Fully Relativistic Convergent Close-Coupling Method for Excitation and Ionization Processes in Electron Collisions with Atoms and Ions

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We report the development of the fully relativistic convergent close-coupling method based on the solution of the Dirac equation. A complete square-integrable Dirac L-spinor basis is used to obtain a set of target states spanning the target discrete and continuous positive- and negative-energy spectra. The present implementation is for quasi-one-electron atoms whose electronic configuration corresponds to the first column of the periodic table. By way of example, we consider elastic scattering of 7 eV electrons on the ground state of cesium, where the full set of spin asymmetries (A_1, A_2, A_{nn}) has been measured. Excellent agreement with experiment is found.

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Over the last two decades it has been our goal to develop a general theory for the description of electron collisions with atoms and ions, for excitation and ionization processes, whose validity is independent of the projectile energy of interest. The convergent close-coupling (CCC) method [1,2] was first developed for electron-hydrogen scattering with the key ingredient being the usage of a complete square-integrable (Laguerre) basis for the description of the target spectrum. This allowed for convergence in the calculations to be examined simply by increasing the basis size. The solution of the close-coupling equations in momentum space allowed the treatment of relatively large systems, which is vital in convergence studies. Subsequently, the CCC method was generalized to the calculation of electron scattering from alkali atoms [3], helium [4], and alkali-earth atoms [5]. Though historically the close-coupling method was intended for purely excitation processes, we showed how the CCC method can also be used to describe ionizing collisions [6–9].

The CCC method was developed as a completely nonrelativistic theory. This restricts its applicability to highly energetic projectiles, highly charged targets, and spin-dependent observables. The CCC method was applied with considerable success to spin-averaged observables such as cross sections, electron-impact coherence parameters, and even exchange spin asymmetries (A_{nn}) for a number of heavy atoms, such as cesium [10–12], barium [13], and mercury [14]. However, the elastic spin asymmetries A_1 and A_2 measured by Baum *et al.* [10] are identically zero in CCC or any other nonrelativistic theory. Hence, these form an ideal testing ground for the relativistic CCC (RCCC) method.

There are few electron-atom theoretical methods that follow the fully relativistic formulation [15–20]. The most advanced of these is the Dirac R-matrix method [15,16]. However, agreement with experiment is rather mixed, with the omission of the ionization channels in the close-coupling expansion likely to be contributing to the discrepancies with experiment. Extensive calculations of electron-atom elastic scattering and excitations have been performed using perturbative techniques [17,18]. These calculations can provide a useful overview of collision processes, but their region of validity is limited to high incident electron energies and their application to low and intermediate incident electron energies can lead to large errors.

The aim of this Letter is to demonstrate how the ideas of the CCC method can be extended to take into account relativistic effects fully *ab initio*. While the presented formulation is general, we choose the e-Cs scattering system as an example which allows us to discuss a number of important computational details and perform detailed comparison with experiment.

The key step in the formulation of the CCC method is the diagonalization of the nonrelativistic Schrödinger Hamiltonian of the target in a finite Laguerre basis. In the case of the Dirac Hamiltonian, diagonalization proves to be a significantly more complicated problem. First, the spectrum of the Dirac Hamiltonian of a hydrogenlike atom does not have a finite lower bound and consists of three distinct energy intervals: continuous spectrum on $(-\infty, -2mc^2)$ corresponding to the negative-energy electrons (positrons), a discrete spectrum on $(-mc^2, 0)$ containing the target bound states, and the target continuum spectrum on $(0, \infty)$; see Fig. 1. Here m is electron mass and c is speed of light.

The absence of the lowest-energy state means that the variational principle cannot be applied to the problem in the same straightforward manner as is achieved in the nonrelativistic case. Also, the choice of the basis proves to be very important, as a simple generalization of the nonrelativistic diagonalization techniques leads to appearance of the so-called ''intruder'' states [21] that carry no physical meaning. This problem has been addressed by Grant and Quiney [22,23], whose work we follow.

