not lead to the splitting of the one-electron energy levels, which is significant in systems consisting of heavy atoms.

In this paper, we present a formulation of the scattered-wave method based on the solution of the one-electron Dirac equation for a muffin-tin potential. The resulting method furnishes us with a fully relativistic description of the wave func-

tions and spin-orbit-split electronic energies, without the need of perturbation calculations. Section II outlines the development of the relativistic secular equations. The approach is parallel to Johnson's nonrelativistic method, and similar to the relativistic Green's-function methods for energy-band⁷ and electron diffraction calculations.¹⁵ In Sec. III, we demonstrate that the present formalism reduces to the nonrelativistic limit when the electronic energies are negligible compared to the rest energy. The expansions of the relativistic Green's function in the angular momentum representation are derived in Appendix A. Appendix B presents a proof of one of the symmetry properties of the "relativistic Gaunt integrals," which is used in our formulation.

II. RELATIVISTIC SCATTERED-WAVE FORMALISM

We start with the one-electron Dirac equation

$$H\Psi(\vec{r}) = [c\vec{\alpha} \cdot \vec{p} + \beta m_0 c^2 + V(\vec{r})I_4] \Psi(\vec{r}) = W\Psi(\vec{r}), \quad (2.1)$$

where the wave function $\Psi(\vec{r})$ is a four-component column vector and \vec{p} is the momentum operator. I_N is the $N \times N$ unit matrix, and $\vec{\alpha}$ and β are given by

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}, \quad (2.2)$$

where $\vec{\sigma}$ are the Pauli spin matrices. Equation (2.1) can be transformed into the integral equation⁷

$$\int_v \vec{G}(\vec{r}, \vec{r}') V(\vec{r}') \Psi(\vec{r}') d\tau' - ic \int \vec{G}(\vec{r}, \vec{r}') \vec{\alpha} \cdot \hat{n}' \Psi(\vec{r}') dS' = \Psi(\vec{r}) \quad \text{for } \vec{r} \text{ inside } v, \\ = 0 \quad \text{for } \vec{r} \text{ outside } v, \quad (2.3)$$

where \hat{n} is the unit outward normal on the surface enclosing the volume v , and $\vec{G}(\vec{r}, \vec{r}')$ is the Dirac free-electron Green's function satisfying the equation

$$(c\vec{\alpha} \cdot \vec{p} + \beta m_0 c^2 - p_0 I_4) \vec{G}(\vec{r}, \vec{r}') = -\delta(\vec{r} - \vec{r}') I_4. \quad (2.4)$$

The Green's function $\vec{G}(\vec{r}, \vec{r}')$ appears in the form of a 4×4 matrix; thus unlike the nonrelativistic case, the quantities in the surface integral in (2.3) do not commute. The free-electron energy p_0 satisfies the classical relativistic energy-momentum relation

$$p_0^2 = k^2 c^2 + m_0^2 c^4, \quad (2.5)$$

where k stands for the magnitude of the free-electron momentum. The eigenfunctions of \vec{p} are the Dirac plane waves

$$\phi_{\vec{k}s}(\vec{r}) = \left(\frac{p_0 + m_0 c^2}{2p_0} \right)^{1/2} \begin{pmatrix} \chi(s) \\ \frac{c\vec{\sigma} \cdot \vec{p}}{p_0 + m_0 c^2} \chi(s) \end{pmatrix} e^{i\vec{k} \cdot \vec{r}}, \quad (2.6)$$

where $\chi(s)$ are the two-component spin functions with $s = \pm \frac{1}{2}$. Since, for a free particle, the energy and momentum operators commute, $\phi_{\vec{k}s}(\vec{r})$ is also an eigenfunction of the free-electron Dirac Hamiltonian with eigenvalue p_0 . Solving the integral equation (2.3) requires a knowledge of the Green's function and the wave function outside some suitable volume v . $\vec{G}(\vec{r}, \vec{r}')$ in principle can be evaluated via an eigenfunction expansion in terms of $\phi_{\vec{k}s}(\vec{r})$.⁷ However, it can be verified by direct substitution into (2.4) that $\vec{G}(\vec{r}, \vec{r}')$ of energy p_0 and corresponding k is obtainable by applying the Hermitian operator $c\vec{\alpha} \cdot \vec{p} + \beta m_0 c^2 + p_0 I_4$ to the nonrelativistic Green's function $G_0(\vec{r}, \vec{r}')$ of the same k , where $k^2 = 2m_0 E$. Since a Green's function is associated with a specific energy,⁸ it seems odd that $\vec{G}(\vec{r}, \vec{r}')$ derives from $G_0(\vec{r}, \vec{r}')$ of a different energy. This apparent discrepancy can be resolved by recognizing that as energies become small, (2.5) reduces to its nonrelativistic counterpart, that is,

$$k^2 c^2 = E(E + 2m_0 c^2) \xrightarrow{E/m_0 c^2 \ll 1} 2m_0 c^2 E, \quad (2.7)$$

where $E \equiv p_0 - m_0 c^2$ is the relativistic free-electron kinetic energy. Besides its simplicity, the aforementioned relation between $\vec{G}(\vec{r}, \vec{r}')$ and $G_0(\vec{r}, \vec{r}')$ has the additional advantage, over the eigenfunction expansion, of preserving the boundary conditions of the Green's functions. Since $G_0(\vec{r}, \vec{r}')$ is known from the nonrelativistic scattered-wave formalism, and since the same set of boundary conditions prevails in our formulation, the task of finding $\vec{G}(\vec{r}, \vec{r}')$ is vastly simplified. In Appendix A, $\vec{G}(\vec{r}, \vec{r}')$ is evaluated and expanded in the spin-orbit-coupled angular momentum representation. We are then left with the problem of choosing the suitable volume and

creating a model potential which simplifies the calculation of the wave function outside this volume.

