THE TIME-DEPENDENT CLOSE-COUPLING METHOD FOR ELECTRON-IMPACT DIFFERENTIAL IONIZATION CROSS SECTIONS FOR ATOMS AND MOLECULES

M.S. PINDZOLA, F. ROBICHEAUX[1], AND J. COLGAN[2]

[1] Department of Physics, Auburn University, Auburn, AL, USA

[2] Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, USA

Abstract: We review the application of the time-dependent close-coupling method to calculate energy and angle differential cross sections for the electron-impact ionization of atoms and molecules.

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1. INTRODUCTION

The time-dependent close-coupling method was developed to study few-body dynamics in atomic and molecular collision processes [1]. Applications include photon, electron, and proton collisions with atoms, molecules, and their ions. In this paper we review the application of the time-dependent close-coupling method to calculate energy and angle differential cross sections for the electron-impact ionization of atoms and molecules.

The time-dependent close-coupling (TDCC) method was first used used to calculate energy and angle differential cross sections for the electron-impact single ionization of the hydrogen [2, 3] and helium [4, 5] atoms. For the electron-impact single ionization of the hydrogen or helium atoms, collision probabilities are found by the projection of a fully time evolved six-dimensional coordinate space wavefunction onto simple products of spatial functions representing two outgoing electrons in the field of H^+ or He^+. The six-dimensional wavefunction for two continuum electrons moving in a stationary spherical Coulomb field is represented by an expansion of two-dimensional (2D) radial functions in coupled spherical harmonics. The TDCC-2D method, along with the converged close-coupling [6] and the exterior complex scaling [7] methods, provide a non-perturbative

solution of this fully differential three-body spherical quantal problem.

The time-dependent close-coupling method was recently used to calculate energy and angle differential cross sections for the electron-impact double ionization of the helium atom [8].

For the electron-impact double ionization of the helium atom, collision probabilities are found by the projection of a fully time evolved nine-dimensional coordinate space wavefunction onto antisymmetric products of spatial and spin functions representing three outgoing electrons in the field of He^{2+}. The nine-dimensional wavefunction for three continuum electrons moving in a stationary spherical Coulomb field is represented by an expansion of three-dimensional (3D) radial functions in coupled spherical harmonics. The TDCC-3D method provides a non-perturbative solution of this fully differential four-body spherical quantal problem.

The time-dependent close-coupling method was also recently used to calculate energy and angle differential cross sections for the electron-impact single ionization of the hydrogen molecule [9, 10]. For the electron-impact single ionization of the hydrogen molecule, collision probabilities are found by the projection of a fully time evolved six-dimensional coordinate space wavefunction

onto simple products of spatial functions representing two outgoing electrons in the field of H_2^+. The six dimensional wavefunction for two continuum electrons moving in a stationary non-spherical Coulomb field is represented by an expansion of four-dimensional (4D) radial and angular functions in rotation functions. The TDCC-4D method provides a non-perturbative solution of this fully differential three-body non-spherical quantal problem.

The remainder of this paper is organized as follows. The close-coupled equations and various total and differential ionization cross section expressions are presented for the TDCC-2D method in Section 2, the TDCC-3D method in Section 3, and the TDCC-4D method in Section 4. Selected total and differential cross section results for the electron-impact ionization of H, He, H_2^+ and H_2 are presented in Section 5. In Section 6, we conclude with a summary and an outlook for future work. Unless otherwise stated, all quantities are given in atomic units.

2. TIME-DEPENDENT CLOSE-COUPLING 2D METHOD

The time-dependent Schrodinger equation for electron scattering from an atom with one active electron is given by:

$$i \frac{\partial \psi(\vec{r}_1, \vec{r}_2, t)}{\partial t} = H(\vec{r}_1, \vec{r}_2) \psi(\vec{r}_1, \vec{r}_2, t), \qquad \dots (1)$$

where the non-relativistic Hamiltonian is given by:

$$H(\vec{r}_1, \vec{r}_2) = -\frac{1}{2} \nabla_1^2 + V(r_1) - \frac{1}{2} \nabla_2^2$$
$$+ V(r_2) + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \qquad \dots (2)$$

For the hydrogen atom:

$$V(r) = -\frac{1}{r}, \qquad \dots (3)$$

while for the helium atom:

$$V(r) = -\frac{2}{r} + V_H(r) - a \left(\frac{24\rho(r)}{\pi} \right)^{\frac{1}{3}}, \qquad \dots (4)$$

where $V_H(r)$ is the direct Hartree potential, a is an adjustable parameter, and $\rho(r)$ is the probability density of the core electron.

The total six-dimensional electronic wavefunction is expanded in coupled spherical harmonics for each LS total orbital and spin angular momentum symmetry:

$$\psi(\vec{r}_1, \vec{r}_2, t) = \sum_{l_1, l_2} \frac{P_{l_1 l_2}^{LS}(r_1, r_2, t)}{r_1 r_2} Y_{(l_1, l_2) L}(\hat{r}_1, \hat{r}_2), \qquad \dots (5)$$

where

$$Y_{(l_1, l_2) L}(\hat{r}_1, \hat{r}_2) = \sum_{m_1, m_2} C_{m_1 m_2 0}^{l_1 l_2 L} Y_{l_1 m_1}(\hat{r}_1) Y_{l_2 m_2}(\hat{r}_2), \qquad \dots (6)$$