In analogy to the CCC method, RCCC calculations model the Cs atom as a quasi-one-electron atom with one

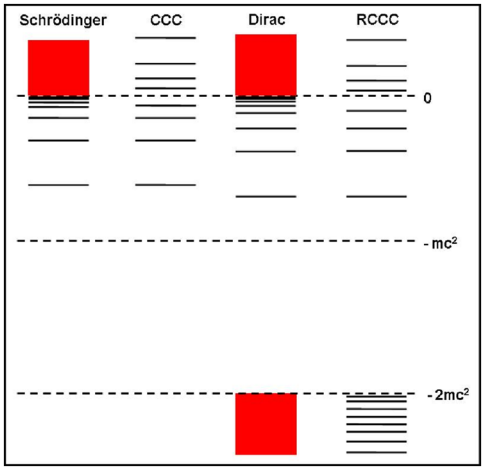

FIG. 1 (color online). A qualitative comparison of the Dirac and Schrödinger target spectra and their discretization using CCC and RCCC methods. The energy was shifted by $-mc^2$ to facilitate comparison with CCC. Note that RCCC generally yields a lower energy ground state and that there is the same number of states with energy below $-2mc^2$ as above.

active electron above a Dirac-Fock core of a Cs^+ ion. The core orbitals are obtained from the relativistic atomic structure GRASP package [24]. A phenomenological one-electron core polarization potential [3] is added to take into account more accurately the effect of the closed inert shells on the active electron. The resulting Dirac equation for the active electron wave function is

$$H_T\phi(\boldsymbol{r}) = [c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2 + V(r)]\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r}), \quad (1)$$

where $\boldsymbol{\alpha}$ and β are the Dirac matrices and $\boldsymbol{p}$ is the momentum operator. In what follows we will use atomic units: $m = 1$ and $c \approx 137$. The potential $V(r)$ describes the interaction of the active electron with the Cs^+ ion as described above.

The Cs atom wave function $\phi(\mathbf{r})$ with relativistic angular momentum quantum number κ and magnetic sublevel m is written as [22]

$$\phi_{\kappa m}(\boldsymbol{r}) = \frac{1}{r}\begin{pmatrix} \phi^L_{n\kappa}(r)\chi_{\kappa m} \\ i\phi^S_{n\kappa}(r)\chi_{-\kappa m}\end{pmatrix} = \frac{1}{r}\begin{pmatrix} \sum_n C^L_n f^L_{n\kappa}(r)\chi_{\kappa m} \\ i\sum_n C^S_n f^S_{n\kappa}(r)\chi_{-\kappa m}\end{pmatrix}. \quad (2)$$

Here $\chi_{\kappa m}$ is a two-component coupled spin-orbit function, $\phi^L_{n\kappa}(r)$ and $\phi^S_{n\kappa}(r)$ are the large and small components of the radial wave function, and C^L_n and C^S_n are expansion coefficients. The $f^L_{n\kappa}(r)$ and $f^S_{n\kappa}(r)$ are the radial parts of Dirac L spinors [22],

$$f^{L/S}_{n\kappa}(r) \propto (2\lambda r)^\gamma e^{-\lambda r}\times\left(-(1-\delta_{n0})L^{2\gamma}_{n-1}(2\lambda r) \pm \frac{N_{n\kappa}-\kappa}{n+2\gamma}L^{2\gamma}_n(2\lambda r)\right), \quad (3)$$

with "+" corresponding to the large component and "−" to the small component; $L^{2\gamma}_n(2\lambda r)$ are the associated Laguerre polynomials, $\gamma = \sqrt{\kappa^2 - (Z/c)^2}$, and $N_{n\kappa} = \sqrt{\kappa^2 + 2n\gamma + n^2}$. Dirac L spinors form a complete square-integrable basis and are the relativistic analogues of the Coulomb Sturmian (Laguerre) functions used in formulation of the nonrelativistic CCC method.

