Symmetry properties of the *S* matrix in a fully relativistic distorted-wave treatment of electron-impact ionization

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The symmetry properties of the *S* matrix in a fully relativistic distorted-wave treatment of electron-impact ionization are investigated. It is shown that the square modulus of the scattering matrix element in which the spin states of all four electrons are determined is not invariant under the reversal of the direction of alignment of all spins. The largest of two contributions to this noninvariance originates from the relativistic modifications of the continuum wave functions induced by the distorting potential of the target atom. A second smaller contribution is manifested on reducing the eight-dimensional matrix elements of the QED covariant propagator to purely spatial two-electron integrals. The triple differential cross section (TDCS) exhibits a spin asymmetry unless the entire scattering process occurs in a single plane. There will be a difference in the TDCS between an $(e,2e)$ event in which the initial beam is polarized parallel or antiparallel with respect to the beam direction even if the target is unpolarized and the final spin states are not determined. The TDCS will remain unchanged if, in addition to reversal of the direction of spin alignment, one appropriate momentum component of one of the two outgoing electrons is reversed.

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I. MOTIVATION

The correct quantum-mechanical description of scattering processes is important in many branches of physics ranging from electron-electron scattering [1] to experiments involving hadronic targets and projectiles [2]. The present paper addresses some of the symmetry properties of the scattering matrix describing the $(e,2e)$ process in which a target atom is ionized by a single incident electron to produce two unbound electrons in the final state [3,4]. Such purely electronic processes form the most suitable subject for initial studies of symmetry properties of the scattering matrix because the fundamental field theory of quantum electrodynamics controlling the scattering is much more firmly established and theoretically tractable than the theories underlying interactions involving hadrons. Furthermore, there is much current interest, both experimental and theoretical, in obtaining a detailed and sophisticated understanding of such electron-impact ionization processes [3,4]. This interest is particularly accentuated [5] for processes in which electrons moving with relativistic energies collide with atoms of high nuclear charge where the behavior of the bound electron is also substantially modified by relativity.

Triple differential cross sections (TDCS's) defining the probabilities with which the two unbound final-state electrons emerge with specific energies in specific directions for a known energy of the incident electron have been measured for copper, silver, gold, and uranium targets [6–8]. The highly relativistic nature of the ionizations of gold and uranium atoms was demonstrated in [9], who showed that theoretical calculations could reproduce the experimental TDCS only if all four electrons were described using Dirac four-component wave functions and their interaction in the ionization process was treated using a covariant propagator derived from quantum electrodynamics. All these experiments and comparisons with numerical calculations were restricted to the coplanar case in which all the three unbound electrons travel in the same plane. The present paper has four main objectives and is primarily concerned with describing scattering in noncoplanar geometries.

The first of the four objectives is to elucidate the time-independent interaction expressed in purely spatial coordinates that is implicit in the photon propagator appearing in the earlier theory [9]. This objective is achieved in Sec. II by showing that this interaction is just that previously derived in [10] (see also [11]).

The second objective is to answer the question as to whether the square magnitude of scattering matrix elements in which the spin states of all four particles are defined would be invariant under reversal of the spins of all the electrons. These square magnitudes directly determine the TDCS's in which the spin states of the outgoing electrons are not determined. These TDCS's are simply proportional to the sums of the scattering matrix element square magnitudes. Although the wave function for a freely traveling relativistic

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particle is only an eigenstate of a spin operator if the axis of spin quantization coincides with the direction of propagation, any linear combination of two such energetically degenerate spin eigenstates can be uniquely defined by its large components. Such a linear combination, although not an eigenstate of any relativistic spin operator, does, in the nonrelativistic limit, reduce to an eigenstate of a Pauli spin operator (σ_q) although the direction $(q=x,y,z)$ defined by this operator does not coincide with the direction of spatial propagation. Furthermore, such a relativistic state would be observed to have its spin aligned along the direction $\pm q$, becoming an eigenstate of the operator Σ_q, defined below, if observed from the rest frame of the electron. Thus it is always possible to refer to the limiting spin state of any relativistic free electron even if the spin is not aligned along the direction of propagation. It is assumed throughout this paper, except in Sec. IV C, that the spins are aligned in the scattering plane, defined by the directions of propagation of the incoming and one of the outgoing electrons. The second objective of the present paper is partly achieved by showing that the square magnitude of the scattering matrix elements is not invariant under spin reversal except for the coplanar case for which a proof of the invariance of these square magnitudes can be advanced. The coplanar case is that in which the entire ionization event occurs in just a single plane. In Sec. IV A it is further shown that this noninvariance survives summation over both the spin states of the final electrons as well as that of the initially bound level. This yields the prediction that the TDCS for ionization by an incident electron of known spin would, excepting the coplanar case, change under reversal of its spin alignment. This result is of interest because such asymmetries could be measured using currently available experimental technologies [12,13]. This lack of invariance was not manifested in previous numerical computations or experiments because all were restricted to coplanar geometries [9,14,15]. In Sec. IV C a link is made between our new results and previous theoretical and experimental studies [12,14] of scattering processes in which all three unbound electrons travel in the same plane with the spins of the incoming electrons being aligned perpendicular to that plane.

The third objective of this paper, emerging as a consequence of achieving the second, is to elucidate the origin of the noninvariance of the scatting matrix under spin reversal in noncoplanar geometries. It is shown in Sec. III C that there are two causes to this asymmetry, both of which are found to be relativistic in origin. By far the largest effect is due to the relativistic interactions between the continuum electrons and the atom in the elastic channels. To lowest order this is the "spin-orbit" interaction. A second smaller contribution is manifested on reducing the eight-dimensional integral elements of the QED covariant propogator to purely spatial two-electron integrals. It will be shown, however, that this contribution also disappears if we use plane waves to describe the continuum electrons.

The fourth objective of the present paper, achieved in Sec. III D, is also raised by the non-spin-reversal invariance of the scattering matrix. This is to elucidate the transformation containing the minimum number of changes, additional to reversal of all spins, under which this matrix does remain unchanged. We will show that for a kinematical arrangement in which one of the final-state electrons is detected out of the scattering plane the TDCS will be sensitive to the direction of *longtitudinal* polarization of the impinging electron. We also predict that the TDCS will be invariant under the simultaneous reversal of the direction of polarization and the out-of-plane component of the momentum of the detected electron.

The relativistic distorted wave Born approximation (rDWBA), as described in detail below, was introduced by Keller *et al.* [9] as a means to understand the inner-shell ionization of heavy-metal targets. Nakel and his collaborators had measured absolute triple differential cross sections in both asymmetric and symmetric geometries on a range of high-Z targets, including cooper, silver, gold, and uranium. Until the first rDWBA calculation agreement between theory and experiment was very poor. However, agreement between the rDWBA in coplanar symmetric and asymmetric geometries [9,16] and for spin-polarized electron experiments in the plane [14] is extremely good.

All evidence indicates that the interaction between the nucleus and incoming and exiting electrons has a dominant effect on the cross section. Explicitly it was shown that, unlike the nonrelativistic low-Z case, the effect of final-state electron-electron interactions is negligible [17]. The properties of the atomic target enter the calculation through the effective static potential generated by the nucleus and bound electrons. In the rDWBA the static potential is used to generate the wave functions for the contiuuum electrons. An important question, therefore, is whether the method of generating the static potential influences the TDCS. In [18], we explored using different ways of generating this potential. In particular, we used the Dirac-Fock approach (see [19]) and the density functional method of [20]. We found negligible difference between the calculations for a range of neutral targets and geometries and found no sensitivity to any realistic discription of the ground target state.

The rDWBA is the only approximation to include the effect of scattering of the incident and outgoing electrons in the field of the nucleus which is the dominant physical effect, and also this approximation is the only one that includes the full QED photon propogator and thus includes magnetic and retardation effects in the electron-electron interaction which is important if we are to get the correct maximum position for the TDCS [21].

II. PHOTON PROPAGATOR AND THE CONFIGURATION-SPACE INTERACTION

In the relativistic $(e,2e)$ process a fast incoming electron in the state denoted by the symbol 0 ionizes a bound electron in the state denoted b to produce a final state containing two continuum electrons in states labeled 1 and 2. The time-dependent wave function $\psi_w(\underline{x})$ for all four states ($w=0$, b, 1, or 2) satisfies the time-dependent Dirac equation containing a spatial potential energy operator $V_w(\mathbf{r})$, which can in principle be either local or nonlocal. These wave functions satisfy

$$i\frac{d\psi_w(\underline{x})}{dt} = [c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}} + \beta c^2 + V_w(\mathbf{r})]\psi_w(\underline{x}), \tag{1}$$

where α_j $(j=1,2,3)$ and β are the usual 4×4 Dirac matrices [22]. Atomic units for which $(\hbar = m_e = e = 4\pi\varepsilon_0 = 1)$ are used

throughout the paper and $\underline{x}$ is the four-vector:

$$\underline{x} = (x^0, x^1, x^2, x^3) = (ct, x, y, z) = (ct, \mathbf{r}). \tag{2}$$

The scalar product between the arbitrary four vectors $\underline{v}$ and $\vec{\hat{\Omega}}^{\dagger}_{AB}{}'$ is defined by

$$\underline{v} \cdot \underline{v}' = g_{\mu\nu} v^{\mu} v'^{\nu}, \tag{3}$$

where $g_{\mu\nu}$=diag(1,−1,−1,−1). Equation (1) has the usual solution

$$\psi_w(\underline{x}) = \psi_w(\mathbf{r}) e^{-iE_w t}, \tag{4}$$

where $\psi_w(\mathbf{r})$ is the solution to the time-independent Dirac equation

$$[c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta c^2 + V_w(\mathbf{r})]\psi_w(\mathbf{r}) = E_w \psi_w(\mathbf{r}). \tag{5}$$

At large distances $\mathbf{r}$ from the target atom, each of the three wave functions $\psi_w(\mathbf{r})$, w=0, 1, or 2, takes the form of a relativistic plane wave having a momentum $\mathbf{k}_w$ and large components defined by the quantum number $\varepsilon_w = \pm\frac{1}{2}$ corresponding to nonrelativistic plane waves having, respectively, spin up or spin down so that $\psi_w(\mathbf{r}) \equiv |\mathbf{k}_w \varepsilon_w\rangle$. The bound state has the usual central-field form and is therefore defined by specifying the principal kappa (κ_b) and m_j (m) quantum numbers so that $\psi_b(\mathbf{r}) \equiv |\kappa_b m\rangle$, leaving the principal quantum number as understood. All spin states are defined with respect to the z axis even though, in general, none of the asymptotically free wave functions has its spatial linear momentum aligned along this axis. For the case of bound s or $p_{1/2}$ orbitals, m can only take the two values $\pm\frac{1}{2}$ and could therefore, as previously [9], be denoted as ε_b.

The TDCS for a spin-averaged scattering process is given by [9]

$$\frac{d\sigma}{d\Omega_1 d\Omega_2 dE_2} = \frac{(2\pi)^2}{c^6}\frac{k_1 k_2}{k_0} E_0 E_1 E_2 \frac{1}{2}\frac{N_B}{N} \times \sum_{\varepsilon_1 \varepsilon_0 \varepsilon_2 m} |\langle \mathbf{k}_2 \varepsilon_2, \mathbf{k}_1 \varepsilon_1 | \hat{S} | \mathbf{k}_0 \varepsilon_0, \kappa m \rangle|^2, \tag{6}$$

where $\hat{S}$ is the S-matrix operator describing the two-electron interaction mediated by exchange of a photon. The scalar k_w (w=0,1,2) is the magnitude of the asymptotic momentum of the wave function ψ_w. The TDCS is averaged over the two possible asymptotic spin states of the incoming electron, thus generating the factor of 2 in the denominator. Furthermore, we have summed over all asymptotic final spin states. The quantity N_B is the number of electrons in subshell B in the target atom, the factor N_B/N enabling Eq. (6) to describe ionization from a subshell which is not closed. The maximum number of electrons that could be accommodated in subshell B is denoted N, so that for ionization from a closed subshell N_B/N reduces to unity.

Since the electronic states are taken to be eigenfunctions of a Dirac equation including an external potential and the $\hat{S}$ operator is applied to first order, evaluation of the TDCS through Eq. (6) corresponds to using the relativistic distorted-wave Born approximation [9]. Thus, although the ionizing electron-electron interaction is retained only to first order, the elastic electron-atom interactions in the incident and final channels are implicitly included to all orders by using distorted waves.