$C_{m_1 m_2 m_3}^{l_1 l_2 l_3}$ is a Clebsch-Gordan coefficient, and $Y_{lm}(\hat{r})$ is a spherical harmonic. Upon substitution of $\psi(\vec{r}_1, \vec{r}_2, t)$ of Eq. (5) into the time-dependent Schrodinger equation and projection onto the coupled spherical harmonics, we obtain the time-dependent close-coupled partial differential equations for each *LS* symmetry:

$$i \frac{\partial P_{l_1 l_2}^{LS}(r_1, r_2, t)}{\partial t} = T_{l_1 l_2}(r_1, r_2) P_{l_1 l_2}^{LS}(r_1, r_2, t)$$
$$+ \sum_{l_1', l_2'} W_{l_1 l_2, l_1' l_2'}^{L}(r_1, r_2) P_{l_1' l_2'}^{LS}(r_1, r_2, t), \dots (7)$$

where

$$T_{l_1 l_2}(r_1, r_2) = \sum_i^2 \left(-\frac{1}{2} \frac{\partial^2}{\partial r_i^2} + \frac{l_i(l_i+1)}{2 r_i^2} + V(r_i) \right) \dots (8)$$

and the coupling operator is given in terms of standard 3*j* and 6*j* symbols by:

$$W_{l_1 l_2, l_1' l_2'}^{L}(r_2, r_2) = (-1)^{l_1 + l_1' + L} \sqrt{(2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)}$$
$$\times \sum_\lambda \frac{(r_1, r_2)_<^\lambda}{(r_1, r_2)_>^{\lambda+1}} \begin{pmatrix} l_1 & \lambda & l_1' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & \lambda & l_2' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ l_2' & l_1' & \lambda \end{Bmatrix}$$
$$\dots (9)$$

An initial condition for the solution of the time-dependent close-coupling equations for electron scattering from an atom with one active electron is given by:

$$P_{l_1 l_2}^{LS}(r_1, r_2, t = 0)$$
$$= \sqrt{\frac{1}{2}} [P_{1s}(r_1) F_{k_0 L}(r_2) \delta_{l_1, 0} \delta_{l_2, L} \qquad \dots (10)$$
$$+ (-1)^S F_{k_0 L}(r_1) P_{1s}(r_2) \delta_{l_1, L} \delta_{l_2, 0}],$$

where k_0 is the initial linear momentum, $F_{kl}(r)$ is a radial wavepacket, and $P_{1s}(r)$ is a bound radial orbital for the ground state of the hydrogen or helium atoms.

Following time evolution of the time-dependent close-coupled partial differential equations into the asymptotic region for each LS symmetry, the total cross section is given by:

$$\sigma = \frac{\pi}{4k_0^2} \int_0^\infty dk_1 \int_0^\infty dk_2$$

$$\times \sum_{L,S} (2L+1)(2S+1) \sum_{l_1,l_2} \left| P_{l_1 l_2}^{LS}(k_1, k_2) \right|^2, \qquad \dots (11)$$

the energy differential cross section is given by:

$$\frac{d\sigma}{d\alpha} = \frac{\pi}{4k_0^2} \int_0^\infty dk_1 \int_0^\infty dk_2 \delta\left(\alpha - \tan^{-1}(k_2/k_1)\right)$$

$$\times \sum_{L,S} (2L+1)(2S+1) \sum_{l_1,l_2} \left| P_{l_1 l_2}^{LS}(k_1, k_2) \right|^2, \qquad \dots (12)$$

and the energy and angle differential cross section is given by:

$$\frac{d\sigma}{d\alpha d\Omega_1 d\Omega_2} = \frac{\pi}{4k_0^2} \int_0^\infty dk_1 \int_0^\infty dk_2 \delta\left(\alpha - \tan^{-1}(k_2/k_1)\right)$$

$$\times \sum_s (2S+1) \left| \sum_L i^L \sqrt{2L+1} \sum_{l_1,l_2} (-i)^{l_1+l_2} \right.$$

$$\left. \times e^{i(\delta_{l_1} + \delta_{l_2})} P_{l_1 l_2}^{LS}(k_1, k_2) Y_{(l_1,l_2)L}(\hat{k}_1, \hat{k}_2) \right|^2. \qquad \dots (13)$$

In the cross section expressions of Eqs (11)–(13), α is the angle in the hyperspherical (k_1, k_2) plane, k_1 and k_2 are the final linear momentum, and δ_1 and δ_2 are scattering phase shifts. The momentum space projection wavefunction for each LS symmetry and $l_1 l_2$ coupled channel is given by:

$$P_{l_1 l_2}^{LS}(k_1, k_2) = \int_0^\infty dr_1 \int_0^\infty dr_2 P_{k_1 l_1}(r_1) P_{k_2 l_2}(r_2)$$

$$\times P_{l_1 l_2}^{LS}(r_1, r_2, t \to \infty), \qquad \dots (14)$$

where $P_{kl}(r)$ is a box normalized continuum radial orbital calculated in the potentials of Eq. (3) for H^+ or Eq. (4) for He^+.

3. TIME-DEPENDENT CLOSE-COUPLING 3D METHOD

The time-dependent Schrodinger equation for electron scattering from an atom with two active electrons is given by:

$$i\frac{\partial \psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, t)}{\partial t} = H(\vec{r}_1, \vec{r}_2, \vec{r}_3) \psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, t), \qquad \dots (15)$$

where the non-relativistic Hamiltonian is given by:

$$H(\vec{r}_1, \vec{r}_2, \vec{r}_3) = -\frac{1}{2}\nabla_1^2 + V(r_1) - \frac{1}{2}\nabla_2^2 + V(r_2) - \frac{1}{2}\nabla_3^2$$

$$+ V(r_3) + \frac{1}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{|\vec{r}_1 - \vec{r}_3|} + \frac{1}{|\vec{r}_2 - \vec{r}_3|} \qquad \dots (16)$$

For the helium atom:

$$V(r) = -\frac{2}{r}. \qquad \dots (17)$$

The total nine-dimensional electronic wavefunction is expanded in coupled spherical harmonics for each $\mathcal{LS}$ total orbital and spin angular momentum symmetry:

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, t) = \sum_{l_1, l_2, L, l_3} \frac{P_{l_1 l_2 L l_3}^{S\mathcal{LS}}(r_1, r_2, r_3, t)}{r_1 r_2 r_3}$$

$$\times Y_{((l_1, l_2)L, l_3)\mathcal{L}}(\hat{r}_1, \hat{r}_2, \hat{r}_3), \qquad \dots (18)$$

where

$$Y_{((l_1, l_2)L, l_3)\mathcal{L}}(\hat{r}_1, \hat{r}_2, \hat{r}_3)$$

$$= \sum_{m_1, m_2, M, m_3} C_{m_1 m_2 M}^{l_1 l_2 L} C_{M m_3 0}^{L l_3 \mathcal{L}} Y_{l_1 m_1}(\hat{r}_1)$$

$$\times Y_{l_2 m_2}(\hat{r}_2) Y_{l_3 m_3}(\hat{r}_3). \qquad \dots (19)$$

Upon substitution of $\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, t)$ of Eq. (18) into the time-dependent Schrodinger equation and projection onto the coupled spherical harmonics, we obtain the time-dependent close-coupled partial differential equations for each $\mathcal{LS}$ symmetry:

$$i \frac{\partial P_{l_1 l_2 L l_3}^{SLS}(r_1, r_2, r_3, t)}{\partial t}$$

$$= T_{l_1 l_2 l_3}(r_1, r_2, r_3) P_{l_1 l_2 L l_3}^{SLS}(r_1, r_2, r_3, t)$$

$$+ \sum_{l_1', l_2', L', l_3'} \sum_{i<j}^{3} W_{l_1 l_2 L l_3, l_1' l_2' L' l_3'}^{L}(r_i, r_j)$$

$$\times P_{l_1' l_2' L' l_3'}^{SLS}(r_1, r_2, r_3, t), \qquad \dots (20)$$

where

$$T_{l_1 l_2 l_3}(r_1, r_2, r_3) = \sum_{i}^{3}\left(-\frac{1}{2}\frac{\partial^2}{\partial r_i^2} + \frac{l_i(l_i+1)}{2r_i^2} + V(r_i)\right),$$
$$\dots (21)$$

$$W_{l_1 l_2 L l_3, l_1' l_2' L' l_3'}^{\mathcal{L}}(r_1, r_2)$$

$$= (-1)^{l_1+l_1'+L} \delta_{l_3, l_3'}\delta_{L, L'}$$

$$\times \sqrt{(2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)}$$

$$\times \sum_{\lambda} \frac{(r_1, r_2)_<^{\lambda}}{(r_1, r_2)_>^{\lambda+1}}\begin{pmatrix} l_1 & \lambda & l_1' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} l_2 & \lambda & l_2' \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} l_1 & l_2 & L \\ l_2' & l_1' & \lambda \end{Bmatrix}, \qquad \dots (22)$$

$$W_{l_1 l_2 L l_3, l_1' l_2' L' l_3'}^{\mathcal{L}}(r_1, r_3)$$

$$= (-1)^{l_2+\mathcal{L}} \delta_{l_2, l_2'}$$

$$\times \sqrt{\frac{(2l_1+1)(2l_1'+1)(2l_3+1)(2l_3'+1)}{(2L+1)(2L'+1)}}$$

$$\times \sum_{\lambda} \frac{(r_1, r_3)_<^{\lambda}}{(r_1, r_3)_>^{\lambda+1}}\begin{pmatrix} l_1 & \lambda & l_1' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_3 & \lambda & l_3' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{Bmatrix} L & l_3 & \mathcal{L} \\ l_3' & L' & \lambda \end{Bmatrix}\begin{Bmatrix} l_1 & l_2 & L \\ L' & \lambda & l_1' \end{Bmatrix}, \qquad \dots (23)$$

and

$$W_{l_1 l_2 L l_3, l_1' l_2' L' l_3'}^{\mathcal{L}}(r_2, r_3)$$

$$= (-1)^{l_1'+l_2+l_2'+L+L'+\mathcal{L}} \delta_{l_1, l_1'}$$

$$\times \sqrt{\frac{(2l_2+1)(2l_2'+1)(2l_3+1)(2l_3'+1)}{(2L+1)(2L'+1)}}$$

$$\times \sum_{\lambda} \frac{(r_2, r_3)_<^{\lambda}}{(r_2, r_3)_>^{\lambda+1}}\begin{pmatrix} l_2 & \lambda & l_2' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_3 & \lambda & l_3' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{Bmatrix} L & l_3 & \mathcal{L} \\ l_3' & L' & \lambda \end{Bmatrix}\begin{Bmatrix} l_1 & l_2 & L \\ \lambda & L' & l_2' \end{Bmatrix}. \qquad \dots (24)$$

An initial condition for the solution of the time-dependent close-coupling equations for electron scattering from an atom with two active electrons is given by:

$$P_{l_1 l_2 L l_3}^{SLS}(r_1, r_2, r_3, t=0)$$

$$= \sum_{l} \bar{P}_u^{00}(r_1, r_2) F_{k_0 \mathcal{L}}(r_3)$$

$$\times \delta_{l_1, l}\delta_{l_2, l}\delta_{L, 0}\delta_{S, 0}\delta_{l_3, \mathcal{L}}, \qquad \dots (25)$$

where $\sum_l \bar{P}_u^{00}(r_1, r_2)$ is a correlated radial wavefunction for the two target electrons of the ground state of helium.

Following time evolution of the time-dependent close-coupled partial differential equations into the asymptotic region for each $\mathcal{LS}$ symmetry, the total cross section for single ionization is given by:

$$\sigma = \frac{\pi}{2k_0^2}\int_0^{\infty} dk_2 \int_0^{\infty} dk_3$$

$$\times \sum_{\mathcal{L}, S}(2\mathcal{L}+1)(2S+1)$$

$$\times \sum_{L, S}\sum_{l_2, l_3}\left|P_{sl_2 L l_3}^{SLS}(1s, k_2, k_3)\right|^2 \dots (26)$$

the energy differential cross section for single ionization is given by:

$$\frac{d\sigma}{d\beta} = \frac{\pi}{2k_0^2}\int_0^{\infty} dk_2 \int_0^{\infty} dk_3 \delta\left(\beta - \tan^{-1}(k_3/k_2)\right)$$