Our formulation of the scattered-wave cluster problem will be based on the muffin-tin potential approximation, although in principle it can be generalized to include non-muffin-tin corrections. In the muffin-tin model, the potential is spherically symmetric inside nonoverlapping atomic spheres and outside an outer sphere enclosing the entire system, and is constant elsewhere. The wave function within each atomic sphere and outside the outer sphere are given in the angular momentum or partial wave representation by

$$\Psi^\alpha(\vec{r}_\alpha) = \sum_Q A_Q^\alpha \begin{pmatrix} g_\kappa^\alpha(r_\alpha) \chi_Q(\hat{r}_\alpha) \\ i f_\kappa^\alpha(r_\alpha) \chi_{\bar{Q}}(\hat{r}_\alpha) \end{pmatrix} \quad \text{for } \alpha = 0, 1, \dots, N, \quad (2.8)$$

where $\vec{r}_\alpha = \vec{r} - \vec{R}_\alpha$, and \vec{R}_α is the position of the center of the α th sphere. N is the total number of atoms and $\alpha = 0$ denotes the outer sphere with \vec{R}_0 being the origin. The radial functions $g_\kappa^\alpha(r_\alpha)$ and $f_\kappa^\alpha(r_\alpha)$ satisfy the pair of coupled differential equations

$$\frac{d}{dr} (c f_\kappa) = \left(\frac{\kappa - 1}{r} \right) c f_\kappa - (E - V) g_\kappa, \quad (2.9)$$

$$\frac{d}{dr} g_\kappa = \left(\frac{E - V}{c^2} + 1 \right) c f_\kappa - \left(\frac{\kappa + 1}{r} \right) g_\kappa,$$

where atomic units ($\hbar = 1$, $m_0 = \frac{1}{2}$, $e^2 = 2$) are used and will be assumed hereafter. The spin-angular functions $\chi_Q(\hat{r}_\alpha)$, where $Q \equiv (\kappa, \mu)$ and $\bar{Q} \equiv (-\kappa, \mu)$, are eigenfunctions of the operators L^2 , S^2 , J^2 , J_z , and $\vec{\sigma} \cdot \vec{L} + 1$ (about the center \vec{R}_α) with eigenvalues $l(l+1)$, $s(s+1)$, $j(j+1)$, μ , and $-\kappa$ respectively. They are given by

$$\chi_Q(\hat{r}_\alpha) = \sum_{s=\pm \frac{1}{2}} C(l \frac{1}{2} j; \mu - s, s) Y_{l, \mu - s}(\hat{r}_\alpha) \chi(s), \quad (2.10)$$

where $C(l \frac{1}{2} j; \mu - s, s)$ is a Clebsch-Gordan (or C) coefficient and $Y_{l, \mu - s}(\hat{r}_\alpha)$ is a spherical harmonic about the center \vec{R}_α . The parameter κ takes on integer values except zero, and is related to l and j by

$$\begin{aligned} l &= \kappa & \text{for } \kappa > 0, \\ &= -\kappa - 1 & \text{for } \kappa < 0, \\ j &= |\kappa| - \frac{1}{2}. \end{aligned} \quad (2.11)$$

If the interstitial region (IR) (where $V = \bar{V} = \text{constant}$) is taken to be the volume v in the integral equation (2.3), and energies are measured with respect to \bar{V} , then (2.3) is reduced to

$$\Psi(\vec{r}) = -ic \int \vec{G}(\vec{r}, \vec{r}') \vec{\alpha} \cdot \hat{n}' \Psi(\vec{r}') dS' \quad \text{for } \vec{r} \in \text{IR}, \quad (2.12)$$

where, by convention, $\vec{r} \in \text{IR}$ means that \vec{r} can lie within IR as well as on its surface. This surface consists of the IR outer sphere boundary S_1 and the IR atomic sphere boundary S_2 . Since the scattered-wave theory requires continuity of the wave function everywhere, the interstitial wave functions on the surfaces S_1 and S_2 can be obtained by matching with the outer and atomic sphere wave functions. In particular, we have

$$\begin{aligned} \Psi(\vec{r})|_{S_1} &= \Psi^0(\vec{r}_0)|_{r_0=b_{0-}}, & \Psi(\vec{r}')|_{S_1} &= \Psi^0(\vec{r}'_0)|_{r'_0=b_{0+}}, \\ \Psi(\vec{r})|_{S_2} &= \Psi^\alpha(\vec{r}_\alpha)|_{r_\alpha=b_{\alpha+}}, & \Psi(\vec{r}')|_{S_2} &= \Psi^\alpha(\vec{r}'_\alpha)|_{r'_\alpha=b_{\alpha-}}, \end{aligned} \quad (2.13)$$

where b_α is the radius of sphere α and the subscripts + and - denote the outer and inner surfaces of the sphere, respectively. The secular equations can now be set up by substituting the boundary conditions (2.13) into (2.12). For the case $\vec{r} \in S_1$, using (2.13) and (2.12), we have

$$\Psi^0(\vec{r}_0)|_{r_0=b_{0-}} = S_{0-0+} + \sum_{\alpha \neq 0} S_{0-\alpha-}, \quad (2.14)$$

where, for example, S_{0-0+} stands for the integral in (2.12) over the surface of the outer sphere with $r_0=b_{0-}$ and $r'=b_{0+}$. In effect, (2.14) means that the sum of the partial waves scattered off all muffin-tin spheres (including the outer sphere) via the propagator $\vec{G}(\vec{r}, \vec{r}')$ are matched with the wave function at the inner surface of the sphere. For the other case, $\vec{r} \in S_2$, where waves scattered off all spheres are matched at the outer surface of the α th sphere ($\alpha \neq 0$), (2.13) and (2.12) lead to

$$\Psi^\alpha(\vec{r}_\alpha)|_{r_\alpha=b_{\alpha+}} = S_{\alpha+0+} + S_{\alpha+\alpha-} + \sum_{\alpha' \neq 0, \alpha} S_{\alpha+\alpha'}. \quad (2.15)$$