The S-matrix element describing the scattering of the relativistic electrons by their attendant electromagnetic fields is derived from QED and found using the previous assumptions [9] to be

$$\langle \mathbf{k}_2 \varepsilon_2, \mathbf{k}_1 \varepsilon_1 | \hat{S} | \mathbf{k}_0 \varepsilon_0, \kappa m \rangle = S^{dir} - S^{ex}, \tag{7}$$

where the direct (S^{dir}) and exchange (S^{ex}) matrix elements are given by

$$S^{dir} = i \int d^4\underline{x}_A \int d^4\underline{x}_B \psi_1^{\dagger}(\underline{x}_A)\gamma^0(A)\gamma^{\mu}(A)\psi_0(\underline{x}_A) \times D_{\mu\nu}(\underline{x}_A - \underline{x}_B)\psi_2^{\dagger}(\underline{x}_B)\gamma^0(B)\gamma^{\nu}(B)\psi_b(\underline{x}_B), \tag{8a}$$

$$S^{ex} = i \int d^4\underline{x}_A \int d^4\underline{x}_B \psi_2^{\dagger}(\underline{x}_A)\gamma^0(A)\gamma^{\mu}(A)\psi_0(\underline{x}_A) \times D_{\mu\nu}(\underline{x}_A - \underline{x}_B)\psi_1^{\dagger}(\underline{x}_B)\gamma^0(B)\gamma^{\nu}(B)\psi_b(\underline{x}_B). \tag{8b}$$

Here $\underline{x}_A$ is the four-vector $(ct_A, \mathbf{r}_A)$ containing the coordinates of electron A and $\gamma^{\mu}(A)$ are the Dirac matrices acting on the wave functions for this electron. These matrices are given by

$$\gamma^0(A) = \beta(A), \tag{9a}$$

$$\gamma^j(A) = \beta(A)\alpha_j(A), \quad j = 1,2,3. \tag{9b}$$

The QED photon propagator $D_{\mu\nu}(\underline{x}_A - \underline{x}_B)$ is given in Feynman gauge [23] as

$$D_{\mu\nu}(\underline{x}_A - \underline{x}_B) = \frac{4\pi}{c} i g_{\mu\nu} \int \frac{d^4q}{(2\pi)^4} \frac{e^{-i\underline{q}\cdot(\underline{x}_A - \underline{x}_B)}}{\underline{q}\cdot\underline{q} + i\eta}, \quad \eta \to 0, \tag{10}$$

where $\underline{q}$ is the momentum four-vector with components

$$\underline{q} = (q^0, q^1, q^2, q^3) = (c^{-1}E, p_x, p_y, p_z) = (c^{-1}E, \mathbf{p}). \tag{11}$$

In order to obtain a useful expression for the interaction operator, we consider first Eq. (8a). Inserting the expression for the photon propagator Eq. (10), and separating the time variables in the wave functions, noting that $dq^0 = c^{-1}dE$ and $dx_A^0 = cdt_A$, gives

$$S^{dir} = -4\pi g_{\mu\nu} \int e^{iE_1 t_A} \psi_1^{\dagger}(\mathbf{r}_A)\gamma^0(A)\gamma^{\mu}(A) e^{-iE_0 t_A}\psi_0(\mathbf{r}_A) \times \int \frac{dE d\mathbf{p}}{(2\pi)^4} \frac{e^{-iE(t_A - t_B)} e^{i\mathbf{p}\cdot(\mathbf{r}_A - \mathbf{r}_B)}}{E^2 c^{-2} - |\mathbf{p}|^2 + i\eta} \times \int e^{iE_2 t_B}\psi_2^{\dagger}(\mathbf{r}_B)\gamma^0(B)\gamma^{\nu}(B) e^{-iE_b t_B}\psi_b(\mathbf{r}_B) d\mathbf{r}_A d\mathbf{r}_B dt_A dt_B. \tag{12}$$

This can be written as

$$S^{dir} = -4\pi g_{\mu\nu} \int f_{\mu\nu}(\mathbf{r}_A, \mathbf{r}_B) I(\mathbf{r}_A, \mathbf{r}_B) d\mathbf{r}_A d\mathbf{r}_B, \tag{13}$$

where

$$f_{\mu\nu}(\mathbf{r}_A,\mathbf{r}_B) = \psi_1^\dagger(\mathbf{r}_A)\gamma^0(A)\gamma^\mu(A)\psi_0(\mathbf{r}_A)\psi_2^\dagger \times(\mathbf{r}_B)\gamma^0(B)\gamma^\nu(B)\psi_b(\mathbf{r}_B), \tag{14a}$$

$$I(\mathbf{r}_A,\mathbf{r}_B) = \int e^{-i(E_0-E_1)t_A}e^{-i(E_b-E_2)t_B}e^{-iE(t_A-t_B)}g(E)dEd\mathbf{p}dt_Adt_B, \tag{14b}$$

with

$$g(E) = \frac{1}{(2\pi)^4}\frac{e^{i\mathbf{p}\cdot(\mathbf{r}_A-\mathbf{r}_B)}}{E^2c^{-2}-|\mathbf{p}|^2+i\eta}, \tag{15}$$

with $g(E)$ implicitly depending on $\mathbf{r}_A$, $\mathbf{r}_B$, and $\mathbf{p}$. One can perform the time integrations in $I(\mathbf{r}_A,\mathbf{r}_B)$ by rearranging the corresponding variables to obtain an integration over Dirac-delta functions:

$$I(\mathbf{r}_A,\mathbf{r}_B) = \int e^{i(E_1-E_0-E)t_A}e^{i(E_2-E_b+E)t_B}g(E)dE\,d\mathbf{p}\,dt_Adt_B \tag{16a}$$

$$=(2\pi)^2\int \delta(E_1-E_0-E)\delta(E_2-E_b+E)g(E)dE\,d\mathbf{p}. \tag{16b}$$

We have to consider the product of two delta functions in Eq. (16b). One can show that the product of a function $f(E)$ with a delta function $\delta(E-\Delta E)$ is given as

$$f(E)\delta(E-\Delta E) = f(\Delta E)\delta(E-\Delta E). \tag{17}$$

Defining the two positive energy differences $\Delta E_A=E_0-E_1$ and $\Delta E_B=E_2-E_b$ and replacing E in Eq. (17) by $E+\Delta E_B$ while also substituting $\Delta E_B-\Delta E_A$ for ΔE yields

$$\delta(E+\Delta E_B)\delta(E+\Delta E_A) = \delta(\Delta E_B-\Delta E_A)\delta(E+\Delta E_A), \tag{18}$$

where the function f in Eq. (17) has itself been taken to be a delta function. Substitution of this result into Eq. (16b) renders trivial the E integration so that one has

$$I(\mathbf{r}_A,\mathbf{r}_B) = \delta(\Delta E_B-\Delta E_A)\frac{1}{(2\pi)^2}\int\frac{e^{i\mathbf{p}\cdot(\mathbf{r}_A-\mathbf{r}_B)}}{\omega^2-|\mathbf{p}|^2+i\eta}d\mathbf{p}, \tag{19}$$

where $\omega=\Delta E_Ac^{-1}$. The quantity $\delta(\Delta E_B-\Delta E_A)$ represents the condition of energy conservation. The remaining integration over $\mathbf{p}$ in Eq. (19) can be evaluated by a transformation of coordinates. Assuming that $\mathbf{r}_A-\mathbf{r}_B$ lies along the z axis and denoting $|\mathbf{r}_A-\mathbf{r}_B|$ by r_{AB} and $|\mathbf{p}|$ by p, the scalar product becomes

$$\mathbf{p}\cdot(\mathbf{r}_A-\mathbf{r}_B) = pr_{AB}\cos\theta, \tag{20}$$

where θ is the angle between $\mathbf{p}$ and the vector $(\mathbf{r}_A-\mathbf{r}_B)$. After performing the integrations over θ and ϕ, Eq. (19) becomes

$$I(\mathbf{r}_A,\mathbf{r}_B) = \delta(\Delta E_B-\Delta E_A)\frac{1}{2\pi}\frac{1}{ir_{AB}}\int_{-\infty}^{\infty}p\,dp\frac{e^{ipr_{AB}}}{\omega^2-p^2+i\eta},$$

$$\eta\to 0. \tag{21}$$

To evaluate Eq. (21) one can apply the residue theorem and evaluate the integral in the upper half plane. There is a pole of order 1 enclosed and the integral is therefore given by

$$I(\mathbf{r}_A,\mathbf{r}_B) = -\,\delta(\Delta E_B-\Delta E_A)\frac{1}{2}\frac{e^{i\omega r_{AB}}}{r_{AB}}. \tag{22}$$

Substitution of this result and the definition (14a) into Eq. (13) yields

$$S^{dir} = 2\pi\delta(E_0+E_b-E_1-E_2)g_{\mu\nu}\int\psi_1^\dagger(\mathbf{r}_A)\gamma^0(A)\gamma^\mu(A)\psi_0(\mathbf{r}_A) \times\psi_2^\dagger(\mathbf{r}_B)\gamma^0(B)\gamma^\nu(B)\psi_b(\mathbf{r}_B)\frac{e^{i\omega r_{AB}}}{r_{AB}}d\mathbf{r}_1d\mathbf{r}_2. \tag{23}$$

Using the relations (9a) and (9b) and noting that $\beta^2=1$ yields

$$S^{dir} = 2\pi\delta(E_0+E_b-E_1-E_2) \times\int\psi_1^\dagger(\mathbf{r}_A)\psi_2^\dagger(\mathbf{r}_B)\hat{\mathcal{H}}\psi_0(\mathbf{r}_A)\psi_b(\mathbf{r}_B)d\mathbf{r}_Ad\mathbf{r}_B, \tag{24}$$

where the operator $\hat{\mathcal{H}}$ is defined as

$$\hat{\mathcal{H}} = [1-\boldsymbol{\alpha}(A)\cdot\boldsymbol{\alpha}(B)]\frac{e^{i\omega r_{AB}}}{r_{AB}} \tag{25a}$$

$$=[1-\boldsymbol{\alpha}(A)\cdot\boldsymbol{\alpha}(B)]\frac{\cos(\omega r_{AB})+i\sin(\omega r_{AB})}{r_{AB}}. \tag{25b}$$

A similar derivation holds true for the exchange matrix element but with the labels 1 and 2 for the outgoing electrons interchanged. The operator (25a) is just the configuration-space interaction originally derived in [10] (see also [11]).

The result (24) shows that the TDCS for spin-averaged energy-conserving processes can be expressed as

$$\frac{d\sigma}{d\Omega_1d\Omega_2dE_2} = c_E\frac{1}{2}\frac{N_B}{N}\sum_{\varepsilon_1\varepsilon_0\varepsilon_2m}|\langle 1,2|\hat{\mathcal{H}}|0,b\rangle-\langle 1,2|\hat{\mathcal{H}}|b,0\rangle|^2, \tag{26}$$

where

$$c_E = \frac{(2\pi)^4}{c^6}\frac{k_1k_2}{k_0}E_0E_1E_2 \tag{27}$$

and

$$\langle 1,2|\hat{\mathcal{H}}|0,b\rangle = \int\psi_1^\dagger(\mathbf{r}_A)\psi_2^\dagger(\mathbf{r}_B)\hat{\mathcal{H}}\psi_0(\mathbf{r}_A)\psi_b(\mathbf{r}_B)d\mathbf{r}_Ad\mathbf{r}_B. \tag{28}$$

For slowly moving electrons $E_0=E_1=E_2=c^2$, $\hat{\mathcal{H}}$ reduces to r_{AB}^{-1}, thus showing that Eq. (26) reduces to the standard non-relativistic expression.

III. SPIN-RESOLVED SCATTERING MATRIX ELEMENTS

A. Overview

The scattering process controlled by the S matrix depends on the spin states of the free electrons and m_j, the quantum number of the bound level. This collection of four quantum numbers is denoted by the symbol $s=(\varepsilon_1\varepsilon_2\varepsilon_0 m)$. We can always choose a coordinate system in which the momentum vectors of the incoming and fast scattered electrons define the scattering plane, chosen to be the xz plane. Hence, these two electrons have y momentum components equal to zero. There are two distinct cases, in which the spins are aligned in the scattering plane, which, however, do not need to be distinguished in the following treatment because they follow exactly the same theoretical development. In the first of these the incoming particle travels along the z direction, so that its direction of propagation is the same as the axis of spin alignment. The second case is physically different because the spin alignment axis (z) is perpendicular to the direction (x) along which the incoming electron is traveling. Furthermore, we introduce the symbol k_{2_y} which denotes the asymptotic y-momentum component of the slow electron at large distances from the nucleus.

The square magnitude of any scattering matrix element entering a TDCS (26) will be denoted by $\mathcal{S}(s,k_{2_y})$ so that

$$\mathcal{S}(s,k_{2_y}) = |\mathcal{M}(s,k_{2_y}) - \mathcal{M}^{Ex}(s,k_{2_y})|^2, \tag{29}$$

where the direct and exchange matrix elements in Eq. (29) are denoted

$$\mathcal{M}(s,k_{2_y}) = \langle \varepsilon_1, \varepsilon_2 k_{2_y} | \hat{\mathcal{H}} | \varepsilon_0, m \rangle, \tag{30a}$$

$$\mathcal{M}^{Ex}(s,k_{2_y}) = \langle \varepsilon_1, \varepsilon_2 k_{2_y} | \hat{\mathcal{H}} | m, \varepsilon_0 \rangle. \tag{30b}$$

Consequently, the square magnitude of the scattering matrix elements in which all four quantum numbers specified by the symbol s are reversed will be denoted by $\mathcal{S}(-s,k_{2_y})$. This process of changing the spins of all four quantum numbers defining the symbol s will be called spin reversal, it being understood that this also involves changing the signs of the appropriate angular momenta in the bound orbital.