The important feature of the expansion (2) is that although the large and small components of the wave function are expanded separately, the Dirac L spinors for large and small components are not independent but satisfy the following system of differential equations:

$$\frac{d}{dr}f^L_{n\kappa} = -\frac{\kappa}{r}f^L_{n\kappa} + \left(\frac{N_{n\kappa}-n-\gamma}{r} + \lambda\right)f^S_{n\kappa}, \quad (4)$$

$$\frac{d}{dr}f^S_{n\kappa} = \frac{\kappa}{r}f^S_{n\kappa} + \left(\frac{-N_{n\kappa}-n-\gamma}{r} + \lambda\right)f^L_{n\kappa}. \quad (5)$$

The consequence of these matching relations is that the representation of the Dirac operator in an L-spinor basis does not suffer from any variational problems. The Dirac spectrum correctly separates into the positive- and negative-energy branches shown in Fig. 1, and the correct transition to the nonrelativistic limit is guaranteed for $c \to \infty$.

For each value of κ a standard eigenvalue problem for expansion coefficients $\{C^L_n, C^S_n\}$, $n = 1, \ldots, N$ can be formulated by substitution of the expansion (2) into Dirac Eq. (1). Note that for N L spinors used in expansion (2) the size of the eigenvalue problem is $2N$. The result of the diagonalization is a set of $2N$ states $\{\phi_n\}$ with N of them describing Cs discrete and positive-energy states and N states that provide a square-integrable discretization of the negative-energy continuum; see Fig. 1. According to Dirac [25] the negative-energy continuum is filled with electrons and the Pauli exclusion principle prohibits decay to the negative-energy continuum from bound and positive-energy continuum parts of the spectrum. Excitation from the negative-energy continuum results in creation of electron-positron pairs. The energy required for such processes ($\sim 2mc^2 \approx 1$ MeV) is much higher than that normally considered in electron-atom collision studies. Consequently, here we neglect the negative-energy continuum states.

The relativistic formulation of scattering is similar to the nonrelativistic case, and so we will concentrate mainly on the differences. For the sake of clarity in the present paper we use Dirac plane waves to describe the projectile electron. The generalization to (Coulomb) distorted waves has been implemented in the RCCC computer code but will be described elsewhere.

Dirac plane waves are solutions of the free Dirac Hamiltonian and are given by [26]

$$|\boldsymbol{k}\mu b\rangle = U^b_\mu \frac{1}{(2\pi)^{3/2}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \quad (6)$$

where $\boldsymbol{k}$ is momentum, μ is spin magnetic number, b is sign of energy, and U^b_μ are four-component spinors. They

satisfy the following orthogonality and completeness condition:

$$\langle \boldsymbol{k}\mu b|\boldsymbol{k}'\mu' b'\rangle = \delta_{\mu\mu'}\delta_{bb'}\delta(\boldsymbol{k}-\boldsymbol{k}'), \tag{7}$$

$$\sum_{b\mu}\int d^3k|\boldsymbol{k}\mu b\rangle\langle \boldsymbol{k}\mu b| = \tilde{1}, \tag{8}$$

where $\tilde{1}$ denotes the 4×4 unit matrix.

The spectral decomposition of the free Dirac Green's function is [26]

$$G(E) = \sum_{\mu}\int d^3k\left(\frac{|\boldsymbol{k}\mu+\rangle\langle \boldsymbol{k}\mu+|}{E-E_k} + \frac{|\boldsymbol{k}\mu-\rangle\langle \boldsymbol{k}\mu-|}{E+E_k}\right), \tag{9}$$

where relativistic energy $E_k = c\sqrt{k^2+c^2}$. Note the presence of an additional ("$-$") term corresponding to the negative-energy continuum.

The Dirac Hamiltonian describing total e-Cs system is given by (with indexes 0 and 1 referring to the projectile and target electron spaces, respectively)

$$H = H_T + K_0 + V(r_0) + 1/|\boldsymbol{r}_0 - \boldsymbol{r}_1|, \tag{10}$$

where H_T is Hamiltonian of the Cs atom [see Eq. (1)], K_0 is the free Dirac Hamiltonian of the projectile electron, and $V(r_0)$ is interaction potential of projectile electron with Cs^+ ion as discussed earlier.