It should be kept in mind that the unit normal \hat{n} in (2.12) points outwards from IR, thus on S_1 , $\hat{n} = \hat{r}_0$, while on S_2 , $\hat{n} = -\hat{r}_\alpha$. Although (2.14) and (2.15) each consists of two sets of algebraic equations (from the upper and lower components of the wave function), they turn out to be identical. Thus, as in the nonrelativistic case, the secular equations consist of only two sets of algebraic equations. The procedure for the explicit generation of these equations is outlined below. The surface integrals are evaluated using the expansions for the Green's functions given in Appendix A and those for the wave functions given by (2.8). Then we multiply (2.14) and (2.15) by the appropriate spin-angular functions and integrate over the sphere surface to eliminate the angular depen-

dence. The results can be simplified using the property of the spherical Bessel and Neumann functions,

$$n_l(x)j_{l+1}(x) - n_{l+1}(x)j_l(x) = 1/x^2. \quad (2.16)$$

Canceling the nonzero common factor ($E/c^2 + 1$) (since $E > -c^2$) and utilizing the symmetry property of the relativistic Gaunt integrals proven in Appendix B, we finally arrive at the secular equations

$$\begin{aligned} [T_\kappa^\alpha]^{-1} C_Q^\alpha - \sum_{\alpha' \neq 0, \alpha} \mathfrak{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'}) C_Q^{\alpha'} \\ + \sum_{\alpha'} \mathfrak{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_\alpha) C_Q^{\alpha'} = 0, \end{aligned} \quad (2.17)$$

$$\sum_{\alpha' \neq 0} \mathfrak{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_\alpha) C_Q^{\alpha'} + T_\kappa^0 C_Q^0 = 0,$$

where

$$\begin{aligned} C_Q^0 &= b_0^2 k^{l+1} A_Q^0 [S_\kappa E n_\tau (kb_0) g_\kappa^0 - kc n_l (kb_0) f_\kappa^0] \\ &\quad \text{for } E > 0 \\ &= b_0^2 (-\gamma)^{l+1} A_Q^0 [|E| k_\tau^{(1)} (\gamma b_0) g_\kappa^0 - \gamma c k_\tau^{(1)} (\gamma b_0) f_\kappa^0] \\ &\quad \text{for } E < 0, \quad k \equiv i\gamma, \end{aligned}$$

$$\begin{aligned} C_Q^\alpha &= b_\alpha^2 k^{-l} A_Q^\alpha [S_\kappa E j_\tau (kb_\alpha) g_\kappa^\alpha - kc j_l (kb_\alpha) f_\kappa^\alpha] \\ &\quad \text{for } E > 0, \\ &= b_\alpha^2 \gamma^{-l} A_Q^\alpha [|E| i_\tau (\gamma b_\alpha) g_\kappa^\alpha - \gamma c i_l (\gamma b_\alpha) f_\kappa^\alpha] \\ &\quad \text{for } E < 0, \end{aligned}$$

$$T_\kappa^\beta = \frac{S_\kappa E j_\tau (kb_\beta) g_\kappa^\beta - kc j_l (kb_\beta) f_\kappa^\beta}{S_\kappa E n_\tau (kb_\beta) g_\kappa^\beta - kc n_l (kb_\beta) f_\kappa^\beta} \Gamma_i^\beta(k)$$

$$= \frac{|E| i_\tau (\gamma b_\beta) g_\kappa^\beta - \gamma c i_l (\gamma b_\beta) f_\kappa^\beta}{|E| k_\tau^{(1)} (\gamma b_\beta) g_\kappa^\beta - \gamma c k_\tau^{(1)} (\gamma b_\beta) f_\kappa^\beta} \Gamma_i^\beta(k) \quad \text{for } E < 0,$$

$$\Gamma_i^\beta(k) \equiv -k^{-2l-1} \quad \text{for } E > 0, \quad \beta = 0, \alpha,$$

$$\equiv \lambda_\beta (-)^l \gamma^{-2l-1} \quad \text{for } E < 0,$$

$$\lambda_\beta = -1 \quad \text{for } \beta = 0,$$

$$= 1 \quad \text{for } \beta = \alpha \neq 0,$$

and

$$\vec{R}_{\alpha\alpha'} \equiv \vec{R}_\alpha, -\vec{R}_\alpha, \quad g_\kappa^0 \equiv g_\kappa^0(b_0), \quad \text{etc.} \quad (2.18)$$

The structure factors $\vec{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'})$, $\mathfrak{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_\alpha)$, and $\mathfrak{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha'})$, where 0, α , α' denote the centers of the outer, the α th, and the α' th spheres, respectively, are potential independent, and are discussed at length in Appendix A. The only other type of quantities in the secular equations consists of the "t matrices" T_κ^β , which, unlike the structure factors, depend on the potential through

the radial functions. As in ordinary scattering theory, T_κ^β is essentially the tangent of the phase shift of the κ th partial wave scattered by the β th sphere. In these equations, the energy parameter $E \equiv p_0 - \frac{1}{2}c^2$ is measured with respect to the constant potential \bar{V} . For a given E , the corresponding k can be deduced from (2.5) to yield

$$\begin{aligned} k &= (E + E^2/c^2)^{1/2} \text{ for } E > 0, \\ &= i(|E| - E^2/c^2)^{1/2} \text{ for } -c^2 < E < 0. \end{aligned} \quad (2.19)$$

From (A21), it is apparent that the secular matrix

$$\begin{pmatrix} \delta_{\alpha\alpha'} \delta_{QQ'} [T_\kappa^\alpha]^{-1} - \bar{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'}) & g_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'}) \\ g_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'}) & \delta_{QQ'} T_\kappa^0 \end{pmatrix} \quad (2.20)$$

is Hermitian in the double set of subscripts βQ and $\beta' Q'$. If $M_{QQ'}^{\beta\beta'}$ is a general element, then

$$M_{QQ'}^{\beta\beta'} = (M_{Q'Q}^{\beta'\beta})^*. \quad (2.21)$$

Hence the determinant of this matrix must be real. This is expected since the one-electron energies of the atomic cluster correspond to the zeros of this determinant.