$$\times \sum_{\mathcal{L}, S}(2\mathcal{L}+1)(2S+1)$$

$$\times \sum_{L, S}\sum_{l_2, l_3}\left|P_{sl_2 L l_3}^{SLS}(1s, k_2, k_3)\right|^2, \qquad \dots (27)$$

and the energy and angle differential cross section for single ionization is given by:

$$\frac{d\sigma}{d\beta d\Omega_2 d\Omega_3} = \frac{\pi}{2k_0^2} \int_0^\infty dk_2 \int_0^\infty dk_3 \delta\left(\beta - \tan^{-1}\left(k_3/k_2\right)\right)$$

$$\times \sum_S (2S+1) \times \sum_S |\sum_{\mathcal{L}} i^{\mathcal{L}} \sqrt{2\mathcal{L}+1}$$

$$\times \sum_L \sum_{l_2, l_3} (-i)^{l_2+l_3} e^{i\left(\delta_{l_2}+\delta_{l_3}\right)}$$

$$\times P_{sl_2 Ll_3}^{S\mathcal{L}S}\left(1s, k_2, k_3\right) Y_{((s,l_2)L,l_3)\mathcal{L}}\left(\hat{k}_1, \hat{k}_2\right)|^2. \qquad \ldots (28)$$

In the cross section expressions of Eqs (26) – (28), β is the angle in the hyperspherical (k_2, k_3) plane, k_2 and k_3 are the final linear momentum, and δ_{l_2} and δ_{l_3} are scattering phase shifts. The momentum space projection wave-function for each $\mathcal{L}S$ symmetry and $sl_2 Ll_3$ coupled channel is given by:

$$P_{sl_2 Ll_3}^{S\mathcal{L}S}\left(1s, k_2, k_3\right)$$

$$= \sum_{L', S'} \sum_{ijk}^6 Q_{l_1 l_2 LSl_3 \, L'S'}^{\mathcal{L}S}\left(ijk\right) \times \int_0^\infty dr_1 \int_0^\infty dr_2$$

$$\times \int_0^\infty dr_3 \, P_{1s}\left(r_1\right) P_{k_2 l_2}\left(r_2\right) P_{k_3 l_3}\left(r_3\right)$$

$$\times P_{sl_2 Ll_3}^{S\mathcal{L}S}\left(r_1, r_2, r_3, t \to \infty\right), \qquad \ldots (29)$$

where $P_{kl}(r)$ is a box normalized continuum radial orbital calculated in the potential of Eq. (4) for He$^+$ and ijk is summed over the six permutations of 123. The probability expansion coefficients, $Q(ijk)$, are obtained using standard algebraic reduction methods.

Similarly, the total cross section for double ionization is given by:

$$\sigma = \frac{\pi}{2k_0^2} \int_0^\infty dk_1 \int_0^\infty dk_2 \int_0^\infty dk_3$$

$$\times \sum_{\mathcal{L}, S} (2\mathcal{L}+1)(2S+1)$$

$$\times \sum_{L, S} \sum_{l_1, l_2, l_3} \left| P_{l_1 l_2 Ll_3}^{S\mathcal{L}S}\left(k_1, k_2, k_3\right)\right|^2, \qquad \ldots (30)$$

the energy differential cross section for double ionization is given by:

$$\frac{d\sigma}{d\alpha d\beta} = \frac{\pi}{2k_0^2} \int_0^\infty dk_1 \int_0^\infty dk_2 \int_0^\infty dk_3$$

$$\times \delta\left(\alpha - \tan^{-1}\left(k_2/k_1\right)\right)$$

$$\times \delta\left(\beta - \tan^{-1}\left(k_3/\sqrt{k_1^2+k_2^2}\right)\right)$$

$$\times \sum_{\mathcal{L}, S} (2\mathcal{L}+1)(2S+1)$$

$$\times \sum_{L, S} \sum_{l_1, l_2, l_3} \left| P_{l_1 l_2 Ll_3}^{S\mathcal{L}S}\left(k_1, k_2, k_3\right)\right|^2, \qquad \ldots (31)$$

and the energy and angle differential cross section for double ionization is given by:

$$\frac{d\sigma}{d\alpha d\beta d\Omega_1 d\Omega_2 d\Omega_3}$$

$$= \frac{\pi}{2k_0^2} \int_0^\infty dk_1 \int_0^\infty dk_2 \int_0^\infty dk_3$$

$$\times \delta\left(\alpha - \tan^{-1}\left(k_2/k_1\right)\right)$$

$$\times \delta\left(\beta - \tan^{-1}\left(k_3/\sqrt{k_1^2+k_2^2}\right)\right)$$

$$\times \sum_S (2S+1) \times \sum_S \left|\sum_{\mathcal{L}} i^{\mathcal{L}} \sqrt{2\mathcal{L}+1} \sum_L \sum_{l_1, l_2, l_3}\right.$$

$$\times (-i)^{l_1+l_2+l_3} e^{i\left(\delta_{l_1}+\delta_{l_2}+\delta_{l_3}\right)}$$

$$\times \left. P_{l_1 l_2 Ll_3}^{S\mathcal{L}S}\left(k_1, k_2, k_3\right) Y_{((l_1,l_2)L,l_3)\mathcal{L}}\left(\hat{k}_1, \hat{k}_2, \hat{k}_3\right)\right|^2 \qquad \ldots (32)$$

In the cross section expressions of Eqs (30) – (32), α is the angle in the hyperspherical (k_1, k_2) plane, β is the angle in the hyperspherical $\left(\sqrt{k_1^2+k_2^2}, k_3\right)$ plane, k_1, k_2, and k_3 are the final linear momentum, and δ_{l_1}, δ_{l_2}, and δ_{l_3} are scattering phase shifts. The momentum space projection wavefunction for each $\mathcal{L}S$ symmetry and $l_1 l_2 Ll_3$ coupled channel is given by:

$$P_{l_1 l_2 Ll_3}^{S\mathcal{L}S}\left(k_1, k_2, k_3\right)$$

$$= \sum_{L', S'} \sum_{ijk}^6 Q_{l_1 l_2 LSl_3 \, L'S'}^{\mathcal{L}S}\left(ijk\right) \int_0^\infty dr_1 \int_0^\infty dr_2$$

$$\times \int_0^\infty dr_3 P_{k_1 l_1}\left(r_1\right) P_{k_2 l_2}\left(r_2\right) P_{k_3 l_3}\left(r_3\right)$$

$$\times P_{l_1 l_2 L l_3}^{SLS}\left(r_1, r_2, r_3, t \to \infty\right), \qquad \dots (33)$$

$P_{kl}(r)$ is a box normalized continuum radial orbital calculated in the potential of Eq. (17) for He^{2+}.