The spin-up $[\psi^+_{pl}(\mathbf{r})]$ and spin-down $[\psi^-_{pl}(\mathbf{r})]$ plane waves to which the distorted waves tend at large distance $\mathbf{r}$ are given by

$$\psi^{\pm}_{pl}(\mathbf{r}) = \begin{pmatrix} \chi^{\pm 1/2} \\ A_s(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\chi^{\pm 1/2} \end{pmatrix} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{31}$$

where the $\chi^{\pm 1/2}$ are the usual two-component spin functions defined on p. 12 of [24] and A_s is the constant defined by $A_s=c(E+c^2)^{-1}$. Here σ_x, σ_y, and σ_z are the usual 2×2 Pauli matrices whose 4×4 equivalents Σ_x, Σ_y, and Σ_z are related [25] to the Dirac matrices by $\alpha_j=\rho_1\Sigma_q$ with $q=x$ for $j=1$, etc. Although the $\psi^{\pm}_{pl}(\mathbf{r})$ are not eigenstates of the relativistic operator Σ_z, they are the relevant energy eigenstates with spin states uniquely defined by the large components as already discussed in Sec. I.

For distorted yet still unbound wave functions, which asymptotically become plane waves of momentum $\mathbf{k}$ traveling along the direction defined by the polar angular variable $\Omega_{\mathbf{k}}$, one must distinguish between incoming $|\mathbf{k}^{in}\varepsilon\rangle$ and outgoing $|\mathbf{k}^{out}\varepsilon\rangle$ solutions. For the states $|\mathbf{k}_0\varepsilon_0\rangle$, $|\mathbf{k}_1\varepsilon_1\rangle$, and $|\mathbf{k}_2\varepsilon_2\rangle$, these superscripts are not required since $|\mathbf{k}_0\varepsilon_0\rangle$ is clearly and incoming state while $|\mathbf{k}_1\varepsilon_1\rangle$ and $|\mathbf{k}_2\varepsilon_2\rangle$ are outgoing ones. It is convenient to expand the $|\mathbf{k}^{i/o}\varepsilon\rangle$ as a sum of partial waves each having the standard relativistic central-field form thus carrying the label κ. This expansion takes the form [9,24]

$$|\mathbf{k}^{i/o}\varepsilon\rangle = (2\pi)^{-1/2}\sum_{j=1/2}^{\infty}\sum_{l=j-1/2}^{j+1/2} i^l e^{\pm i\delta'_\kappa}\sum_{m=-j}^{j} C\left(l,\frac{1}{2},j,m-\varepsilon,\varepsilon,m\right) \times [Y_{l,m-\varepsilon}(\Omega_{\mathbf{k}})]^* \begin{pmatrix} g_\kappa\chi_{\kappa,m} \\ if_\kappa\chi_{-\kappa,m} \end{pmatrix}. \tag{32}$$

Here a positive sign is taken in $e^{\pm i\delta'_\kappa}$ for an outgoing wave ($i/o=out$) and the negative sign for the incoming case ($i/o=in$). Each $\chi_{\kappa,m}$ is a standard two component spin-angular function which is an eigenfunction of j^2 with eigenvalue $j(j+1)$ and l is the orbital angular momentum entering the large components of the partial wave defined by the quantum number κ. The spatial angular variables (θ and ϕ) upon which the $\chi_{\kappa,m}$ and $\chi_{-\kappa,m}$ depend are implied by the notation in Eq. (32) as is the radial distance argument upon which both g_κ and f_κ depend. For $\kappa=-1$, the quantities $\chi_{-1,\pm 1/2}$ reduce to the pure spin functions $\chi^{\pm 1/2}$ introduced in Eq. (31). The real quantity δ'_κ is the difference between the phase shift δ_κ and that equal to $-\pi(l+1)/2$ occurring in the plane-wave case, so that for the latter, $\delta'_\kappa=0$. The phase shift δ_κ, defined and discussed more fully on pp. 205–207 of [24], can include the logarithmic Coulomb contribution arising when the potential experienced by the electron reduces to a Coulomb field at large distances from the nucleus.

B. Transformations under pure spin inversion

1. Spin reversal operator

In physical terms, time reversal changes the sign of both the spin and spatial linear momentum of a particle. The observation that a subsequent purely spatial inversion would restore the spatial linear momentum to its original value suggests that the operator $\vec{\hat{\Omega}}$ for spin reversal is the product of that for time reversal with that for spatial inversion, so that

$$\vec{\hat{\Omega}} = \hat{I}_D\vec{\hat{T}}. \tag{33}$$

The relativistic operators, denoted $\hat{I}_D$ and $\vec{\hat{T}}$, corresponding to spatial inversion and time reversal are given by [26]

$$\hat{I}_D = \beta\hat{I}, \tag{34a}$$

$$\vec{\hat{T}} = i\Sigma_y\vec{\hat{K}}, \tag{34b}$$

where $\hat{I}$ is the operator for purely spatial inversion and $\vec{\hat{K}}$ is the complex conjugation operator acting to the right as denoted by the arrow.

The spin-reversing properties of $\vec{\hat{\Omega}}$ in the simplest case, that of the plane-wave states $\psi^{\pm}_{pl}(\mathbf{r})$, is demonstrated by using

the anticommutation relations obeyed by the Pauli matrices and the result is $i\sigma_y\chi^{\pm 1/2} = \mp\chi^{\mp 1/2}$. It then follows that

$$\vec{\hat{\Omega}}\psi^{\pm}_{pl}(\mathbf{r}) = \beta\hat{I}i\Sigma_y\vec{\hat{K}}\psi^{\pm}_{pl}(\mathbf{r}) = \beta\hat{I}i\Sigma_y\begin{pmatrix}\chi^{\pm 1/2}\\ A_s(-\sigma_x\hat{p}_x+\sigma_y\hat{p}_y-\sigma_z\hat{p}_z)\chi^{\pm 1/2}\end{pmatrix}e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{35a}$$

$$= \beta\hat{I}\begin{pmatrix}\mp\chi^{\mp 1/2}\\ A_s(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})i\sigma_y\chi^{\pm 1/2}\end{pmatrix}e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{35b}$$

$$= \beta\begin{pmatrix}\mp\chi^{\mp 1/2}\\ \pm A_s(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\chi^{\mp 1/2}\end{pmatrix}e^{i\mathbf{k}\cdot\mathbf{r}} = \mp\psi^{\mp}_{pl}(\mathbf{r}). \tag{35c}$$

2. Transformations of atomic eigenstates under spin reversal

The action of $\vec{\hat{\Omega}}$ on a single Dirac central field orbital, such as the $|\kappa,m\rangle$ bound state, is derived by combining the results (2.18) and (2.16) of [27] for $\vec{\hat{T}}|\kappa,m\rangle$ with the phase factor $(-1)^l$ arising when $\hat{I}_D$ acts on $|\kappa,m\rangle$ [19]. This yields

$$\vec{\hat{\Omega}}|\kappa,m\rangle = (-1)^l(-1)^{m+1/2}(-1)^{(1-a)/2}|\kappa,-m\rangle. \tag{36}$$

Here l is the orbital angular momentum associated with the large components and $a=1$ for $\kappa<0$ and $a=-1$ for $\kappa>0$. Thus the phase factor is always ± 1. We note that $\vec{\hat{\Omega}}$ flips the spin of a plane wave and reverses the m_j quantum number of a bound state.

The effect of the $\vec{\hat{\Omega}}$ operator on the unbound states is elucidated by considering the partial-wave expansion (32). For a spin-up $\varepsilon=\frac{1}{2}$ state, it follows that

$$\vec{\hat{\Omega}}\left|\mathbf{k}^{i/o}\frac{1}{2}\right\rangle = (2\pi)^{-1/2}\sum_{j=1/2}^{\infty}\sum_{l=j-1/2}^{j+1/2}(-i)^l e^{\mp i\delta'_\kappa} \times\sum_{m=-j}^{j} C\left(l,\frac{1}{2},j,m-\frac{1}{2},\frac{1}{2},m\right) \times Y_{l,m-1/2}(\Omega_{\mathbf{k}})\vec{\hat{\Omega}}\begin{pmatrix}g_\kappa\chi_{\kappa,m}\\ if_\kappa\chi_{-\kappa,m}\end{pmatrix} \tag{37a}$$

$$= (2\pi)^{-1/2}\sum_{j=1/2}^{\infty}\sum_{l=j-1/2}^{j+1/2}(-i)^l e^{\mp i\delta'_\kappa} \times\sum_{m=-j}^{j} C\left(l,\frac{1}{2},j,m-\frac{1}{2},\frac{1}{2},m\right) \times Y_{l,m-1/2}(\Omega_{\mathbf{k}})(-1)^l(-1)^{m+1/2}(-1)^{(1-a)/2} \times\begin{pmatrix}g_\kappa\chi_{\kappa,-m}\\ if_\kappa\chi_{-\kappa,-m}\end{pmatrix} \tag{37b}$$

$$= (2\pi)^{-1/2}\sum_{j=1/2}^{\infty}\sum_{l=j-1/2}^{j+1/2} i^l e^{\mp i\delta'_\kappa} \times\sum_{m=-j}^{j} C\left(l,\frac{1}{2},j,-m-\frac{1}{2},\frac{1}{2},-m\right) \times Y_{l,-m-1/2}(\Omega_{\mathbf{k}})(-1)^{-m+1/2}(-1)^{(1-a)/2} \times\begin{pmatrix}g_\kappa\chi_{\kappa,-m}\\ if_\kappa\chi_{-\kappa,-m}\end{pmatrix}, \tag{37c}$$

where Eq. (36) was used in the second step and the order of summation over the dummy variable m has been reversed in the third step. By using the two results

$$C\left(l,\frac{1}{2},j,-m-\frac{1}{2},\frac{1}{2},-m\right) = (-1)^{j-l-1/2}C\left(l,\frac{1}{2},j,m+\frac{1}{2},-\frac{1}{2},m\right), \tag{38a}$$

$$(-1)^{-m-1/2}Y_{l,-m-1/2}(\Omega_{\mathbf{k}}) = [Y_{l,m+1/2}(\Omega_{\mathbf{k}})]^* \tag{38b}$$

and then noting that for both $a=1$ $\left(j=l+\frac{1}{2}\right)$ and $a=-1$ $\left(j=l-\frac{1}{2}\right)$

$$(-1)^{j-l-1/2}(-1)^{(1-a)/2} = 1, \tag{39}$$

it follows that Eq. (37c) can be developed as

$$\vec{\hat{\Omega}}\left|\mathbf{k}^{i/o}\frac{1}{2}\right\rangle = (-1)(2\pi)^{-1/2}\sum_{j=1/2}^{\infty}\sum_{l=j-1/2}^{j+1/2} i^l e^{\mp i\delta'_\kappa} \times\sum_{m=-j}^{j} C\left(l,\frac{1}{2},j,m+\frac{1}{2},-\frac{1}{2},m\right) \times[Y_{l,m+1/2}(\Omega_{\mathbf{k}})]^*\begin{pmatrix}g_\kappa\chi_{\kappa,m}\\ if_\kappa\chi_{-\kappa,m}\end{pmatrix}. \tag{40}$$

Comparison of this result with that provided by Eq. (32) for $|\mathbf{k}^{i/o}-\frac{1}{2}\rangle$ shows that Eq. (40) differs from $|\mathbf{k}^{i/o}-\frac{1}{2}\rangle$ only in the overall -1 phase factor and in that the sign of every phase-shift term has become reversed. This shows that

$$\vec{\hat{\Omega}}\left|\mathbf{k}^{in}\tfrac{1}{2}\right\rangle = -\left|\mathbf{k}^{out}-\tfrac{1}{2}\right\rangle, \tag{41a}$$

$$\vec{\hat{\Omega}}\left|\mathbf{k}^{out}\tfrac{1}{2}\right\rangle = -\left|\mathbf{k}^{in}-\tfrac{1}{2}\right\rangle. \tag{41b}$$

Thus the action of $\vec{\hat{\Omega}}$ on a incoming spin-up state produces an outgoing spin-down one. This might have been expected in view of the time reversal operator $\vec{\hat{T}}$ component of $\vec{\hat{\Omega}}$. An essentially identical calculation to that just presented shows that

$$\vec{\hat{\Omega}}\left|\mathbf{k}^{in}-\tfrac{1}{2}\right\rangle = \left|\mathbf{k}^{out}\tfrac{1}{2}\right\rangle, \tag{42a}$$

$$\hat{\vec{\Omega}}\left|\mathbf{k}^{in}-\tfrac{1}{2}\right\rangle=\left|\mathbf{k}^{out}\tfrac{1}{2}\right\rangle. \tag{42b}$$

For the case of plane waves, δ'_κ vanishes so that the results (41) and (42) then become identical to those Eq. (35c) derived directly.