As in the nonrelativistic case,⁴ the secular matrix (2.20) is contracted to the form

$$\delta_{\alpha\alpha'} \delta_{QQ'} [T_\kappa^\alpha]^{-1} - [\bar{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'}) + Z_{QQ'}^{\alpha\alpha'}], \quad (2.22)$$

where $\alpha, \alpha' \neq 0$. The information concerning the outer sphere is lumped together in the "pseudo-structure-factor"

$$Z_{QQ'}^{\alpha\alpha'} = \sum_{Q''} g_{QQ''}^{\alpha\alpha'}(\vec{R}_\alpha) T_\kappa^0 g_{Q''Q'}^{\alpha\alpha'}(\vec{R}_{\alpha'}), \quad (2.23)$$

which can be interpreted to describe the propagation of partial waves that travel between spheres α and α' via an intermediate scattering off the outer sphere. Thus in the absence of an outer sphere in the model potential, $Z_{QQ'}^{\alpha\alpha'}$ must vanish since there is no outer surface for the partial waves to "bounce back" from. The secular matrix will then be reduced to

$$\delta_{\alpha\alpha'} \delta_{QQ'} [T_\kappa^\alpha]^{-1} - \bar{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'}). \quad (2.24)$$

In the free-atom limit ($R_{\alpha\alpha'} \rightarrow \infty$), $\bar{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'})$ in (2.24) vanishes, and we are left with the t matrices, the zeros of which determine the relativistic one-electron energies for isolated atoms.

III. THE NONRELATIVISTIC LIMIT

Our treatment of the relativistic scattered-wave method based on the Dirac equation has been entirely analogous to that based on the Schrödinger

equation.² However, the relativistic formulation requires only the continuity of the wave function, whereas in the nonrelativistic case, the first derivative of the wave function has to be continuous as well. Nevertheless, because of the two-component nature of the relativistic wave function in the partial wave representation, the number of quantities to be matched remains equal to two.

The four-component Dirac equation can be reduced to a two-component equation via the Foldy-Wouthuysen transformation,⁹ which in turn reduces to the Schrödinger equation when c is taken to be infinite. Thus it is natural to conclude that the secular matrix (2.20) must also reduce to its nonrelativistic counterpart in the corresponding limit. Since the two secular matrices have identical forms,⁴ we can compare the structure factors and t matrices separately. The relations between the relativistic and nonrelativistic structure factors are given by (A15), the first of which can be rewritten as

$$\begin{aligned} \bar{g}_{QQ'}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'}) &= \sum_{\mu-m=\mu'-m'=\pm\frac{1}{2}} C(l\frac{1}{2}j; m, \mu-m) \bar{G}_{LL}^{\alpha\alpha'}(\vec{R}_{\alpha\alpha'}) \\ &\quad \times C(l'\frac{1}{2}j'; m', \mu'-m'). \end{aligned} \quad (3.1)$$

In the nonrelativistic limit, the total angular momentum is simply the orbital angular momentum, that is, $j=l$ and $Q=(l, m)=L$. Thus in this limit,

$$\bar{g}_{QQ'}^{\alpha\alpha'} \xrightarrow{j=l} \bar{G}_{LL}^{\alpha\alpha'}. \quad (3.2)$$

The potential-dependent t matrices T_κ^β given by (2.18) also reduces to its nonrelativistic counterpart

$$t_i^\beta = \frac{w_i(kb_\beta)R_i^{\beta'}(b_\beta) - kw_i'(kb_\beta)R_i^\beta(b_\beta)}{u_i(kb_\beta)R_i^{\beta'}(b_\beta) - ku_i'(kb_\beta)R_i^\beta(b_\beta)} \Gamma_i^\beta(k), \quad (3.3)$$

where w_i, u_i stand for appropriate spherical functions j_i, n_i, i_i , or $k_i^{(1)}$. R_i^β is the Schrödinger radial function within sphere β , and the "prime" denotes the first derivative with respect to the entire argument. To show this, we make use of the second of the Dirac radial equations (2.9), and the recurrence relations

$$w_i'(x) = a_\kappa w_{i-1}(x) - [(k+1)/x] w_i(x),$$

where

$$\begin{aligned} a_\kappa &= S_\kappa \quad \text{for } w_i = j_i, n_i, \\ &= 1 \quad \text{for } w_i = i_i, k_i^{(1)}. \end{aligned} \quad (3.4)$$

For example, the nonrelativistic limit of the numerator of a t matrix is given by

$$S_{\kappa} E j_{\Gamma}(k b_{\beta}) g_{\kappa}^{\beta}(b_{\beta}) - k c j_{\Gamma}(k b_{\beta}) f_{\kappa}^{\beta}(b_{\beta}) \xrightarrow{c \rightarrow \infty} k^2 j_{\Gamma}(k b_{\beta}) g_{\kappa}^{\beta}(b_{\beta}) - k j_{\Gamma}(k b_{\beta}) g_{\kappa}^{\beta'}(b_{\beta}), \quad (3.5)$$

where (2.7) is used. Recognizing that the larger component g_{κ}^{β} simply becomes the nonrelativistic radial function R_l^{β} in the nonrelativistic limit, one can easily verify that

$$T_{\kappa}^{\beta} \xrightarrow{c \rightarrow \infty} t_l^{\beta} \quad (3.6)$$

for both the outer and atomic spheres and for positive and negative E .