4. TIME-DEPENDENT CLOSE-COUPLING 4D METHOD

The time-dependent Schrodinger equation for electron scattering from a homonuclear diatomic molecule with one active electron is given by:

$$i \frac{\partial \psi\left(\vec{r}_1, \vec{r}_2, t\right)}{\partial t} = H\left(\vec{r}_1, \vec{r}_2\right) \psi\left(\vec{r}_1, \vec{r}_2, t\right), \qquad \dots (34)$$

where the non-relativistic Hamiltonian is given by:

$$H\left(\vec{r}_1, \vec{r}_2\right) = -\frac{1}{2}\nabla_1^2 + V\left(r_1, \theta_1\right) - \frac{1}{2}\nabla_2^2$$
$$+ V\left(r_2, \theta_2\right) + \frac{1}{|\vec{r}_1 - \vec{r}_2|}. \qquad \dots (35)$$

For the hydrogen molecular ion:

$$V(r, \theta) = -\frac{1}{\sqrt{r^2 + \frac{1}{4}R^2 - rR\cos\theta}}$$
$$-\frac{1}{\sqrt{r^2 + \frac{1}{4}R^2 + rR\cos\theta}}, \qquad \dots (36)$$

while for the hydrogen molecule:

$$V(r, \theta) = -\frac{1}{\sqrt{r^2 + \frac{1}{4}R^2 - rR\cos\theta}}$$
$$-\frac{1}{\sqrt{r^2 + \frac{1}{4}R^2 + rR\cos\theta}} + V_H(r, \theta)$$
$$-a\left(\frac{24\rho(r, \theta)}{\pi}\right)^{\frac{1}{3}}, \qquad \dots (37)$$

where R is the internuclear distance, $V_H(r, \theta)$ is the direct Hartree potential, a is an adjustable parameter,

and $\rho(r, \theta)$ is the probability density of the core electron.

The total six-dimensional electronic wavefunction is expanded in simple products of rotational functions for each MS total projection onto the internuclear axis and spin angular momentum symmetry:

$$\Psi\left(\vec{r}_1, \vec{r}_2, t\right) = \sum_{m_1, m_2} \frac{P_{m_1 m_2}^{l_0 MS}\left(r_1, \theta_1, r_2, \theta_2, t\right)}{r_1 \sqrt{\sin\theta_1}\, r_2 \sqrt{\sin\theta_2}}$$
$$\times \Phi_{m_1}\left(\phi_1\right)\Phi_{m_2}\left(\phi_2\right), \qquad \dots (38)$$

where

$$\Phi_m\left(\phi\right) = \frac{e^{im\phi}}{\sqrt{2\pi}}, \qquad \dots (39)$$

and $M = m_1 + m_2$. Upon substitution of $\psi\left(\vec{r}_1, \vec{r}_2, t\right)$ of Eq. (38) into the time-dependent Schrodinger equation and projection onto the simple products of rotational functions, we obtain the time-dependent close-coupled partial differential equations for each *MS* symmetry:

$$i\frac{\partial P_{m_1 m_2}^{l_0 MS}\left(r_1, \theta_1, r_2, \theta_2, t\right)}{\partial t}$$
$$= T_{m_1 m_2}\left(r_1, \theta_1, r_2, \theta_2\right) P_{m_1 m_2}^{l_0 MS}\left(r_1, \theta_1, r_2, \theta_2, t\right)$$
$$+ \sum_{m_1', m_2'} W_{m_1 m_2, m_1' m_2'}^{M}\left(r_1, \theta_1, r_2, \theta_2\right)$$
$$\times P_{m_1' m_2'}^{l_0 MS}\left(r_1, \theta_1, r_2, \theta_2, t\right), \qquad \dots (40)$$

where

$$T_{m_1 m_2}\left(r_1, \theta_1, r_2, \theta_2\right)$$
$$= \sum_i^2 \left(K\left(r_i\right) + \bar{K}\left(r_i, \theta_i\right) + \frac{m_i^2}{2r_i^2 \sin^2\theta_i} + V\left(r_i, \theta_i\right)\right), \qquad \dots (41)$$

and $K(r)$, $\bar{K}(r, \theta)$ are kinetic energy operators. The coupling operator is given by:

$$W_{m_1 m_2, m_1' m_2'}^{M}\left(r_1, \theta_1, r_2, \theta_2\right)$$
$$= \sum_\lambda \frac{\left(r_1, r_2\right)_<^\lambda}{\left(r_1, r_2\right)_>^{\lambda+1}} \sum_q \frac{\left(\lambda - |q|\right)!}{\left(\lambda + |q|\right)!} P_\lambda^{|q|}\left(\cos\theta_1\right)$$
$$\times P_\lambda^{|q|}\left(\cos\theta_2\right) \times \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \Phi_{m_1}\left(\phi_1\right)$$

$$\times \Phi_{m_2}(\phi_2)\, e^{iq(\phi_2 - \phi_1)}\, \Phi_{m_1'}(\phi_1)\Phi_{m_2'}(\phi_2), \quad ... (42)$$

where $P_\lambda^{|q|}(\cos\theta)$ is an associated Legendre function.