3. Transformation properties of the scattering matrix elements

One can attempt to relate the states in the matrix elements $\mathcal{M}(s,k_{2_y})$ to their spin-reversed counterparts by introducing the operators $\hat{\vec{\Omega}}$ followed by using Eqs. (41), (42), and (36). It follows immediately from the definition (33) that the square of the $\hat{\vec{\Omega}}$ operator containing the coordinates of any one electron is −1. Inserting into Eq. (30a) this representation of −1 for both electrons and then invoking Eqs. (41), (42), and (36) yields

$$\mathcal{M}(s,k_{2_y})=\langle\varepsilon_1,\varepsilon_2 k_{2_y}|\hat{\mathcal{H}}[\hat{\vec{\Omega}}(A)]^2[\hat{\vec{\Omega}}(B)]^2|\varepsilon_0,m\rangle \tag{43a}$$

$$=(-1)^{\Delta_a}\langle\varepsilon_1,\varepsilon_2 k_{2_y}|\hat{\mathcal{H}}\hat{\vec{\Omega}}(A)\hat{\vec{\Omega}}(B)|-\varepsilon_0^{out},-m\rangle, \tag{43b}$$

where Δ_a is a phase factor resulting from a combination of those in Eqs. (36), (41), and (42). Here the state $|-\varepsilon_0^{out},-m\rangle$ differs from the state $|-\varepsilon_0,-m\rangle$, in which the incoming electron has spin $-\varepsilon_0$, only in that the unbound wave function is that for an outgoing state still with momentum $\mathbf{k}_0$ and spin state $-\varepsilon_0$. The operator product $\hat{\vec{\Omega}}(A)\hat{\vec{\Omega}}(B)$, to be denoted $\hat{\vec{\Omega}}_{AB}$, must be moved to the left of $\hat{\mathcal{H}}$ in Eq. (43b) before one can attempt to reverse the spins in the final state by invoking Eqs. (41), (42), and (36). It is therefore necessary to define the transformed operator $\hat{\mathcal{H}}'$:

$$\hat{\mathcal{H}}'=\hat{\vec{\Omega}}^\dagger_{AB}\hat{\mathcal{H}}\hat{\vec{\Omega}}_{AB}. \tag{44}$$

Multiplication of both sides of this equation from the left by $\hat{\vec{\Omega}}_{AB}$ and noting that $\hat{\vec{\Omega}}^\dagger_{AB}\hat{\vec{\Omega}}_{AB}=1$ yields

$$\hat{\mathcal{H}}\hat{\vec{\Omega}}_{AB}=\hat{\vec{\Omega}}_{AB}\hat{\mathcal{H}}'. \tag{45}$$

Substituting back the definition of $\hat{\mathcal{H}}'$ in Eq. (45) yields

$$\hat{\mathcal{H}}\hat{\vec{\Omega}}_{AB}=\hat{\vec{\Omega}}_{AB}\tilde{\vec{\Omega}}^\dagger{}_{AB}\hat{\mathcal{H}}\hat{\vec{\Omega}}_{AB}. \tag{46}$$

It is useful to decompose the operator $\hat{\vec{\Omega}}_{AB}$ into the product of a linear operator $\hat{U}_{AB}$ and the complex conjugation $\hat{\vec{K}}$ which, acting on any two-electron function appearing on its right, changes factors of i into $-i$ regardless of whether these originated from the wave function of electron A or that of electron B. Thus

$$\hat{\vec{\Omega}}_{AB}=\hat{U}_{AB}\hat{\vec{K}}, \tag{47}$$

where the linear two-electron operator $\hat{U}_{AB}$ is given by

$$\hat{U}_{AB}=-\beta(A)\hat{I}(A)\Sigma_y(A)\beta(B)\hat{I}(B)\Sigma_y(B). \tag{48}$$

Using the expression for $\hat{\vec{\Omega}}_{AB}$ given by Eq. (47), Eq. (46) can be developed as

$$\hat{\mathcal{H}}\hat{\vec{\Omega}}_{AB}=\hat{\vec{\Omega}}_{AB}\hat{U}^\dagger_{AB}\hat{\vec{K}}^\dagger\hat{\mathcal{H}}\hat{\vec{K}}\hat{U}_{AB} \tag{49a}$$

$$=\hat{\vec{\Omega}}_{AB}\hat{U}^\dagger_{AB}\hat{\mathcal{H}}^*\hat{U}_{AB}. \tag{49b}$$

The only imaginary unit in the Møller interaction (25b) is that multiplying $\sin\omega r_{AB}$ because, although $\alpha_2(A)$ and $\alpha_2(B)$ are both imaginary, their product is real. Standard manipulations using the anticommutation properties of the Dirac matrices shows that $\hat{U}_{AB}$ commutes with $\hat{\mathcal{H}}^*$ which, after noting that $\hat{U}^\dagger_{AB}\hat{U}_{AB}=1$, yields

$$\hat{\mathcal{H}}\hat{\vec{\Omega}}_{AB}=\hat{\vec{\Omega}}_{AB}\hat{U}^\dagger_{AB}\hat{U}_{AB}\hat{\mathcal{H}}^*=\hat{\vec{\Omega}}_{AB}\hat{\mathcal{H}}^*. \tag{50}$$

Use of this result in Eq. (43b) shows that

$$\mathcal{M}(s,k_{2_y})=(-1)^{\Delta_a}\langle\varepsilon_1,\varepsilon_2 k_{2_y}|\hat{U}_{AB}\hat{\vec{K}}\hat{\mathcal{H}}^*|-\varepsilon_0^{out},-m\rangle. \tag{51}$$

Using the relation $\langle a|\hat{\vec{K}}|b\rangle=\langle a|\hat{\overleftarrow{K}}|b\rangle^*$ (see [26]) and the result for both electrons that $(\beta i\Sigma_y)^\dagger=-\beta i\Sigma_y$ followed by invoking the adjoints of Eqs. (41), (42), and (36) yields

$$\mathcal{M}(s,k_{2_y})=(-1)^{\Delta_a}\langle\varepsilon_1,\varepsilon_2 k_{2_y}|\hat{U}_{AB}\hat{\overleftarrow{K}}\hat{\mathcal{H}}^*|-\varepsilon_0^{out},-m\rangle^* \tag{52a}$$

$$=(-1)^{\Delta_a}\langle\varepsilon_1,\varepsilon_2 k_{2_y}|\hat{\overleftarrow{\Omega}}^\dagger(A)\hat{\overleftarrow{\Omega}}^\dagger(B)\hat{\mathcal{H}}^*|-\varepsilon_0^{out},-m\rangle^* \tag{52b}$$

$$=(-1)^{\tilde{\Delta}_a}\langle-\varepsilon_1^{in},-\varepsilon_2^{in}k_{2_y}|\hat{\mathcal{H}}^*|-\varepsilon_0^{out},-m\rangle^*. \tag{52c}$$

The same type of relation with the same phase factor $(-1)^{\tilde{\Delta}_a}$ applies to $\mathcal{M}^{Ex}(s,k_{2_y})$. Substitution of this result and Eq. (52c) into the expression (29) for the quantity $\mathcal{S}(s,k_{2_y})$ shows that this can be written as

$$\mathcal{S}(s,k_{2_y})=|\langle-\varepsilon_1^{in},-\varepsilon_2^{in}k_{2_y}|\hat{\mathcal{H}}^*|-\varepsilon_0^{out},-m\rangle - \langle-\varepsilon_1^{in},-\varepsilon_2^{in}k_{2_y}|\hat{\mathcal{H}}^*|-m,-\varepsilon_0^{out}\rangle|^2. \tag{53}$$

However, relations (29) and (30) show that $\mathcal{S}(-s,k_{2_y})$ with all the spins reversed is given by

$$\mathcal{S}(-s,k_{2_y})=|\mathcal{M}(-s,k_{2_y})-\mathcal{M}^{Ex}(-s,k_{2_y})|^2 \tag{54a}$$

$$=|\langle-\varepsilon_1,-\varepsilon_2 k_{2_y}|\hat{\mathcal{H}}|-\varepsilon_0,-m\rangle - \langle-\varepsilon_1,-\varepsilon_2 k_{2_y}|\hat{\mathcal{H}}|-m,-\varepsilon_0\rangle|^2. \tag{54b}$$

Comparison of the results (53) and (54b) shows that there are two different and distinct effects which cause $\mathcal{S}(s,k_{2_y})$ to differ from its spin-reversed counterpart. The first of these is that Eq. (53) contains the outward-going wave function of a particle with spin state $-\varepsilon_0$ and asymptotic momentum $\mathbf{k}_0$

rather than the inward-going function that appears in Eq. (54b). Similarly, Eq. (53) contains inward-going wave functions with momenta $\mathbf{k}_1$ and $\mathbf{k}_2$ rather than the outward-going ones appearing in Eq. (54b). All three of these differences arise from the complex conjugation in the time reversal operator changing the sign of the exponent in each phase shift term $e^{\pm i\delta'_\kappa}$. The second factor causing $\mathcal{S}(s,k_{2_y})$ to differ from its spin-reversed counterpart is the complex conjugation of the operator $\hat{\mathcal{H}}$ in Eq. (53). In the event that $\hat{\vec{\Omega}}_{AB}$ were to commute with $\hat{\mathcal{H}}$ then the order of these operators in Eq. (43b) could be reversed. Since standard manipulations using Dirac matrices show that $\hat{I}_D$ and $\hat{U}_{AB}$ both commute with $\hat{\mathcal{H}}$, it is only the complex conjugation in the time reversal operator which prevents $\hat{\vec{\Omega}}_{AB}$ from commuting with $\hat{\mathcal{H}}$. Thus, if only the real part of the operator $\hat{\mathcal{H}}$ were to be considered, $\hat{\vec{\Omega}}_{AB}$ would commute with $\hat{\mathcal{H}}$ with the consequence that only the first (the phase shifts in the continuum wave functions) factor would cause $\mathcal{S}(s,k_{2_y})$ to change under reversal of all spins.

C. Interactions responsible for spin asymmetry

1. Relativistic contributions to the phase shifts

The first factor, causing $\mathcal{S}(s,k_{2_y})$ to differ from its spin reversed counterpart—namely, the phase shifts in the continuum wave functions—is seen to be relativistic in origin by considering the entirely nonrelativistic case. In the latter each of the four wave functions entering a scattering matrix element can be factorized into a product of a purely spatial function and a spin function which can either be $\chi^{+1/2}$ corresponding to spin up or $\chi^{-1/2}$ corresponding to spin down as defined after Eq. (31). Here the operator $i\sigma_y$ alone acts as a spin-inversion operator; it only failed to fulfill that role in the relativistic case on account of the small components of the wave functions in Eq. (31) which necessitated introducing the more complicated operator $\hat{\vec{\Omega}}$. Since the Møller interaction reduces to just the Coulomb interaction r_{AB}^{-1} in the nonrelativistic limit, $i\sigma_y(A)i\sigma_y(B)$ commutes with r_{AB}^{-1}. This in conjugation with the result $i\sigma_y\chi^{\pm 1/2}=\mp\chi^{\mp 1/2}$ immediately shows, using the methods followed in demonstrating that Eq. (43a) can be written as Eq. (54b), that, in the nonrelativistic theory, the scattering matrix elements are unchanged under reversal of all spins. This conclusion coupled with the previous result—that it is the phase shifts in the continuum wave functions which introduce the spin asymmetry—shows that this arises from relativistic modifications of the phase shifts.