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APPENDIX A: GREEN'S FUNCTIONS AND THEIR EXPANSIONS

The Schrödinger free-particle Green's function is given by

$$G_0(\vec{r}, \vec{r}') = -\frac{\cos(k|\vec{r} - \vec{r}'|)}{4\pi|\vec{r} - \vec{r}'|} \text{ for } k^2 > 0, \\ = -\frac{e^{-\gamma|\vec{r} - \vec{r}'|}}{4\pi|\vec{r} - \vec{r}'|} \text{ for } k^2 < 0, \quad k \equiv i\gamma. \quad (A1)$$

The single-center (\vec{r} and \vec{r}' originate from the same point) expansion of $G_0(\vec{r}, \vec{r}')$ in orbital angular momentum space $L \equiv (l, m)$ can be written as

$$G_0(\vec{r}, \vec{r}') = \sum_L H_L(k\vec{r}_>) J_L(k\vec{r}_<)^*, \quad (A2)$$

where $H_L(k\vec{r}_>)$, $J_L(k\vec{r}_<)$ are each products of the spherical harmonics with suitable spherical functions (depending on the sign of k^2), and $r_>$ and $r_<$ denote, respectively, the larger and smaller of r and r' . In particular, we have

$$H_L(k\vec{r}_>) = k^{l+1} Y_L(\hat{r}_>) n_l(kr_>) \text{ for } k^2 > 0, \\ = (-\gamma)^{l+1} Y_L(\hat{r}_>) k_l^{(1)}(\gamma r_>) \text{ for } k^2 < 0, \\ J_L(k\vec{r}_<) = k^{-1} Y_L(\hat{r}_<) j_l(kr_<) \text{ for } k^2 > 0, \\ = \gamma^{-1} Y_L(\hat{r}_<) i_l(\gamma r_<) \text{ for } k^2 < 0, \quad (A3)$$

where the modified spherical functions $k_l^{(1)}(\gamma r) \equiv -i^{-1} h_l^{(1)}(i\gamma r)$ and $i_l(\gamma r) \equiv i^{-1} j_l(i\gamma r)$ are real for real arguments.

We now wish to transform this one-center expansion of G_0 into spin-orbit-coupled angular mo-

mentum space $Q \equiv (l, j, \mu) \equiv (\kappa, \mu)$. To do this, we first use the definition of the spin-angular function

$$\chi_Q(\hat{r}) = \sum_{s=\pm\frac{1}{2}} C(l\frac{1}{2}j; \mu - s, s) Y_{l, \mu - s}(\hat{r}) \chi(s), \quad (A4)$$

and the orthonormality of the Clebsch-Gordan coefficients $C(l\frac{1}{2}j; \mu - s, s)$ to show that

$$\sum_{j\mu} \chi_Q(\hat{r}) \chi_Q(\hat{r}')^* = \sum_{sm} \chi(s) \chi(s)^* Y_L(\hat{r}) Y_L(\hat{r}')^* \\ = I_2 \sum_m Y_L(\hat{r}) Y_L(\hat{r}')^*, \quad (A5)$$

where $\chi(s)$ is the spin function with $s = \pm\frac{1}{2}$ and I_2 is the 2×2 unit matrix. We note that the sums in (A5) are real and they are invariant under interchange of \vec{r} and \vec{r}' . Substituting (A5) into (A2), bearing in mind the equivalence of the summations $\sum_{ij\mu}$ and $\sum_{\kappa\mu}$, we obtain

$$G_0(\vec{r}, \vec{r}') I_2 = \sum_Q H_Q(k\vec{r}_>) J_Q(k\vec{r}_<)^*, \quad (A6)$$

where H_Q and J_Q are the spin-orbit analogs of H_L and J_L obtained by replacing Y_L by χ_Q .

To begin the derivation of the two-center expansions of $G_0(\vec{r}, \vec{r}')$, we let \vec{r} (or \vec{r}') be $\vec{\rho} + \vec{R}$, where \vec{r} (or \vec{r}') and \vec{R} have the same origin 0, but $\vec{\rho}$ is measured from the point specified by \vec{R} . From the plane-wave expansion

$$e^{i\vec{k} \cdot \vec{r}} = 4\pi \sum_L (ik)^L Y_L(\hat{k})^* J_L(k\vec{r}), \quad (A7)$$

we derive the useful expansion

$$J_L''[k(\vec{r} - \vec{\rho})] = \sum_{LL'} i^{l-l'-1} k^{l+l'-1} I(LL'L'') \\ \times J_L(k\vec{r}) J_{L'}(k\vec{\rho})^*, \quad (A8)$$

where $I(LL'L'')$ are the Gaunt integrals

$$I(LL'L'') \equiv 4\pi \int d\Omega Y_L(\Omega)^* Y_{L'}(\Omega) Y_{L''}(\Omega), \quad (A9)$$

which are always real, and nonvanishing only if the conditions

$$m = m' + m'', \quad l + l' + l'' = \text{even integer},$$

and

$$|l - l'| \leq l'' \leq l + l' \text{ or } \Delta(l'l'') \quad (A10)$$

are satisfied. Using (A2) and (A8), we obtain two-center expansions of $G_0(\vec{r}, \vec{r}')$ in L space for the following cases of interest:

(a) $\vec{r}' = \vec{\rho} + \vec{R}$, $R > |\vec{r} - \vec{\rho}|$

$$G_0(\vec{r}, \vec{\rho} + \vec{R}) = \sum_{LL'} J_L(k\vec{r}) \bar{G}_{LL'}^{OP}(\vec{R}) J_{L'}(k\vec{\rho})^*, \quad (\text{A11a})$$

$$(b) \quad \vec{r}' = \vec{\rho} + \vec{R}, \quad r' > |\vec{\rho} + \vec{R}|$$

$$G_0(\vec{r}, \vec{\rho} + \vec{R}) = \sum_{LL'} H_L(k\vec{r}) G_{LL'}^{OP}(\vec{R}) J_{L'}(k\vec{\rho})^*, \quad (\text{A11b})$$

$$(c) \quad \vec{r} = \vec{\rho} + \vec{R}, \quad r' > |\vec{\rho} + \vec{R}|$$

$$G_0(\vec{\rho} + \vec{R}, \vec{r}') = \sum_{LL'} J_L(k\vec{\rho}) G_{LL'}^{OP}(\vec{R}) H_{L'}(k\vec{r}')^*, \quad (\text{A11c})$$

where

$$\begin{aligned} \bar{G}_{LL'}^{OP}(\vec{R}) &\equiv \sum_{L''} i^{l'-l'-l''} k^{l'+l'-l''} I(LL'L'') H_{L''}(k\vec{R})^* \\ &\equiv \bar{G}_{LL'}^{PO}(-\vec{R}) \quad \text{for } O \neq P, \end{aligned} \quad (\text{A12a})$$

$$G_{LL'}^{OP}(\vec{R}) \equiv \sum_{L''} i^{l'-l'-l''} k^{-l'+l'+l''} I(LL'L'') J_{L''}(k\vec{R})^*, \quad (\text{A12b})$$

$$G_{LL'}^{PO}(\vec{R}) \equiv \sum_{L''} i^{l'-l'-l''} k^{l'-l'+l''} I(LL'L'') J_{L''}[k(-\vec{R})]^*, \quad (\text{A12c})$$

$$\bar{G}_{LL'}^{OO}(0) \equiv 0, \quad \text{and } G_{LL'}^{OO} = \delta_{LL'}. \quad (\text{A12d})$$