An initial condition for the solution of the time-dependent close-coupling equations for electron scattering from a homonuclear diatomic molecule with one active electron is given by:

$$P_{m_1 m_2}^{l_0 MS}(r_1, \theta_1, r_2, \theta_2, t = 0)$$

$$= \sqrt{\frac{1}{2}}\Big[P_{1s0}(r_1, \theta_1)\, F_{k_0 l_0 M}(r_2, \theta_2)\, \delta_{m_1, 0}$$

$$\times \delta_{m_2, M} + (-1)^S\, F_{k_0 l_0 M}(r_1, \theta_1)$$

$$\times P_{1s0}(r_2, \theta_2)\, \delta_{m_1, M}\delta_{m_2, 0}\Big] \qquad ... (43)$$

where $P_{1s0}(r, \theta)$ is a bound orbital for the ground state of the H_2^+ or H_2 molecules.

Following time evolution of the time-dependent close-coupled partial differential equations into the asymptotic region for each MS symmetry, the total cross section is given by:

$$\sigma = \frac{\pi}{4k_0^2}\int_0^\infty dk_1 \int_0^\infty dk_2 \sum_{l_0, M, S}(2S+1)$$

$$\times \sum_{l_1, m_1}\sum_{l_2, m_2}\left|P_{l_1 m_1 l_2 m_2}^{l_0 M S}(k_1, k_2)\right|^2, \qquad ... (44)$$

the energy differential cross section is given by:

$$\frac{d\sigma}{d\alpha} = \frac{\pi}{4k_0^2}\int_0^\infty dk_1 \int_0^\infty dk_2\, \delta\left(\alpha - \tan^{-1}(k_2/k_1)\right)$$

$$\times \sum_{l_0, M, S}(2S+1)\sum_{l_1, m_1}\sum_{l_2, m_2}\left|P_{l_1 m_1 l_2 m_2}^{l_0 MS}(k_1, k_2)\right|^2,$$

$$... (45)$$

and the energy and angle differential cross section is given by:

$$\frac{d\sigma}{d\alpha d\Omega_1 d\Omega_2} = \frac{\pi}{4k_0^2}\int_0^\infty dk_1 \int_0^\infty dk_2\, \delta\left(\alpha - \tan^{-1}(k_2/k_1)\right)$$

$$\times \sum_S (2S+1)\times\left|\sum_{l_0, M}i^{l_0}Y_{l_0 M}^*(\theta_k, \phi_k)\right.$$

$$\times \sum_{l_1, m_1}\sum_{l_2, m_2}(-i)^{l_1 + l_2}\, e^{i(\delta_{l_1} + \delta_{l_2})}\times P_{l_1 m_1 l_2 m_2}^{l_0 MS}(k_1, k_2)$$

$$\times Y_{l_1 m_1}(\hat{k}_1)\, Y_{l_2 m_2}(\hat{k}_2)\, \delta_{m_1 + m_2, M}\Bigg|^2. \quad ... (46)$$

α is the angle in the hyperspherical (k_1, k_2) plane, k_1 and k_2 are the final linear momentum, θ_k and ϕ_k are angles the incoming electron makes with the internuclear (z) axis, and δ_{l_1} and δ_{l_2} are scattering phase shifts. The momentum space projection wavefunction for each MS symmetry and $m_1 m_2$ coupled channel is given by:

$$P_{l_1 m_1 l_2 m_2}^{l_0 M S}(k_1, k_2) = \int_0^\infty dr_1 \int_0^\pi d\theta_1 \int_0^\infty dr_2 \int_0^\pi d\theta_2 P_{k_1 l_1 m_1}^*(r_1, \theta_1)$$

$$\times P_{k_2 l_2 m_2}^*(r_2, \theta_2)$$

$$\times P_{m_1 m_2}^{l_0 MS}(r_1, \theta_1, r_2, \theta_2, t \to \infty), \quad ... (47)$$

where $P_{klm}(r, \theta)$ is a box normalized continuum orbital calculated in the potentials of Eq. (36) for H_2^{2+} or Eq. (37) for H_2^+.

5. SELECTED RESULTS

The TDCC-2D method was first applied to the electron-impact single ionization of the hydrogen atom. The total cross section calculated [11] using Eq. (11) is compared with experiment [12] in Fig. 1. Previous converged close-coupling calculations [13] had also achieved excellent agreement with experiment.
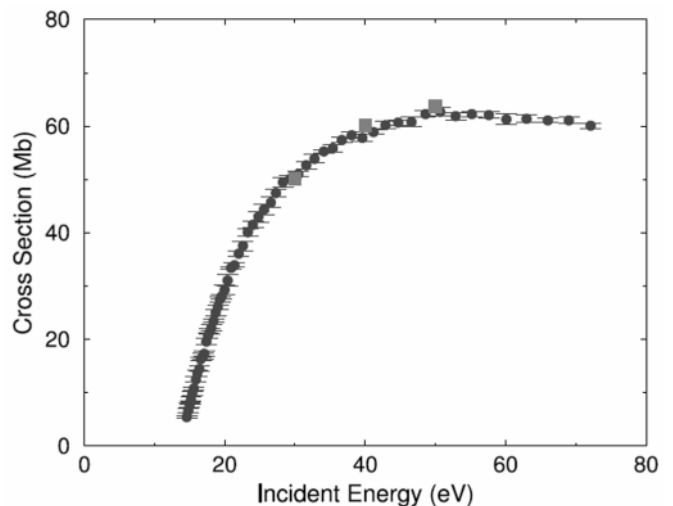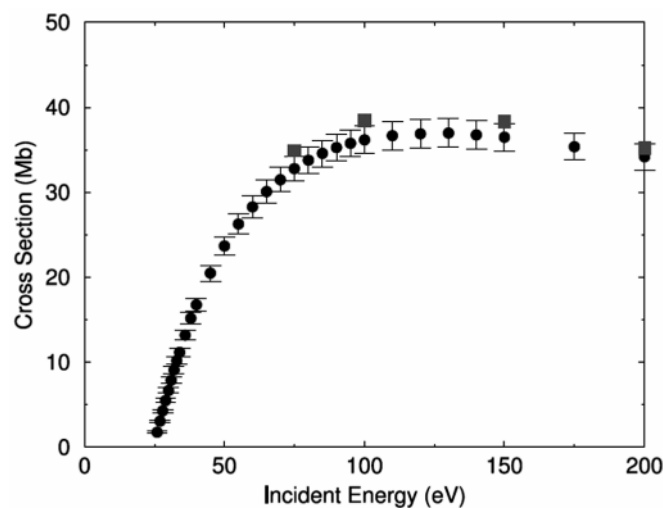