The set of square-integrable states $\{\phi_n\}$, $n = 1,\ldots,N$, is used to perform close-coupling expansion of the total scattering electron-target atom wave function. Each term of the close-coupling expansion is antisymmetrized to ensure that the Pauli principle is satisfied. The Lippmann-Schwinger equation for the T matrix can be obtained from the corresponding Dirac equation for the total wave function in a standard manner [using relativistic Green's function (9)] with the result

$$\begin{aligned} T_{fi}^{++}(\boldsymbol{k}_f,\boldsymbol{k}_i) &= V_{fi}^{++}(\boldsymbol{k}_f,\boldsymbol{k}_i) \\ &+ \sum_{n=1}^{N}\int d^3k\frac{V_{fn}^{++}(\boldsymbol{k}_f,\boldsymbol{k})T_{ni}^{++}(\boldsymbol{k},\boldsymbol{k}_i)}{E-E_n-E_k+i0} \\ &+ \sum_{n=1}^{N}\int d^3k\frac{V_{fn}^{+-}(\boldsymbol{k}_f,\boldsymbol{k})T_{ni}^{-+}(\boldsymbol{k},\boldsymbol{k}_i)}{E-E_n+E_k+i0} \end{aligned} \tag{11}$$

$$\begin{aligned} T_{fi}^{-+}(\boldsymbol{k}_f,\boldsymbol{k}_i) &= V_{fi}^{-+}(\boldsymbol{k}_f,\boldsymbol{k}_i) \\ &+ \sum_{n=1}^{N}\int d^3k\frac{V_{fn}^{-+}(\boldsymbol{k}_f,\boldsymbol{k})T_{ni}^{++}(\boldsymbol{k},\boldsymbol{k}_i)}{E-E_n-E_k+i0} \\ &+ \sum_{n=1}^{N}\int d^3k\frac{V_{fn}^{--}(\boldsymbol{k}_f,\boldsymbol{k})T_{ni}^{-+}(\boldsymbol{k},\boldsymbol{k}_i)}{E-E_n+E_k+i0}, \end{aligned}$$

where

$$T_{fi}^{bb'}(\boldsymbol{k},\boldsymbol{k}') = \langle k\mu b\phi_f|T|\boldsymbol{k}'\mu' b'\phi_i\rangle, \tag{12}$$

$$\begin{aligned} V_{fi}^{bb'}(\boldsymbol{k},\boldsymbol{k}') &= \langle \boldsymbol{k}\mu b\phi_f|V|\boldsymbol{k}\mu' b'\phi_i\rangle \\ &= \langle \boldsymbol{k}\mu b\phi_f|V(r_0) + \frac{1}{|\boldsymbol{r}_0-\boldsymbol{r}_1|} \\ &\quad - (H-E)P_{01}|\boldsymbol{k}'\mu' b'\phi_i\rangle, \end{aligned} \tag{13}$$

with P_{01} denoting the space exchange operator.

This is considerably more complicated than in the CCC method. The T matrix $T_{ni}^{-+}(\boldsymbol{k},\boldsymbol{k}_i)$ describes transition to a negative-energy continuum state. For a positive total energy E of the scattering system the Green's function associated with term $T_{ni}^{-+}(\boldsymbol{k},\boldsymbol{k}_i)$ has no singularity ($E - E_n + E_k > 0$; i.e., we assume here that the energies of target bound states are much less than the electron rest energy) and therefore it corresponds to closed states. Hence, we drop all negative-energy continuum terms in the Lippmann-Schwinger Eq. (11). For electron-atom or ion scattering processes the error associated with this approximation is negligible as the Green's function for the negative energy terms is of order $1/2mc^2$. The resulting form of the Lippmann-Schwinger equation is then the same as for the nonrelativistic case and involves only the "$++$" matrix elements, and the calculations can proceed as previously described [2].

Elastic scattering of polarized electrons from polarized Cs atoms has been studied in a series of experiments [10]. The scattered electron intensities were measured for all four possible combinations of relative polarization (with respect to the scattering plane) of incident electron (up or down) and target Cs atom (up or down). This allows determination of the relative differential cross section (DCS) for scattering of unpolarized electrons on Cs, as well as three spin asymmetries describing scattering of unpolarized electrons from polarized Cs atoms (A_1), polarized electrons from unpolarized atoms (A_2), and antiparallel-parallel asymmetry (A_{nn}) for scattering of polarized electrons from polarized Cs atoms. Asymmetries A_1 and A_2 are identically zero in nonrelativistic calculations and offer a sensitive test to account for relativistic effects in theoretical models. We also note that all spin asymmetries are zero when calculated in the first Born approximation, thus also providing a test of the importance of channel coupling in e-Cs scattering.