The double superscript OP is chosen to mean that the "structure factor" $G_{LL'}^{OP}$ is "measured" from point O to point P as demonstrated by comparing (A12b) and (A12c).

To obtain the Q -space two-center expansions of $G_0(\vec{r}, \vec{r}')$, we multiply (A4) by $C(l\frac{1}{2}j; \mu - s', s')$ and sum over j . From the orthonormality of the C coefficients, we get

$$Y_L(\hat{r})\chi(s) = \sum_j C(l\frac{1}{2}j; m, \mu - m)\chi_Q(\hat{r}). \quad (\text{A13})$$

Substituting for Y_L and $Y_{L'}$ in (A11) with (A13) and changing the indices of summation from mm' to $\mu\mu'$ ($\mu - m = \mu' - m' = s$), we arrive at the following expansions of $G_0(\vec{r}, \vec{r}')$ corresponding to cases (a), (b) and (c):

$$G_0(\vec{r}, \vec{\rho} + \vec{R})_{I_2} = \sum_{QQ'} J_Q(k\vec{r}) \bar{\mathfrak{G}}_{QQ'}^{OP}(\vec{R}) J_{Q'}(k\vec{\rho})^+, \quad (\text{A14a})$$

$$G_0(\vec{r}, \vec{\rho} + \vec{R})_{I_2} = \sum_{QQ'} J_Q(k\vec{r}) \mathfrak{G}_{QQ'}^{PO}(\vec{R}) J_{Q'}(k\vec{\rho})^+, \quad (\text{A14b})$$

$$G_0(\vec{\rho} + \vec{R}, \vec{r}')_{I_2} = \sum_{QQ'} J_Q(k\vec{\rho}) \mathfrak{G}_{QQ'}^{PO}(\vec{R}) H_{Q'}(k\vec{r}')^+, \quad (\text{A14c})$$

where

$$\begin{aligned} \bar{\mathfrak{G}}_{QQ'}^{OP}(\vec{R}) &\equiv \sum_s C(l\frac{1}{2}j; \mu - s, s) \bar{G}_{l, \mu - s; l', \mu' - s}^{OP}(\vec{R}) \\ &\quad \times C(l'\frac{1}{2}j'; \mu' - s, s) \\ &\equiv \sum_{L''} k^{l'+l'-l''} B(QQ'L'') H_{L''}(k\vec{R})^* \\ &\equiv \bar{\mathfrak{G}}_{QQ'}^{PO}(-\vec{R}) \quad \text{for } O \neq P, \end{aligned} \quad (\text{A15a})$$

$$\begin{aligned} \mathfrak{G}_{QQ'}^{PO}(\vec{R}) &\equiv \sum_s C(l\frac{1}{2}j; \mu - s, s) G_{l, \mu - s; l', \mu' - s}^{PO}(\vec{R}) \\ &\quad \times C(l'\frac{1}{2}j'; \mu' - s, s) \\ &\equiv \sum_{L''} k^{-l'+l'+l''} B(QQ'L'') J_{L''}(k\vec{R})^*, \end{aligned} \quad (\text{A15b})$$

$$\begin{aligned} \mathfrak{G}_{QQ'}^{PO}(\vec{R}) &\equiv \sum_s C(l\frac{1}{2}j; \mu - s, s) G_{l, \mu - s; l', \mu' - s}^{PO}(\vec{R}) \\ &\quad \times C(l'\frac{1}{2}j'; \mu' - s, s) \\ &\equiv \sum_{L''} k^{l'-l'+l''} B(QQ'L'') J_{L''}[k(-\vec{R})]^*, \end{aligned} \quad (\text{A15c})$$

$$\bar{\mathfrak{G}}_{QQ'}^{OO}(0) \equiv 0, \quad \mathfrak{G}_{QQ'}^{OO}(0) = \delta_{QQ'}, \quad (\text{A15d})$$

and

$$\begin{aligned} B(QQ'L'') &\equiv i^{l'-l'-l''} \sum_s C(l\frac{1}{2}j; \mu - s, s) \\ &\quad \times I(l, \mu - s; l', \mu' - s; L'') \\ &\quad \times C(l'\frac{1}{2}j'; \mu' - s, s). \end{aligned} \quad (\text{A16})$$

Thus the "relativistic structure factors" $\bar{\mathfrak{G}}_{QQ'}^{OP}(\vec{R})$, $\mathfrak{G}_{QQ'}^{PO}(\vec{R})$ can be derived from their nonrelativistic counterparts $\bar{G}_{QQ'}^{OP}(\vec{R})$, $G_{QQ'}^{PO}(\vec{R})$ using only the C coefficients. The modified "relativistic Gaunt integrals" $B(QQ'L'')$ are real since the C coefficients and the Gaunt integrals are real, and $l - l' - l'' = \text{even integer}$.