Fig. 1: Total electron-impact single ionization cross section for hydrogen, square boxes: TDCC-2D calculations [11], solid circles: experiment [12] (1.0 Mb = 1.0×10^{-18} cm^2)

The TDCC-2D method was then applied to the electron-impact single ionization of the helium atom. The

total cross section calculated [14] using Eq. (11) is compared with experiment [15] in Fig. 2. Previous . . . . *R*-matrix with pseudo-states [17] calculations had also achieved excellent agreement with experiment.

The energy and differential cross section calculated [4] using Eq. (13) is compared with experiment [18] in Fig. 3. The differential cross section is at an incident energy of $E_0 = 44.6$ eV, equal energy sharing with $E_1 = E_2 = 10.0$ eV, co-planar with $\phi_1 = \phi_2 = 0°$, and with $\theta_1 = 147°$ Good agreement is found between theory and experiment.

The TDCC-3D method was first applied to the electron-impact double ionization of the helium atom. The total cross section calculated [19, 20] using Eq. (30) is compared with experiment [21] in Fig. 4. Excellent agreement is found between theory and experiment.

Fig. 2: Total electron-impact single ionization cross section for helium. Square boxes: TDCC-2D calculations [14], solid circles: experiment [15] (1.0 Mb = 1.0×10^{-18} cm^2)

The energy and differential cross section calculated [8] using Eq. (32) is compared with experiment [22] in Fig. 5. The differential cross section is at an incident energy of $E_0 = 109$ eV, equal energy sharing with $E_1 = E_2 = E_3 = 9.0$ eV, co-planar with $\phi_1 = \phi_2 = \phi_3 = 0°$, and with $\theta_1 = 45°$ and $\theta_2 = 315°$. Good relative agreement is found between theory and experiment, although the measurement magnitudes have been divided by a factor of 25.

The TDCC-4D method was first applied to the . . . . $^+_2$. The total cross section calculated [23] using Eq. (44) is compared with experiment [24] in Fig. 6. Excellent agreement is found between theory and experiment.
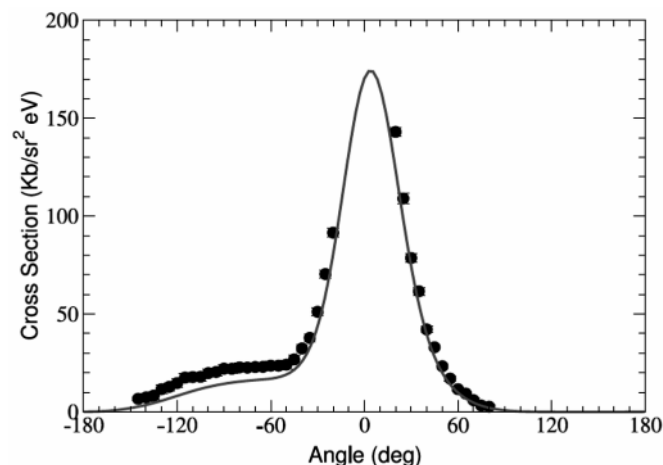

Fig. 3: Energy and angle differential electron-impact single ionization cross section for helium. Solid line: TDCC-2D calculations [4], solid circles: Experiment [18] (1.0 Kb = 1.0×10^{-21} cm^2).
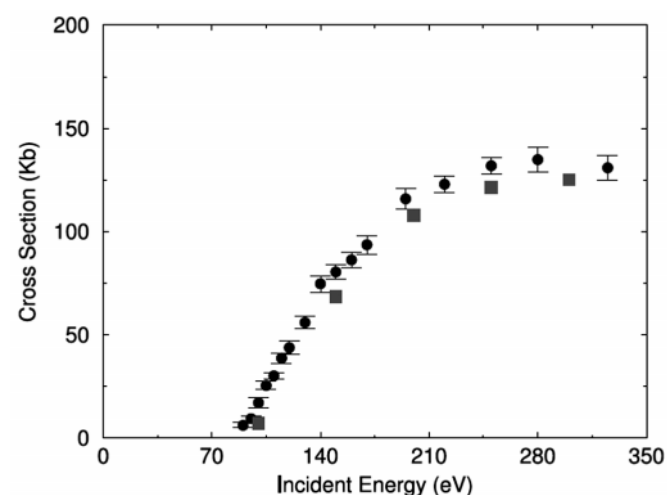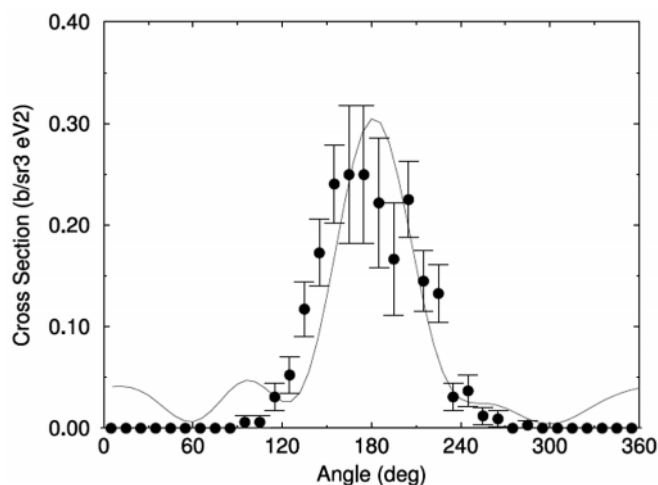

Fig. 4: Total electron-impact double ionization cross section for helium. Square boxes: TDCC-3D calculations [20], solid circles: Experiment [21] (1.0 Kb = 1.0×10^{-21} cm^2)

The TDCC-4D method was then applied to the electron-impact single ionization of H$_2$. The total cross section calculated [25] using Eq. (44) is compared with experiment [26] in Fig. 7. Previous *R*-matrix with pseudo-states [27] calculations had also achieved excellent agreement with experiment near the ionization threshold.