We have performed a series of calculations of e-Cs scattering at 7 eV incident electron energies until convergence in all of the parameters of interest has been obtained, and present the results of just the largest (89 state) calculation in Fig. 2. Agreement with experiment is excellent for all four parameters, though we note that the experimental DCS data are relative and have been normalized to the RCCC theory. Comparison with a number of previous calculations for e-Cs elastic scattering is also presented. Nonrelativistic CCC calculations [27] are in very good agreement with the present results for the DCS and the spin asymmetry A_{nn}, but are identically zero for A_1 and A_2. The 40-state Breit-Pauli R-matrix calculation [28] does not give as good agreement with the DCS, A_1 and A_2, but

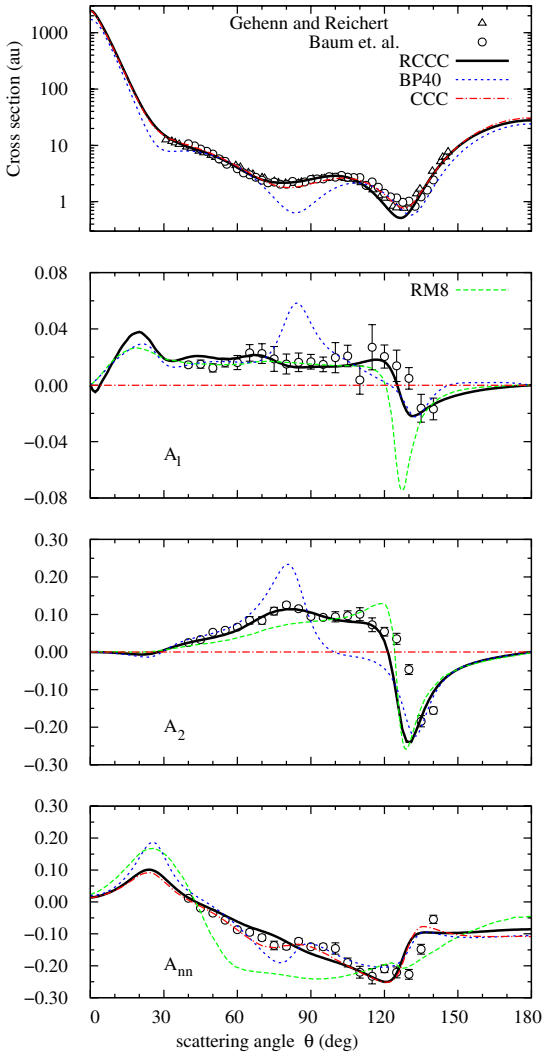

FIG. 2 (color online). Differential cross section and spin asymmetries for elastic 7 eV electron scattering on Cs. Present calculations (RCCC) are described in the text, Breit-Pauli (BP40) R-matrix calculations are due to Bartschat and Fang *et al.*, [28], Dirac R-matrix (RM8) calculations are due to Baum *et al.* [29], and nonrelativistic CCC calculations are due to Bartschat and Bray [27]. The measurements are due to Baum *et al.* [10] and Gehenn and Reichert [30].

comparable with RCCC for A_{nn}. The Dirac-based R-matrix calculation, presented by Baum *et al.* [29] only for the spin asymmetry parameters, shows better agreement with the A_1 and A_2 parameters than A_{nn}. These discrepancies indicate the importance of having a method whose convergence can be systematically verified.

In conclusion, we have developed a fully relativistic CCC method and demonstrated its utility by considering 7 eV elastic electron scattering from cesium. The excellent agreement of RCCC with the A_1 and A_2 spin asymmetries, which are identically zero in the nonrelativistic CCC method, indicates that the relativistic formalism has been incorporated correctly while maintaining the important channel-coupling effects. The new formalism considerably extends our capacity to consider problems with high projectile energies, highly-charged or heavy targets and spin-resolved phenomena. Extension of RCCC to quasi two-electron targets is underway.

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