The Dirac free-electron Green's function $\tilde{G}(\vec{r}, \vec{r}')$ is related to the nonrelativistic one $G_0(\vec{r}, \vec{r}')$ by¹⁰

$$\begin{aligned} \tilde{G}(\vec{r}, \vec{r}') &= (c\vec{\alpha} \cdot \vec{p} + \beta m_0 c^2 + \rho_0 I_4) G_0(\vec{r}, \vec{r}') / c^2 \\ &= \left[\begin{array}{cc} (\rho_0 + m_0 c^2) I_2 & c\vec{\sigma} \cdot \vec{p} \\ c\vec{\sigma} \cdot \vec{p} & (\rho_0 - m_0 c^2) I_2 \end{array} \right] \frac{G_0(\vec{r}, \vec{r}')}{c^2} I_2. \end{aligned} \quad (\text{A17})$$

Using (A17), (A6), (A14) and the relation

$$\vec{\sigma} \cdot \vec{p} F_Q(k\vec{r}) = i S_\kappa k F_{\bar{Q}}(k\vec{r}), \quad (\text{A18})$$

where $F_Q(k\vec{r})$ stands for either $H_Q(k\vec{r})$ or $J_Q(k\vec{r})$, $S_\kappa = \text{sign of } \kappa$, and $\bar{Q} \equiv (\bar{l}, \bar{j}, \bar{\mu}) \equiv (-\kappa, \mu)$, we can expand $\tilde{G}(\vec{r}, \vec{r}')$ to yield the one-center expansion

$$\bar{G}(\vec{r}, \vec{r}') = \sum_{\vec{Q}} \begin{bmatrix} (E/c^2 + 1)H_Q(k\vec{r}_>)J_Q(k\vec{r}_<)^+ & iS_\kappa(k/c)H_{\bar{Q}}(k\vec{r}_>)J_Q(k\vec{r}_<)^+ \\ iS_\kappa(k/c)H_{\bar{Q}}(k\vec{r}_>)J_Q(k\vec{r}_<)^+ & (E/c^2)H_Q(k\vec{r}_>)J_Q(k\vec{r}_<)^+ \end{bmatrix}, \quad (\text{A19})$$

and the two-center expansions

(a) $\vec{r} = \vec{\rho} + \vec{R}$, $R > |\vec{r} - \vec{\rho}|$

$$\bar{G}(\vec{r}, \vec{\rho} + \vec{R}) = \sum_{\vec{Q}\vec{Q}'} \bar{g}_{\vec{Q}\vec{Q}'}^{OP}(\vec{R}) \begin{bmatrix} (E/c^2 + 1)J_Q(k\vec{r})J_{Q'}(k\vec{\rho})^+ & iS_\kappa(k/c)J_{\bar{Q}}(k\vec{r})J_{Q'}(k\vec{\rho})^+ \\ iS_\kappa(k/c)J_{\bar{Q}}(k\vec{r})J_{Q'}(k\vec{\rho})^+ & (E/c^2)J_Q(k\vec{r})J_{Q'}(k\vec{\rho})^+ \end{bmatrix}, \quad (\text{A20a})$$

(b) $\vec{r}' = \vec{\rho} + \vec{R}$, $r > |\vec{\rho} + \vec{R}|$

$$\bar{G}(\vec{r}, \vec{\rho} + \vec{R}) = \sum_{\vec{Q}\vec{Q}'} g_{\vec{Q}\vec{Q}'}^{OP}(\vec{R}) \begin{bmatrix} (E/c^2 + 1)H_Q(k\vec{r})J_{Q'}(k\vec{\rho})^+ & iS_\kappa(k/c)H_{\bar{Q}}(k\vec{r})J_{Q'}(k\vec{\rho})^+ \\ iS_\kappa(k/c)H_{\bar{Q}}(k\vec{r})J_{Q'}(k\vec{\rho})^+ & (E/c^2)H_Q(k\vec{r})J_{Q'}(k\vec{\rho})^+ \end{bmatrix}, \quad (\text{A20b})$$

(c) $\vec{r} = \vec{\rho} + \vec{R}$, $r' > |\vec{\rho} + \vec{R}|$

$$\bar{G}(\vec{\rho} + \vec{R}, \vec{r}') = \sum_{\vec{Q}\vec{Q}'} g_{\vec{Q}\vec{Q}'}^{PO}(\vec{R}) \begin{bmatrix} (E/c^2 + 1)J_Q(k\vec{\rho})H_{Q'}(k\vec{r}')^+ & iS_\kappa(k/c)J_{\bar{Q}}(k\vec{\rho})H_{Q'}(k\vec{r}')^+ \\ iS_\kappa(k/c)J_{\bar{Q}}(k\vec{\rho})H_{Q'}(k\vec{r}')^+ & (E/c^2)J_Q(k\vec{\rho})H_{Q'}(k\vec{r}')^+ \end{bmatrix}, \quad (\text{A20c})$$

where $E \equiv p_0 - m_0 c^2$ and atomic units are assumed. We have also assumed that \vec{R} is a constant vector so that $\nabla_{\vec{\rho} + \vec{R}} = \nabla_{\vec{\rho}}$.

The structure factors $\bar{G}_{LL'}^{OP}$, $G_{LL'}^{OP}$, $\bar{g}_{\vec{Q}\vec{Q}'}^{OP}$, and $g_{\vec{Q}\vec{Q}'}^{OP}$ possess the symmetry

$$\bar{G}_{L'L}^{PO}(\vec{R}) = \bar{G}_{LL'}^{OP}(\vec{R})^*, \text{ etc.} \quad (\text{A21})$$

This property can be easily verified for each structure factor using the conditions (A10) for nonvanishing Gaunt integrals. This symmetry is to be expected in view of the Hermiticity of both $G_0(\vec{r}, \vec{r}')$ and $\bar{G}(\vec{r}, \vec{r}')$ in \vec{r} and \vec{r}' .