The conclusion of the previous paragraph is confirmed by demonstrating that each continuum wave function (32) does indeed reduce a pure spin-up or a pure spin-down state in the nonrelativistic limit. In the nonrelativistic limit the small components f_κ in the partial wave expansion (32) become negligible while the δ'_κ phase factors and unbound wave functions depend only on l becoming independent of j [24]. The use of these results enables the order of the two outer summations in Eq. (32) to be interchanged, so that this becomes

$$|\mathbf{k}_0^{i/o}\varepsilon\rangle = (2\pi)^{-1/2}\sum_{l=0}^{\infty} i^l e^{\pm i\delta'_l} g_l \sum_{j=l-1/2}^{l+1/2}\sum_{m=-j}^{j} C\left(l,\frac{1}{2},j,m-\varepsilon,\varepsilon,m\right) \times[Y_{l,m-\varepsilon}(\Omega_{\mathbf{k}})]^*\chi_{\kappa,m}. \tag{55}$$

Introducing the explicit form of the $\chi_{\kappa,m}$ functions as

$$\chi_{l-1/2,m} = C\left(l,\frac{1}{2},l-\frac{1}{2},m+\frac{1}{2},-\frac{1}{2},m\right)Y_{l,m+1/2}|\beta\rangle + C\left(l,\frac{1}{2},l-\frac{1}{2},m-\frac{1}{2},\frac{1}{2},m\right)Y_{l,m-1/2}|\alpha\rangle, \tag{56a}$$

$$\chi_{l+1/2,m} = C\left(l,\frac{1}{2},l+\frac{1}{2},m+\frac{1}{2},-\frac{1}{2},m\right)Y_{l,m+1/2}|\beta\rangle + C\left(l,\frac{1}{2},l+\frac{1}{2},m-\frac{1}{2},\frac{1}{2},m\right)Y_{l,m-1/2}|\alpha\rangle \tag{56b}$$

and substituting these into Eq. (55) converts this to

$$|\mathbf{k}_0^{i/o}\varepsilon\rangle = (2\pi)^{-1/2}\sum_{l=0}^{\infty} i^l e^{\pm i\delta'_l} g_l \sum_{m=-j}^{j}[Y_{l,m-\varepsilon}(\Omega_{\mathbf{k}})]^*\left\{C\left(l,\frac{1}{2},l-\frac{1}{2},m-\varepsilon,\varepsilon,m\right)\right.$$
$$\times\left[C\left(l,\frac{1}{2},l-\frac{1}{2},m+\frac{1}{2},-\frac{1}{2},m\right)Y_{l,m+1/2}|\beta\rangle + C\left(l,\frac{1}{2},l-\frac{1}{2},m-\frac{1}{2},\frac{1}{2},m\right)Y_{l,m-1/2}|\alpha\rangle\right] + C\left(l,\frac{1}{2},l+\frac{1}{2},m-\varepsilon,\varepsilon,m\right)$$
$$\left.\times\left[C\left(l,\frac{1}{2},l+\frac{1}{2},m+\frac{1}{2},-\frac{1}{2},m\right)Y_{l,m+1/2}|\beta\rangle + C\left(l,\frac{1}{2},l+\frac{1}{2},m-\frac{1}{2},\frac{1}{2},m\right)Y_{l,m-1/2}|\alpha\rangle\right]\right\}, \tag{57}$$

which can be rearranged as

$$|\mathbf{k}_0^{i/o}\varepsilon\rangle = (2\pi)^{-1/2}\sum_{l=0}^{\infty} i^l e^{\pm i\delta_l'} g_l \sum_{m=-j}^{j} [Y_{l,m-\varepsilon}(\Omega_{\mathbf{k}})]^* \Bigg\{ \Bigg[C\left(l,\frac{1}{2},l-\frac{1}{2},m-\varepsilon,\varepsilon,m\right) C\left(l,\frac{1}{2},l-\frac{1}{2},m+\frac{1}{2},-\frac{1}{2},m\right)$$
$$+ C\left(l,\frac{1}{2},l+\frac{1}{2},m-\varepsilon,\varepsilon,m\right) C\left(l,\frac{1}{2},l+\frac{1}{2},m+\frac{1}{2},-\frac{1}{2},m\right) \Bigg] Y_{l,m+1/2}|\beta\rangle$$
$$+ \Bigg[C\left(l,\frac{1}{2},l-\frac{1}{2},m-\varepsilon,\varepsilon,m\right) C\left(l,\frac{1}{2},l-\frac{1}{2},m-\frac{1}{2},\frac{1}{2},m\right)$$
$$+ C\left(l,\frac{1}{2},l+\frac{1}{2},m-\varepsilon,\varepsilon,m\right) C\left(l,\frac{1}{2},l+\frac{1}{2},m-\frac{1}{2},\frac{1}{2},m\right) \Bigg] Y_{l,m-1/2}|\alpha\rangle \Bigg\}. \tag{58}$$

However, one can write

$$\sum_j C\left(l,\frac{1}{2},j,m_l,m_s,m_l+m_s\right) C\left(l,\frac{1}{2},j,m_l',m_s',m_l+m_s\right)$$
$$= \sum_j \sum_M C\left(l,\frac{1}{2},j,m_l,m_s,M\right) C\left(l,\frac{1}{2},j,m_l',m_s',M\right)$$
$$\times \delta_{m_l,m_l'}\delta_{m_s,m_s'}, \tag{59}$$

where the last step uses a standard result [28]. This converts Eq. (58) into

$$|\mathbf{k}_0^{i/o}\varepsilon\rangle = (2\pi)^{-1/2}\sum_l i^l e^{\pm i\delta_l'} g_l \sum_m Y_{l,m-\varepsilon}(\Omega_{\mathbf{k}})[\delta_{\varepsilon,-1/2}Y_{l,m+1/2}|\beta\rangle$$
$$+ \delta_{\varepsilon,1/2}Y_{l,m-1/2}|\alpha\rangle], \tag{60}$$

where all the implicitly referred $Y_{l,m'}$ with $|m'|>l$ are defined to be zero. This result shows that

$$\left|\mathbf{k}_0^{i/o}\frac{1}{2}\right\rangle = (2\pi)^{-1/2}\sum_l i^l e^{\pm i\delta_l'} g_l \sum_m [Y_{l,m_l}Y_{l,m_l}^*(\Omega_{\mathbf{k}})]|\alpha\rangle, \tag{61a}$$

$$\left|\mathbf{k}_0^{i/o}-\frac{1}{2}\right\rangle = (2\pi)^{-1/2}\sum_l i^l e^{\pm i\delta_l'} g_l \sum_m [Y_{l,m_l}Y_{l,m_l}^*(\Omega_{\mathbf{k}})]|\beta\rangle, \tag{61b}$$

as would be expected since $|\mathbf{k}_0^{i/o}\frac{1}{2}\rangle$ is purely a $|\alpha\rangle$ spin and $|\mathbf{k}_0^{i/o}-\frac{1}{2}\rangle$ is a pure $|\beta\rangle$ spin.

The overall conclusion of this subsection is that it is the relativistic modifications of the phase shifts in the continuum wave functions which provide one mechanism for introducing spin asymmetry into the scattering matrix elements. Since the phase shifts δ_κ' are zero for relativistic plane waves, it follows that this mechanism would not arise if all the continuum states were described by such functions. This shows that it is the relativistic modifications of the distortions of the continuum wave functions induced by the potential originating from the target atom which generates the first mechanism producing spin asymmetry.

2. Non-time-reversal-invariant part of the Møller interaction

It is apparent from the arguments advanced in Sec. III B 3 that the form (25b) for the Møller interaction is particularly useful. Furthermore, if $\sin \omega r_{AB}$ is expanded as its power series, the leading term proportional to ωr_{AB} contributes zero to the matrix elements $\mathcal{M}(s,k_{2_y})$ and $\mathcal{M}^{Ex}(s,k_{2_y})$ due to the orthogonality between the initial and final states. We can therefore, without changing the overall result, subtract this term from the operator $\hat{\mathcal{H}}$, which can then be written as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{TI} + \hat{\mathcal{H}}_{NTI}, \tag{62}$$

where

$$\hat{\mathcal{H}}_{TI} = r_{AB}^{-1}[1 - \boldsymbol{\alpha}(A)\cdot\boldsymbol{\alpha}(B)]\cos \omega r_{AB}, \tag{63a}$$

$$\hat{\mathcal{H}}_{NTI} = i r_{AB}^{-1}[\sin \omega r_{AB} - \omega r_{AB} - \boldsymbol{\alpha}(A)\cdot\boldsymbol{\alpha}(B)\sin \omega r_{AB}] = i\hat{\mathcal{H}}_R. \tag{63b}$$

It is readily shown using the commutation properties of the Dirac matrices that both $\hat{\mathcal{H}}_{TI}$ and $\hat{\mathcal{H}}_R$ are invariant under time reversal because both these operators are entirely real, so that $\hat{\vec{T}}^\dagger\hat{\mathcal{H}}_{TI}\hat{\vec{T}}=\hat{\mathcal{H}}_{TI}$ and $\hat{\vec{T}}^\dagger\hat{\mathcal{H}}_R\hat{\vec{T}}=\hat{\mathcal{H}}_R$. The result (62) thus decomposes $\hat{\mathcal{H}}$ into its time-reversal-invariant ($\hat{\mathcal{H}}_{TI}$) and non-time-reversal-invariant ($\hat{\mathcal{H}}_{NTI}$) parts. It is only the explicit imaginary unit in $i\hat{\mathcal{H}}_R$ which renders $\hat{\mathcal{H}}_{NTI}$ noninvariant under time reversal and makes $\hat{\mathcal{H}}^*$ different from $\hat{\mathcal{H}}$, thus introducing a noncommutation between $\hat{\mathcal{H}}$ and $\hat{\vec{\Omega}}_{AB}$ and thereby introducing, as described in Sec. III B 3, the second factor causing the spin-reversed quantity $\mathcal{S}(-s,k_{2_y})$ to differ from $\mathcal{S}(s,k_{2_y})$.

The operator $\hat{\mathcal{H}}_{NTI}$ is of higher order in $1/c$ than the well-known Breit interaction which is of order $1/c^2$ [see, for example, Eq. (3.5) of [19]]. Thus, when $\hat{\mathcal{H}}_{NTI}$ is expressed as its power series expansion in ωr_{AB}, the leading term is of order $1/c^3$. This shows that the second factor introducing a spin asymmetry into the quantity $\mathcal{S}(s,k_{2_y})$ is relativistic in origin.

The contribution from $\hat{\mathcal{H}}_{NTI}$ to the direct matrix element is nonzero but only if the distorting effect of the potential on either of the incoming or the fast-outgoing electron is con-

sidered. If both these wave functions are plane waves, then the matrix elements of $\hat{\mathcal{H}}_{NTI}$ will contain kernels of the form

$$I_{\mathbf{k}}(\mathbf{r}_B) = \int \frac{e^{i\mathbf{k}\cdot\mathbf{r}_A}\sin(\omega|\mathbf{r}_A - \mathbf{r}_B|)}{|\mathbf{r}_A - \mathbf{r}_B|} d\mathbf{r}_A. \tag{64}$$

It has been shown [29] that for the case considered here in which $\mathbf{k}$ corresponds to the vector of momentum transfer $\mathbf{k} = \mathbf{k}_0 - \mathbf{k}_1$, the integral is given by

$$I_{\mathbf{k}}(\mathbf{r}_B) = \frac{2\pi^2}{|\mathbf{k}|} e^{i\mathbf{k}\cdot\mathbf{r}_B}[\delta(|\mathbf{k}| - \omega) + \delta(|\mathbf{k}| + \omega)], \tag{65}$$

which clearly is zero since $|\mathbf{k}|$ is never equal to the positive ω. Hence $\hat{\mathcal{H}}_{NTI}$ does not contribute to the scattering matrix elements unless at least one of the continuum functions is not defined as a plane wave. Similarly, the contribution of $\hat{\mathcal{H}}_{NTI}$ to the exchange scattering matrix elements vanishes if both the incoming and slow-outgoing electrons are described by plane waves. Thus, $\hat{\mathcal{H}}_{NTI}$ does not contribute to the scattering matrix elements if all three continuum wave functions are described by plane waves.

Since the distinction in Eq. (53) between incoming and outgoing states disappears for plane waves for which the phase shift δ'_κ is zero, it follows that no spin asymmetry arises from the $\hat{\mathcal{H}}_{TI}$ term, as described in the previous section. Thus coupled with the vanishing contribution from the $\hat{\mathcal{H}}_{NTI}$ term this shows that there is no spin asymmetry in the all-plane-wave case and hence that all spin asymmetries must arise from the effect of the distorting potential on the unbound electrons.

D. Invariance under reversal of spin and a *y*-momentum component

It has been shown above that the simplest operator reversing the spins of all the wave functions does not leave the quantity $\mathcal{S}(s,k_{2_y})$ unchanged. To examine possible symmetries in spin-resolved two-electron scattering experiments, one seeks an operator which reverses the spins of all the wave functions while containing the minimum number of such other transformations as is needed to leave the *S*-matrix element invariant. Such an operator will allow us to identify a symmetry property of $\mathcal{S}(s,k_{2_y})$ which would have experimentally observable consequences.