The energy and angle differential cross section calculated [9] using Eq. (46) is compared with experiment [9] in Fig. 8. The differential cross section is at an incident energy of $E_0 = 35.4$ eV, equal energy sharing with $E_1 = E_2 = 10.0$ eV, co-perpendicular with $\theta_1 = \theta_2 = 90°$, and with $\phi_1 = -\phi_2 = \xi$. Good relative agreement is found between theory and experiment, where experiment is normalized to theory at $\xi = 90°$ and theory is averaged over all molecular orientations.

Fig. 5: Energy and angle differential electron-impact double ionization cross section for helium. Solid line: TDCC-3D calculations [8], solid circles: Experiment [22] (1.0 b = 1.0×10^{-24} cm^2)
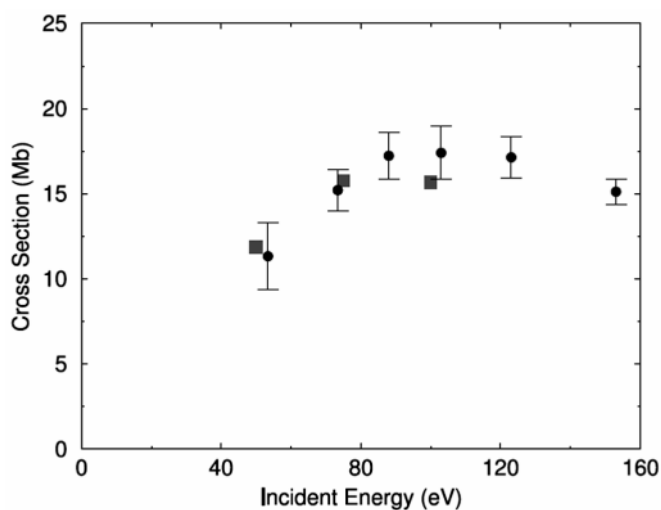

Fig. 6: Total electron-impact single ionization cross section for H_2^+. Square boxes: TDCC-4D calculations [23], solid circles: Experiment [24] (1.0 Mb = 1.0×10^{-18} cm^2)
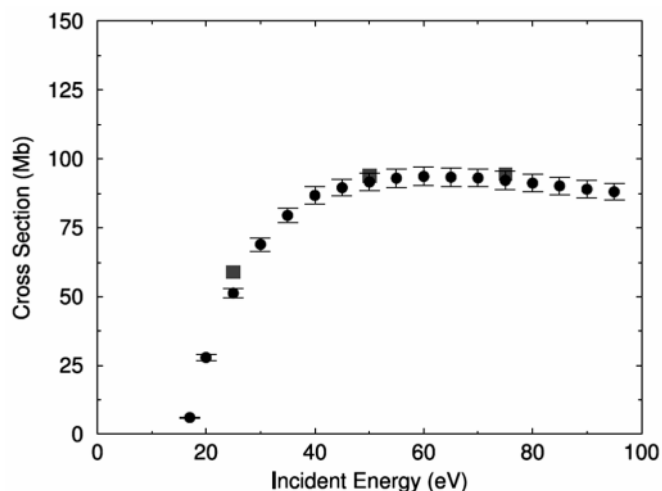

Fig. 7: Total electron-impact single ionization cross section for H_2. Square boxes: TDCC-4D calculations [25], solid circles: experiment [26] (1.0 Mb = 1.0×10^{-18} cm^2)
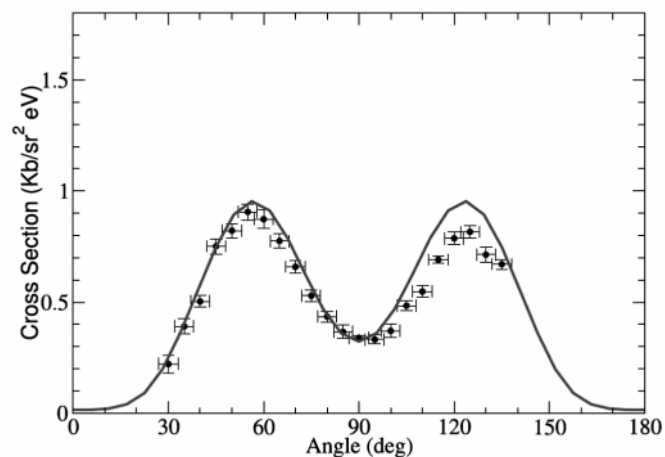

Fig. 8: Energy and angle differential electron-impact single ionization cross section for H_2. Solid line: TDCC-4D calculations [9], solid circles: Experiment [9] (1.0 Kb = 1.0×10^{-21} cm^2).

6. SUMMARY

The time-dependent close-coupling method has been successfully applied to calculate electron-impact differential ionization cross sections for atoms and molecules. In this paper we reviewed the formulation of the TDCC-2D method for the single ionization of atoms, the TDCC-3D method for the double ionization of atoms, and the TDCC-4D method for the single ionization of diatomic molecules. Each TDCC method goes beyond perturbation theory to achieve an exact numerical description of a scattered electron moving in the field of one or two ejected electrons and the field of the ionized core of the atom or molecule. Few-body quantal effects

are strongest for certain energy and angle differential cross sections, as for example, when the scattered and ejected electrons move off with the same energy and close to the same angular direction. In the future, we plan to apply the TDCC methods to calculate differential cross sections for the electron-impact single ionization of several different alkali atoms, the electron-impact double ionization of Be, and the electron-impact single ionization of Li_2^+ and Li_2.

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