APPENDIX B: PROOF OF $S_\kappa B(\bar{Q}\bar{Q}'L'') = S_\kappa B(QQ'L'')$

In arriving at the secular equations (2.17), we have made use of the following property of the relativistic Gaunt integrals:

$$S_\kappa B(\bar{Q}\bar{Q}'L'') = S_\kappa B(QQ'L''), \quad (\text{B1})$$

where $B(QQ'L'')$ is given by (A16). Defining $B' \equiv i^{l''-l'-l} B(QQ'L'')$ and $\bar{B}' \equiv i^{l''-l'-l} B(\bar{Q}\bar{Q}'L'')$, and using the identity $\bar{l} = l - S_\kappa$, we see that

$$i^{\bar{l}-l'-l''}/i^{l'-l'-l''} = i^{S_\kappa'-S_\kappa} = S_\kappa'/S_\kappa. \quad (\text{B2})$$

Hence we need only to show that $\bar{B}' = B'$. The Gaunt integral can be expressed as a product of Clebsch-Gordan coefficients,¹¹ that is,

$$I(L_3 L_2 L_1) = \left(\frac{4\pi(2L_1+1)(2L_2+1)}{2L_3+1} \right)^{1/2} C(l_1 l_2 l_3; m_1 m_2 m_3) C(l_1 l_2 l_3; 000). \quad (\text{B3})$$

Substituting (B3) into B' , with $L_3 = (l, \mu - s)$, $L_2 = (l', \mu' - s)$, $L_1 = L''$, we obtain

$$B' = \left(\frac{4\pi(2l'+1)(2l'+1)}{2l+1} \right)^{1/2} C(l'' l' l; 00) \sum_{s=\pm\frac{1}{2}} C(l'' l' l; \mu - \mu', \mu' - s) C(l'' \frac{1}{2} j; \mu - s, s) C(l' \frac{1}{2} j'; \mu' - s, s), \quad (\text{B4})$$

where the selection rule $m_3 = m_2 + m_1$ has been used in rewriting the C coefficients. The summation over s can be simplified using a single Racah recoupling¹²

$$\begin{aligned} \sum_{\mu_2} C(j_1 j_2 j'; \mu_1 \mu_2) C(j' j_3 j; \mu_1 + \mu_2, \mu_3) C(j_2 j_3 j''; \mu_2 \mu_3) \\ \mu_2 + \mu_3 = \mu'' \text{ fixed} \end{aligned} = [(2j''+1)(2j'+1)]^{1/2} W(j_1 j_2 j j_3; j' j'') C(j_1 j'' j; \mu_1 \mu''), \quad (\text{B5})$$

where $W(j_1 j_2 j_3; j' j'')$ are the Racah coefficients for the coupling of three angular momenta $\vec{J}_1, \vec{J}_2, \vec{J}_3$, with intermediate angular momenta $\vec{J}' = \vec{J}_1 + \vec{J}_2$, $\vec{J}'' = \vec{J}_2 + \vec{J}_3$. Substituting (B5) into (B4) using the correspondence of $(j_1 j_2 j_3 j' j'')$ to $(l'' l' l \frac{1}{2} j j')$ and changing the index of summation from $s = \pm \frac{1}{2}$ to $m' = \mu' \mp \frac{1}{2}$, we find that

$$B' = [4\pi(2l'+1)(2l''+1)(2j'+1)]^{1/2} C(l'' l' l; 00) \times W(l'' l' j \frac{1}{2}; l j') C(l'' j' j; \mu - \mu', \mu'). \quad (\text{B6})$$

The product $[4\pi(2l''+1)(2j'+1)]^{1/2} C(l'' j' j; \mu - \mu', \mu')$ is independent of both l and l' , so to prove $\bar{B}' = B'$,

it is sufficient to show the invariance of

$$\mathfrak{B}(S_\kappa, S_{\kappa'}) \equiv (2l'+1)^{1/2} C(l'' l' l; 00) W(l'' l j \frac{1}{2}; l j'), \quad (\text{B7})$$

under simultaneous changing of signs of κ and κ' . In other words, all that is left to be done is to verify the relations

$$\mathfrak{B}(++)/\mathfrak{B}(--) = \mathfrak{B}(+-)/\mathfrak{B}(-+) = 1. \quad (\text{B8})$$

To achieve this, we simplify the notation by the replacement of $(l'' l' j \frac{1}{2} l j')$ by $(abcd ef)$ in the expressions^{13,14}

$$C(abe; 00) = (-)^{(a+b-e)/2} (2e+1)^{1/2} \Delta_R(abe) \frac{[\frac{1}{2}(a+b+e)]!}{[\frac{1}{2}(a+b-e)]! [\frac{1}{2}(a-b+e)]! [\frac{1}{2}(-a+b+e)]!}, \quad (\text{B9})$$

$$W(abcd; ef) = \Delta_R(abe) \Delta_R(cde) \Delta_R(acf) \Delta_R(bdf) \sum_n \left(\frac{(-)^{n+a+b+c+d} (n+1)!}{(n-a-b-e)! (n-c-d-e)! (n-a-c-f)! (n-b-d-f)!} \times \frac{1}{(a+b+c+d-n)! (a+d+e+f-n)! (b+c+e+f-n)!} \right), \quad (\text{B10})$$

where

$$\Delta_R(abe) = \frac{(a+b-e)! (a-b+e)! (-a+b+e)!}{(a+b+e+1)!}, \quad (\text{B11})$$

and the index of summation assumes all integral values as long as none of the factorial arguments are negative. $C(abe; 00)$ vanishes unless the conditions $a+b+e = \text{even integer}$ and $\Delta(abe)$ [see (A10)] are satisfied, while $W(abcd; ef)$ vanishes unless we have $\Delta(abe)$, $\Delta(edc)$, $\Delta(bdf)$, and $\Delta(afc)$. The

relation $l = j + \frac{1}{2} S_\kappa$ is used to substitute $b = f + \frac{1}{2} S_{\kappa'}$ and $e = c + \frac{1}{2} S_\kappa$ into \mathfrak{B} making its dependence on $(S_\kappa, S_{\kappa'})$ exclusively explicit. The summation in (B10) looks forbidding, but upon closer examination, it can be reduced to only one term for $d = \frac{1}{2}$. This is true for all combinations of $(S_\kappa, S_{\kappa'})$, namely, $++$, $--$, $+-$, $-+$. The combination $(++)$ consists of the term specified by $n = a + f + c + 1$, while for the remaining three, $n = a + f + c$. Then substituting the simplified (B9) and (B10) into (B7) for each of the four combinations, we verify (B8).

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