For a single electron, the relativistic equivalent ($\hat{H}_{y,D}$) of the operator for spatial reflection in the *xz* plane is given by [30]

$$\hat{H}_{y,D} = i\Sigma_y \beta \hat{H}_y, \tag{66}$$

where $\hat{H}_y$ acting on any function depending on $\mathbf{r}$ reverses its *y* component. It can be shown that $\hat{H}_{y,D}$ converts a spin-up plane wave into a spin-down state but having a negative *y*-momentum component:

$$\hat{H}_{y,D}\psi_{pl}^{(\pm)}(\mathbf{r}) = i\Sigma_y\beta\hat{H}_y\psi_{pl}^{(\pm)}(\mathbf{r}) \tag{67a}$$

$$= i\Sigma_y\beta\begin{pmatrix} \chi^{\pm 1/2} \\ A_s[\sigma_x\hat{p}_x - \sigma_y\hat{p}_y + \sigma_z\hat{p}_z]\chi^{\pm 1/2}\end{pmatrix} e^{i[k_x x - k_y y + k_z z]} \tag{67b}$$

$$= \beta\begin{pmatrix} i\sigma_y\chi^{\pm 1/2} \\ A_s[-\sigma_x\hat{p}_x - \sigma_y\hat{p}_y - \sigma_z\hat{p}_z]i\sigma_y\chi^{\pm 1/2}\end{pmatrix} \times e^{i[k_x x - k_y y + k_z z]} \tag{67c}$$

$$= \mp\begin{pmatrix} \chi^{\mp 1/2} \\ A_s(\sigma\cdot\hat{\mathbf{p}})\chi^{\mp 1/2}\end{pmatrix} e^{i[k_x x - k_y y + k_z z]} \equiv \mp\psi'^{(\mp)}_{pl}(\mathbf{r}). \tag{67d}$$

Here $\psi'(\mathbf{r})$ denotes a wave function in which the *y* component of the momentum is reversed compared with that in $\psi(\mathbf{r})$. It has been shown [30] that the action of $\hat{H}_{y,D}$ on a Dirac central-field state is given by

$$\hat{H}_{y,D}|\kappa,m\rangle = (-1)^{m+1/2}(-1)^{1/2(1-a)}|\kappa,-m\rangle. \tag{68}$$

Thus, although $\hat{H}_{y,D}$ reverses all the electron spins in the same fashion as $\hat{\vec{\Omega}}$, the former also changes the *y*-momentum components.

The result (68) taken in conjunction with the partial-wave expansion (32) can be used to show that distorted continuum waves are interconverted under $\hat{H}_{y,D}$ in exactly the same way as plane waves:

$$\hat{H}_{y,D}\left|\mathbf{k},\frac{1}{2}\right\rangle = (2\pi)^{-1/2}\sum_{j=1/2}^{\infty}\sum_{l=j-1/2}^{j+1/2} i^l e^{\pm i\delta'_\kappa}\sum_{m=-j}^{j} C\left(l,\frac{1}{2},j,m - \frac{1}{2},\frac{1}{2},m\right) Y^*_{l,m-1/2}(\Omega_{\mathbf{k}})\hat{H}_{y,D}\begin{pmatrix} g_\kappa\chi_{\kappa,m} \\ if_\kappa\chi_{-\kappa,m}\end{pmatrix} \tag{69a}$$

$$= (2\pi)^{-1/2}\sum_{j=1/2}^{\infty}\sum_{l=j-1/2}^{j+1/2} i^l e^{\pm i\delta'_\kappa}\sum_{m=-j}^{j} C\left(l,\frac{1}{2},j,m - \frac{1}{2},\frac{1}{2},m\right) Y^*_{l,m-1/2}(\Omega_{\mathbf{k}}) \times (-1)^{m+1/2}(-1)^{(1-a)/2}\begin{pmatrix} g_\kappa\chi_{\kappa,-m} \\ if_\kappa\chi_{-\kappa,-m}\end{pmatrix} \tag{69b}$$

$$= (2\pi)^{-1/2}\sum_{j=1/2}^{\infty}\sum_{l=j-1/2}^{j+1/2} i^l e^{\pm i\delta'_\kappa}\sum_{m=-j}^{j} C\left(l,\frac{1}{2},j,-m - \frac{1}{2},\frac{1}{2},-m\right) Y^*_{l,-m-1/2}(\Omega_{\mathbf{k}}) \times (-1)^{-m+1/2}(-1)^{(1-a)/2}\begin{pmatrix} g_\kappa\chi_{\kappa,m} \\ if_\kappa\chi_{-\kappa,m}\end{pmatrix} \tag{69c}$$

$$= (2\pi)^{-1/2} \sum_{j=1/2}^{\infty} \sum_{l=j-1/2}^{j+1/2} i^l e^{\pm i\delta'_\kappa} \sum_{m=-j}^{j} C\left(l, \frac{1}{2}, j, m+\frac{1}{2}, -\frac{1}{2}, m\right)(-1)^{j-l-1/2} Y^*_{l,-m-1/2}(\Omega_{\mathbf{k}}) \times (-1)^{-m+1/2}(-1)^{(1-a)/2}\begin{pmatrix} g_\kappa \chi_{\kappa,m} \\ i f_\kappa \chi_{-\kappa,m} \end{pmatrix}. \quad (69d)$$

The operator $\hat{H}_y$ for purely spatial reflection in the *xz* plane reverses the sign of the k_{2_y} so that $\Omega_{\mathbf{k}}$ becomes $\Omega_{\mathbf{k}'}$, so that one has

$$\hat{H}_y Y_{l,m+1/2}(\Omega_{\mathbf{k}}) = Y_{l,m+1/2}(\Omega_{\mathbf{k}'}). \quad (70)$$

Use of the result [30]

$$\hat{H}_y Y_{l,m+1/2}(\Omega_{\mathbf{k}}) = (-1)^{m+1/2} Y_{l,-m-1/2}(\Omega_{\mathbf{k}}) \quad (71)$$

shows that

$$(-1)^{-m+1/2}[Y_{l,-m-1/2}(\Omega_{\mathbf{k}})]^* = -[Y_{l,m+1/2}(\Omega_{\mathbf{k}'})]^*. \quad (72)$$

Substitution of this result into Eq. (69d) shows after invoking Eq. (39) that

$$\hat{H}_{y,D}\left|\mathbf{k}, \frac{1}{2}\right\rangle = -(2\pi)^{-1/2} \sum_{j,l} i^l e^{\pm i\delta'_\kappa} C\left(l, \frac{1}{2}, j, m+\frac{1}{2}, -\frac{1}{2}, m\right) \times Y^*_{l,m+1/2}(\Omega_{\mathbf{k}'})\begin{pmatrix} g_\kappa \chi_{\kappa,m} \\ i f_\kappa \chi_{-\kappa,m} \end{pmatrix}. \quad (73)$$

Comparison of the right-hand side of this result with Eq. (32) yields

$$\hat{H}_{y,D}\left|\mathbf{k}\frac{1}{2}\right\rangle = -\left|\mathbf{k}' - \frac{1}{2}\right\rangle, \quad (74a)$$

$$\hat{H}_{y,D}\left|\mathbf{k} - \frac{1}{2}\right\rangle = \left|\mathbf{k}'\frac{1}{2}\right\rangle. \quad (74b)$$

The transformation properties of the *S*-matrix elements related to reflection in the *xz* plane are derived by first noting that the square of the operator $\hat{H}_{y,D}$ is −1. Introducing this result for the squares of the operators $\hat{H}_{y,D}(A)$ and $\hat{H}_{y,D}(B)$ for the electrons *A* and *B* and then using Eqs. (74) and (68) shows that

$$\mathcal{M}(s, k_{2_y}) = \langle \varepsilon_1, \varepsilon_2 k_{2_y} | \hat{\mathcal{H}}[\hat{H}_{y,D}(A)]^2[\hat{H}_{y,D}(B)]^2 | \varepsilon_0, m\rangle \quad (75a)$$

$$= (-1)^{\Delta_b}\langle \varepsilon_1, \varepsilon_2 k_{2_y} | \hat{\mathcal{H}}\hat{H}_{y,D}(A)\hat{H}_{y,D}(B)| - \varepsilon_0, -m\rangle. \quad (75b)$$

Using the properties of the Dirac matrices, it is readily shown that the Møller interaction commutes with the product of the two transformation operators occurring in Eq. (75b), so that

$$[\hat{\mathcal{H}}, \hat{H}_{y,D}(A)\hat{H}_{y,D}(B)] = 0. \quad (76)$$

By introducing this result into Eq. (75b) and then using the adjoints of Eqs. (74) and (68) yields

$$\mathcal{M}(s, k_{2_y}) = (-1)^{\Delta_b}\langle \varepsilon_1, \varepsilon_2 k_{2_y} | \hat{H}_{y,D}(A)\hat{H}_{y,D}(B)\hat{\mathcal{H}}| - \varepsilon_0, -m\rangle \quad (77a)$$

$$= (-1)^{\tilde{\Delta}_b}\langle -\varepsilon_1, -\varepsilon_2 - k_{2_y} | \hat{\mathcal{H}}| - \varepsilon_0, -m\rangle. \quad (77b)$$

Since the matrix element in the last line is seen from the definition (30a) to be nothing but $\mathcal{M}(-s, -k_{2_y})$, it follows that the spin-resolved quantity $\mathcal{S}(s, k_{2_y})$ satisfies the equality

$$\mathcal{S}(s, k_{2_y}) = \mathcal{S}(-s, -k_{2_y}). \quad (78)$$

The equality (78) holds true whether the direction of spin alignment is along or perpendicular to the direction of propagation of the incoming electron. For the coplanar case only, this result shows that $\mathcal{S}(s, k_{2_y})$ is invariant under just the reversal of all spins because here the *y* momentum component (k_{2_y}) of the slow-outgoing electron is zero. This identity has been observed in previous numerical calculations [14].

E. Global symmetry

The presence in the Møller interaction of a non-time-reversal-invariant part does not imply that time reversal invariance is violated. Thus, considering the entire ionization event, time reversal would produce the process in which two electrons of momenta $-\mathbf{k}_1$ and $-\mathbf{k}_2$ impinge on an ion which captures one of these electrons while scattering the other into a state of momentum $-\mathbf{k}_0$. Direct consideration of this process would introduce a Møller interaction differing from Eq. (25) only in that the sign of the complex exponential in Eq. (25a) is changed because the sign of the energy change ΔE_A is reversed. However, the scattering matrix element (29) for this entire process can be directly generated from Eq. (30) by introducing the time reversal operators (34b) which would convert each of the states $|\mathbf{k}_1\varepsilon_1\rangle$, $|\mathbf{k}_2\varepsilon_2\rangle$, $|\mathbf{k}_0\varepsilon_0\rangle$, and $|\kappa m\rangle$ into $|-\mathbf{k}_1 - \varepsilon_1\rangle$, $|-\mathbf{k}_2 - \varepsilon_2\rangle$, $|-\mathbf{k}_0 - \varepsilon_0\rangle$, and $|\kappa - m\rangle$, respectively while changing the sign of the exponent in the $e^{i\omega r_{AB}}$ term. This shows that time reversal invariance is not violated on the fundamental level. This should have been expected given that the origin of the Møller interaction might be regarded as lying in either QED or, even more fundamentally, in classical relativistic theory coupled with standard quantum mechanics, all theories invariant under time reversal.

In problems involving time dependences, the derivation of an effective operator acting within a subspace of the states needed to define a complete theory often yields effective operators which are not Hermitian, like the Møller interaction (25). In this case one derivation of this interaction [11] involves eliminating the field variables from the full QED description to produce an operator acting entirely within the subset of non-second-quantized electronic wave functions.

Arguments can be advanced that the origins of the Møller interaction lie in classical relativistic theory coupled with standard quantum mechanics. In this event, the Møller interaction should not be regarded as a specific consequence of QED but rather as a result that this theory must of necessity generate. Thus, for example, no one would regard Coulomb's law as a consequence of covariant QED even though the

former could be derived from the latter. The origins of the non-time-invariant part of the Møller interaction lie in the retarded potentials of classical electromagnetic theory. Thus, as discussed in [31], the electrostatic interaction between the charge density $\rho(\mathbf{r}_2,t)$ with that characterized by a density $\rho(\mathbf{r}_1,t)$ at time t involves the product of $\rho(\mathbf{r}_2,t)$ with the retarded potential generated at $\mathbf{r}_2$ by the charge density $\rho(\mathbf{r}_1,t)$. This retarded potential is given by $\int r_{12}^{-1}\rho(\mathbf{r}_1,t-r_{12}/c)\,d\mathbf{r}_1$. Substitution for $\rho(\mathbf{r}_1,t-r_{12}/c)$ of the time-dependent quantum-mechanical charge density $\psi_a^*(\mathbf{r}_1)\psi_b(\mathbf{r}_1)\exp\{i(E_a-E_b)(t-r_{12}/c)\}$ then yields a factor of the type $\exp\{-i(E_a-E_b)r_{12}/c\}$ entering the Møller interaction. A similar treatment of the interaction between two currents yields the retarded current-current interaction in Eq. (25) after also introducing the Dirac current operators.

IV. SPIN-AVERAGED FINAL STATES

A. Experimental outlook for measuring TDCS spin reversal asymmetries

The measurement of cross sections where the m_j quantum number of the bound level and the spins of all the free electrons are resolved would not currently appear to be feasible. However, TDCS's, so far in entirely coplanar geometries, have been measured [12,13] for known spin states of the incident electron. In the experiments in [13] spin-polarized electrons were used to ionize spin-polarized Li targets at nonrelativistic energies, while in the experiments in [12] spin-polarized fast electrons were fired at heavy-atom targets and the spin asymmetry arising from the ionization of $j=3/2$ electrons in the L shell was resolved. Although the spins of the incoming electrons were aligned perpendicular to the scattering plane, there would appear to be no fundamental reasons against experiments with spin alignments in the scattering plane corresponding to the processes of primary concern here. It is therefore of great interest to see if the results of such experiments would reflect the spin asymmetries in the matrix elements of the type elucidated in Sec. III B 3.

It is convenient to examine the case where the bound electron, which becomes ionized, resides in an s or $p_{1/2}$ orbital so that its m_j quantum number $\left(\pm\frac{1}{2}\right)$ is defined solely by its sign. It is then apparent from Eq. (29) that there are 16 possible spin configurations as labeled in Table I. The configuration bearing the label $-s$ is derived from that labeled s by reversal of all spins. The TDCS for processes in which only ε_0 and m are defined is derived from the fully spin-resolved quantities $\mathcal{S}(s,k_{2_y})$ by summing over the possible spin states of the two outgoing electrons and multiplying by the factor c_E given by Eq. (27). This process generates a result for the TDCS differing from Eq. (26) only in the omission of the sums over ε_0 and m with their attendant statistical factor of $N_B/(2N)$. The four different TDCS's measurable in such experiments are therefore given by

$$\mathcal{T}(++,k_{2_y}) = c_E\{\mathcal{S}(1,k_{2_y}) + \mathcal{S}(2,k_{2_y}) + \mathcal{S}(3,k_{2_y}) + \mathcal{S}(4,k_{2_y})\}, \tag{79a}$$

TABLE I. Possible spin configurations of Eq. (29). Each label s defines the spin configuration appearing immediately to its right, with + and − representing spin-up and spin-down states, respectively. Each configuration is given in the order of fast-scattered, slow-ejected, incoming, and bound electrons.

Label s	1 2 0 m	Label s	1 2 0 m
1	+ + + +	−1	− − − −
2	+ − + +	−2	− + − −
3	− + + +	−3	+ − − −
4	− − + +	−4	+ + − −
5	+ + + −	−5	− − − +
6	+ − + −	−6	− + − +
7	− + + −	−7	+ − − +
8	− − + −	−8	+ + − +

$$\mathcal{T}(+-,k_{2_y}) = c_E\{\mathcal{S}(5,k_{2_y}) + \mathcal{S}(6,k_{2_y}) + \mathcal{S}(7,k_{2_y}) + \mathcal{S}(8,k_{2_y})\}, \tag{79b}$$

$$\mathcal{T}(-+,k_{2_y}) = c_E\{\mathcal{S}(-5,k_{2_y}) + \mathcal{S}(-6,k_{2_y}) + \mathcal{S}(-7,k_{2_y}) + \mathcal{S}(-8,k_{2_y})\}, \tag{79c}$$

$$\mathcal{T}(--,k_{2_y}) = c_E\{\mathcal{S}(-1,k_{2_y}) + \mathcal{S}(-2,k_{2_y}) + \mathcal{S}(-3,k_{2_y}) + \mathcal{S}(-4,k_{2_y})\}. \tag{79d}$$

The first two arguments + or − of the partially averaged ($\mathcal{T}$) cross sections denote, respectively, the spins of the incoming and bound electrons. Each of the contributions on the right-hand side of Eq. (79d) is derived from the corresponding term in Eq. (79a) by reversal of all the spins, with Eqs. (79b) and (79c) being similarly related.

Consideration of reflections in the xz plane yields some equalities between the partially spin-resolved cross sections. Application of the result (78) to each of the four contributions in both Eqs. (79a) and (79b) immediately yields

$$\mathcal{T}(++,k_{2_y}) = \mathcal{T}(--,-k_{2_y}), \tag{80a}$$

$$\mathcal{T}(+-,k_{2_y}) = \mathcal{T}(-+,-k_{2_y}). \tag{80b}$$

The main purpose of this section, probing possible spin asymmetries in the partially spin-averaged TDCS, is achieved by first considering the two differences $\mathcal{T}(++,k_{2_y})-\mathcal{T}(--,k_{2_y})$ and $\mathcal{T}(+-,k_{2_y})-\mathcal{T}(-+,k_{2_y})$. The first of these two is seen to contain the sum of the four differences $\mathcal{S}(s,k_{2_y})-\mathcal{S}(-s,k_{2_y})$ having $s=1$, 2, 3, and 4. The quantity $\mathcal{T}(++,k_{2_y})-\mathcal{T}(--,k_{2_y})$ is nonzero because there are no special relations between the differences $\mathcal{S}(s,k_{2_y})-\mathcal{S}(-s,k_{2_y})$ having different values of s which would cause $\mathcal{T}(++,k_{2_y})-\mathcal{T}(--,k_{2_y})$ to vanish. This has been confirmed by numerical computations. The difference $\mathcal{T}(+-,k_{2_y})-\mathcal{T}(-+,k_{2_y})$ is similarly nonzero.

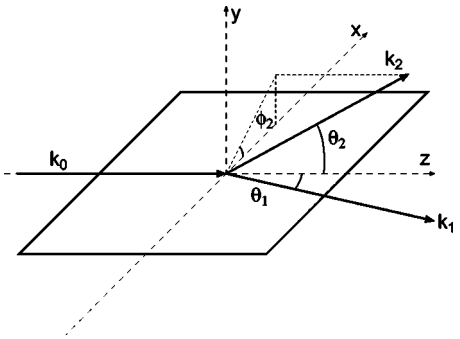

FIG. 1. The scattering geometry and the definition of the momenta for the incoming, fast-scattered, and slow-ejected electron.

It might not be easy to perform an experiment on a highly relativistic system in which the spin of the bound electron to be ionized is known in addition to that of the incoming electron because it would be necessary to prepare hydrogenlike or lithiumlike ions of species having very high nuclear charges. Consequently, the experiments [12] involving targets of very high nuclear charge have involved ionization from an inner shell of a neutral or near-neutral species with consequent averaging over the two possible m_j states of the s or $p_{1/2}$ electron which becomes ionized. It is therefore interesting to consider the TDCS for the process in which only the asymptotic spin of the incident electron is known. The sums

$$\mathcal{T}'(+,k_{2_y}) = \mathcal{T}(++,k_{2_y}) + \mathcal{T}(+-,k_{2_y}), \tag{81a}$$

$$\mathcal{T}'(-,k_{2_y}) = \mathcal{T}(--,k_{2_y}) + \mathcal{T}(-+,k_{2_y}) \tag{81b}$$

denote the TDCS for the processes corresponding to known up- and down-spin states of the incident electron. Since there is no special relationship between the two differences $\mathcal{T}(++,k_{2_y})-\mathcal{T}(--,k_{2_y})$ and $\mathcal{T}(+-,k_{2_y})-\mathcal{T}(-+,k_{2_y})$, the TDCS $\mathcal{T}'(+,k_{2_y})$ is still different from $\mathcal{T}'(-,k_{2_y})$ for noncoplanar geometries.

B. Numerical results

Here we consider the ionization of a 1*s* electron from hydrogenlike uranium. The incoming electron has an impact energy of $E_0=500$ keV, the fast-scattered electron has an energy of $E_1=285$ keV, and the slow has an energy of $E_2=100$ keV. The momentum vector of the incoming electron, $\mathbf{k}_0$, is aligned along the z axis and it is assumed that the momentum vector of the fast scattered, $\mathbf{k}_1$, lies in the xz *scattering plane* as shown in Figure 1. We assume that the fast electron has been scattered through an angle of $\theta_1=-10°$. In Fig. 2 we present spin-resolved cross TDCS's. The slow-outgoing electron is assumed to be in a plane that forms an angle θ_p to the scattering plane. In each case the cross section is shown as a function of the angle ϕ_2 of the slow-outgoing electron. All calcualtions are performed in the rDWBA approximation with Coulombic boundary conditions. The points having $\phi_2=0,180°$ are the points in common with the scattering plane and, as expected, the TDCS for these points is unchanged under reversal of spins. We have confirmed numerically that in all cases $\mathcal{T}(s_1,s_2,k_{2_y})=\mathcal{T}(-s_1,-s_2,-k_{2_y})$. These results together with the predictions presented earlier [32] for spin asymmetry offer an immediate test of the theory developed here.

C. TDCS in coplanar geometries for incident electrons spin resolved perpendicular to the scattering plane

The main objective in this subsection is to examine the spin dependence of the TDCS for scattering processes in coplanar geometries with the electron spins aligned perpendicular to the scattering plane. This situation is of interest as that examined in previous work [14].

The incident electron will always be taken to be traveling along the z direction with the scattering occurring entirely in the xz plane. The partially spin-resolved TDCS $[\mathcal{T}'_q(\pm)]$ in which the spin of the incident electron is aligned either parallel or antiparallel to the direction q $(q=x,y,z)$ can be calculated by summing over the possible spin states of the other three electrons. Consequently, the states of these three electrons can be taken to be those defined in Sec. III A with z taken to be the axis of spin alignment. Hence, from Eq. (29) one has, suppressing the label k_{2_y} which is always zero for the coplanar case considered here,

$$\mathcal{T}'_q(\pm) = c_E \sum_{\varepsilon_1,\varepsilon_2,m} |\langle\varepsilon_1,\varepsilon_2|\hat{\mathcal{H}}|\pm q,m\rangle - \langle\varepsilon_1,\varepsilon_2|\hat{\mathcal{H}}|m,\pm q\rangle|^2. \tag{82}$$

Here the incident states $|\pm q\rangle$ asymptotically become plane waves with the spin states of the large components aligned along the directions $\pm q$. For $q=x,y$, these states are given in term of those Eq. (32) in which the spin is aligned along z by

$$|\pm x\rangle = \frac{1}{\sqrt{2}}\left(\left|\mathbf{k}_0,\frac{1}{2}\right\rangle \pm \left|\mathbf{k}_0,-\frac{1}{2}\right\rangle\right), \tag{83a}$$

$$|\pm y\rangle = \frac{1}{\sqrt{2}}\left(\left|\mathbf{k}_0,\frac{1}{2}\right\rangle \pm i\left|\mathbf{k}_0,-\frac{1}{2}\right\rangle\right). \tag{83b}$$

The states in Eq. (83b) differ from those used previously [14] by the omission of a phase factor which is irrelevant here. For the case in Eq. (82) where $q=z$ the matrix elements are just those defined by Eqs. (30a) and (30b).

The two TDCS's corresponding to the processes in which the spin of the incident electron is aligned asymptotically along the $+y$ and $-y$ directions are found by substituting Eq. (83b) into Eq. (82). The results are

$$\mathcal{T}'_y(\pm) = c_E \sum_{\varepsilon_1,\varepsilon_2,m} \left|\mathcal{M}\left(\varepsilon_1,\varepsilon_2,\frac{1}{2},m\right) \pm i\mathcal{M}\left(\varepsilon_1,\varepsilon_2,-\frac{1}{2},m\right) - \mathcal{M}^{ex}\right|^2. \tag{84}$$

Here all four quantum numbers defining the symbol s introduced in Sec. III A have been introduced explicitly and $\mathcal{M}^{ex}$ denotes the corresponding matrix elements that arise from the exchange term $\langle\varepsilon_1,\varepsilon_2|\hat{\mathcal{H}}|m,\pm q\rangle$. By extracting an irrelevant factor of $|-i|$, $\mathcal{T}'_y(-)$ can be written as

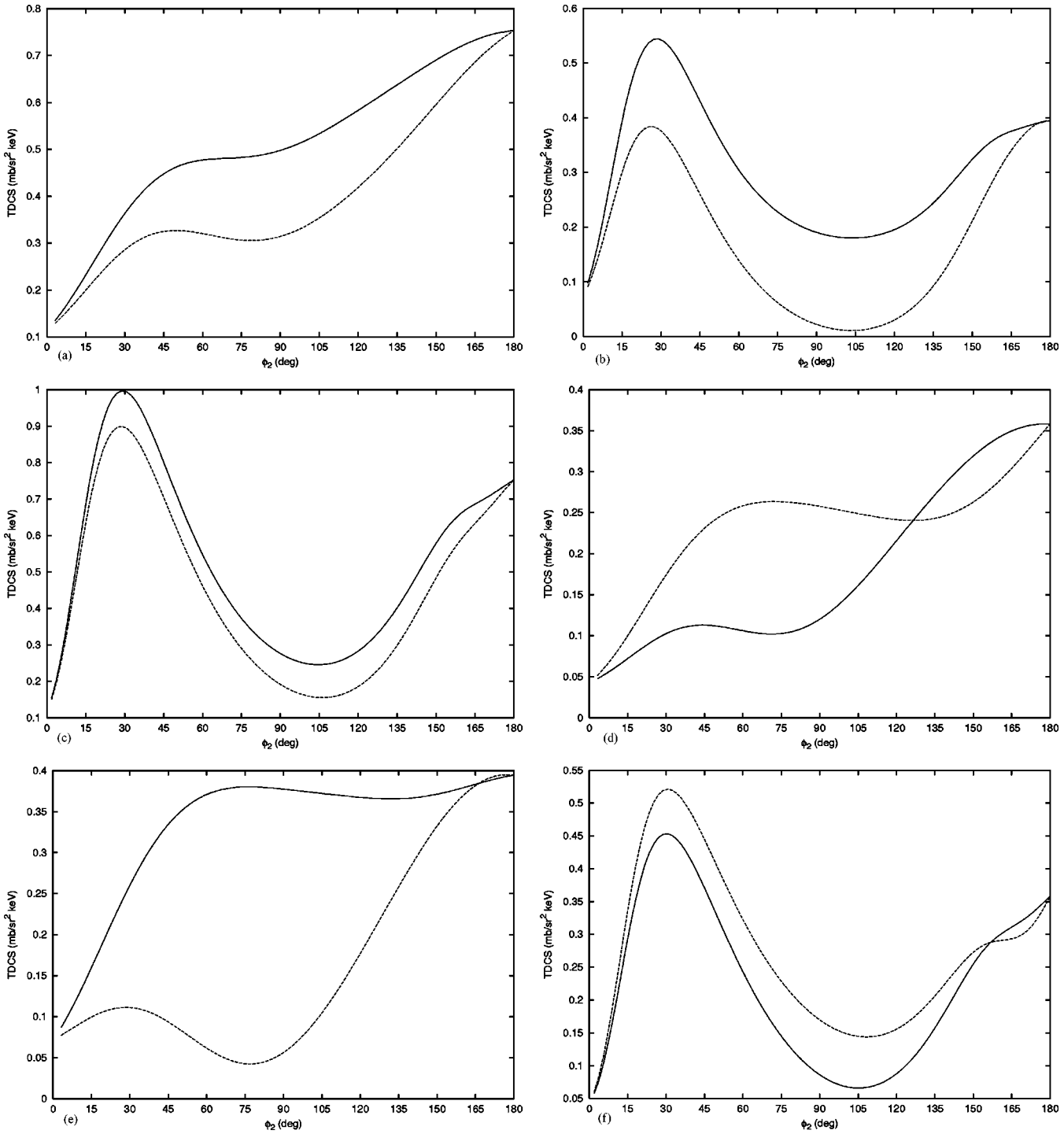

FIG. 2. The spin-resolved TDC's for $(e,2e)$ on hydrogenlike uranium with $E_0=500$ keV, $E_1=285$ keV, $E_2=100$ keV, and $\theta_1=-10°$. The slow-outgoing electron is calculated in a plane that forms an angle θ_p with the scattering plane. The cross section is shown as a function of the angle ϕ_2 of the slow-outgoing electron. The points having $\phi_2=0°$ and $\phi_2=180°$ are the points in common with the scattering plane and, as expected, the TDCS for these points is unchanged under reversal of spins. (a) $\mathcal{T}'(+,k_{2_y})$ (solid) and $\mathcal{T}'(-,k_{2_y})$ (dashed) $\theta_p=64°$, (b) $\mathcal{T}'(+,k_{2_y})$ (solid) and $\mathcal{T}'(-,k_{2_y})$ (dashed) $\theta_p=32°$, (c) $\mathcal{T}(++,k_{2_y})$ (solid) and $\mathcal{T}(--,k_{2_y})$ (dashed) $\theta_p=64°$, (d) $\mathcal{T}(++,k_{2_y})$ (solid) and $\mathcal{T}(--,k_{2_y})$ (dashed) $\theta_p=32°$, (e) $\mathcal{T}(+-,k_{2_y})$ (solid) and $\mathcal{T}(-+,k_{2_y})$ (dashed) $\theta_p=64°$, (f) $\mathcal{T}(+-,k_{2_y})$ (solid) and $\mathcal{T}(-+,k_{2_y})$ (dashed) $\theta_p=32°$.

$$\mathcal{T}'_y(-) = c_E \sum_{\varepsilon_1,\varepsilon_2,m} \left| \mathcal{M}\left(\varepsilon_1,\varepsilon_2,-\frac{1}{2},m\right) + i\mathcal{M}\left(\varepsilon_1,\varepsilon_2,\frac{1}{2},m\right) - \mathcal{M}^{ex}\right|^2. \quad (85)$$

The bound electron will initially be taken to reside in an *s* orbital. The terms in Eq. (85) in which either only one of ε_1, ε_2, or m is $-\frac{1}{2}$ or all three of theses quantities are $-\frac{1}{2}$ will be denoted by a prime. For such terms, the result (77b) with $k_{2_y}=0$ shows after calculating the phase factor $(-1)^{\tilde{\Delta}_b}$ using Eqs. (67d) and (68) that $\mathcal{M}(\varepsilon_1,\varepsilon_2,\mp\frac{1}{2},m)=\pm\mathcal{M}(-\varepsilon_1, -\varepsilon_2,\pm\frac{1}{2},-m)$. For the remaining terms in Eq. (85), to be denoted by a double prime, one has $\mathcal{M}(\varepsilon_1,\varepsilon_2,\mp\frac{1}{2},m) = \mp\mathcal{M}(-\varepsilon_1,-\varepsilon_2,\pm\frac{1}{2},-m)$. Use of these results in Eq. (85) yields

$$\mathcal{T}'_y(-) = c_E \sum_{\varepsilon_1,\varepsilon_2,m}{}' \left| \mathcal{M}\left(-\varepsilon_1,-\varepsilon_2,\frac{1}{2},-m\right) - i\mathcal{M}\left(-\varepsilon_1,-\varepsilon_2,-\frac{1}{2},-m\right) - \mathcal{M}^{ex}\right|^2 + c_E \sum_{\varepsilon_1,\varepsilon_2,m}{}'' \left| -\mathcal{M}\left(-\varepsilon_1,-\varepsilon_2,\frac{1}{2},-m\right) + i\mathcal{M}\left(-\varepsilon_1,-\varepsilon_2,-\frac{1}{2},-m\right) - \mathcal{M}^{ex}\right|^2 \quad (86a)$$

$$= c_E \sum_{\varepsilon_1,\varepsilon_2,m} \left| \mathcal{M}\left(-\varepsilon_1,-\varepsilon_2,\frac{1}{2},-m\right) - i\mathcal{M}\left(-\varepsilon_1,-\varepsilon_2,-\frac{1}{2},-m\right) - \mathcal{M}^{ex}\right|^2. \quad (86b)$$

Since the three summations are over all possible spin states, Eq. (86b) can be written as

$$\mathcal{T}'_y(-) = c_E \sum_{\varepsilon_1,\varepsilon_2,m} \left| \mathcal{M}\left(\varepsilon_1,\varepsilon_2,\frac{1}{2},m\right) - i\mathcal{M}\left(\varepsilon_1,\varepsilon_2,-\frac{1}{2},m\right) - \mathcal{M}^{ex}\right|^2, \quad (87)$$

where the changed signs merely cause the terms in the summation in Eq. (86b) to be generated in a different order. Since $|z_1+iz_2|\neq|z_1-iz_2|$ if z_1 and z_2 are complex, this result shows, when compared with that Eq. (84) for $\mathcal{T}'_y(+)$, that the difference $\mathcal{T}'_y(+)-\mathcal{T}'_y(-)$ is nonzero. The resulting expression for this difference becomes identical with that given in the previous density matrix formulation [14] when the polarization parameter P in that work is set to unity.

In the formulation in this Sec. IV C in which the incident electron propagates along the z direction, the difference $\mathcal{T}'_x(+)-\mathcal{T}'_x(-)$ is found using Eqs. (82) and (83a) to be

$$\mathcal{T}'_x(+) - \mathcal{T}'_x(-) = c_E \sum_{\varepsilon_1,\varepsilon_2,m} \left| \mathcal{M}\left(\varepsilon_1,\varepsilon_2,\frac{1}{2},m\right) + \mathcal{M}\left(\varepsilon_1,\varepsilon_2,-\frac{1}{2},m\right) - \mathcal{M}^{ex}\right|^2 - c_E \sum_{\varepsilon_1,\varepsilon_2,m} \left| \mathcal{M}\left(\varepsilon_1,\varepsilon_2,\frac{1}{2},m\right) - \mathcal{M}\left(\varepsilon_1,\varepsilon_2,-\frac{1}{2},m\right) - \mathcal{M}^{ex}\right|^2. \quad (88)$$

By relating the matrix elements $\mathcal{M}(\varepsilon_1,\varepsilon_2,\varepsilon_0,m)$ to those in which all the spins are reversed by using the equalities described in the last paragraph, it readily follows from the absence of the explicit imaginary unit which appears in Eq. (84) that $\mathcal{T}'_x(+)-\mathcal{T}'_x(-)$ is zero. This agrees with the more direct derivation in Sec. III D using the coordinate system with the x and z axes interchanged.

For ionization from subshells other than those of *s* symmetry, arguments differing from those just presented only through the occurrence of a different phase factor in Eq. (68) yield the same overall conclusion. Thus in coplanar geometries, although $\mathcal{T}'_x(+)$ remains equal to $\mathcal{T}'_x(-)$, $\mathcal{T}'_y(-)$ differs from $\mathcal{T}'_y(+)$.

V. SUMMARY

In the relativistic theory of $(e,2e)$ scattering as presented previously [5], the TDCS is expressed in terms of eight-dimensional matrix elements of a covariant propagator which was derived from QED. In the present paper, it has been shown that these matrix elements reduce to two-electron integrals of the interaction derived by Møller in 1931. These integrals contain purely spatial variables and Dirac matrices but no time coordinates.

It has been shown, for cases in which the spins of the electrons are aligned in the scattering plane as defined in Sec. III A, that the quantity $\mathcal{S}(s,k_{2_y})$ differs from its counterpart $\mathcal{S}(-s,k_{2_y})$ in which both the m_j quantum number and spins of all asymptotically free electrons have been reversed. The difference between these two scattering matrix elements, called the spin asymmetry, has been shown to vanish in coplanar geometries. Two factors generating spin asymmetry in noncoplanar geometries have been elucidated. The first of these is the relativistic modification of the distortion of any one of the three continuum wave functions induced by the potential originating from the target atom. The particular distortions giving rise to the spin asymmetry are those originating from the relativistic modification of the difference between the partial-wave scattering phase shift with the distorting potential and that for the corresponding plane wave. This contribution to the spin asymmetry is therefore predicted to vanish if all the continuum wave functions are described by relativistic plane waves. The second factor generating spin asymmetry is the presence in the Møller interaction of a non-time-reversal-invariant part $\hat{\mathcal{H}}_{NTI}$. Since the orders of this term of $1/c^3$ and higher are larger than that $(1/c^2)$ of the leading relativistic modifications of the phase-shift differences, the

first factor generating spin asymmetry is predicted to make a larger contribution than the second. Since both the first and second contributions to the spin asymmetry have been shown to vanish if all three continuum wave functions are described by plane waves, it follows that it is the effects of the distorting potential on the continuum wave functions which are ultimately responsible for any spin asymmetries.

The extra conditions required to produce scattering matrix-element-square moduli unchanged under reversal of all spins have been elucidated. It has been shown that these quantities are invariant under inversion of both all spins and the *y* momentum component of the slow-outgoing electron when the incoming and fast-outgoing electrons are propagating in the scattering *xz* plane in which the spins of the electrons are aligned. This explains why, in coplanar geometries necessarily having zero *y*-momentum components, the moduli of the scattering matrix elements are unchanged under reversal of just all spins, provided these are aligned in the scattering plane. However, as shown previously [14] the TDCS's in such coplanar cases with the incoming beam polarized along the *y* axis perpendicular to the plane do change under reversal of all the spins.

We have also considered TDCS's with spins polarized in the scattering plane in which only the spins of the electrons in the initial state have been specified. Such TDCS's are therefore generated from the fully spin-resolved quantities $\mathcal{S}(s,k_{2_y})$ by summing over all possible spin states of the electrons in the final state. It has been shown that the difference between such a TDCS and that produced by reversal of the two spins in the initial state remains finite in noncoplanar geometries. The same result has been shown to hold even if one sums over the spin states of the bound electron leaving specified only that of the incident electron. Thus consider the ionization process in which an electron is produced with an asymptotic spin alignment parallel to its direction of propagation. This electron is used to eject a further one from the *K* shell of an unpolarized atom and the two outgoing electrons are detected in coincidence with their spins not resolved. Consequently, the TDCS for this process is not the same as for a scattering event where the initial spin alignment is chosen to be antiparallel to the beam direction, unless all the electrons travel in the same plane. However, the TDCS will remain unchanged under the combination of reversal of the initial spin alignment and reflection with respect to the scattering plane such that $k_{2_y} \rightarrow -k_{2_y}$. From the analysis presented in this work one would expect to observe the same phenomena if the direction of the spin alignment is chosen to be perpendicular to the direction of propagation but still in the scattering plane. These properties of the TDCS's are of interest because it would appear to be feasible to detect them using the technologies available in currently existing experimental setups. Our conclusions are based on a detailed study of the relativistic distorted-wave Born approximation but given that this approximation fully contains the effect of elastic electron nuclear scattering, as well as the retardation and magnetic terms in the propagator for the electron-electron interactions, and that the earlier work shows that these are the dominant effects at high energies and for high-*Z* targets where there is the near-perfect agreement between theory and all existing measurements, we are encouraged to believe that the effects predicted in this paper will be observable and recommend that our experimental colleagues seek them out.

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