

Time-Dependent Close-Coupling Calculations using a Core-Orthogonalization Method for the Electron-Impact Ionization of Atoms and Molecules

M. S. PINDZOLA¹, J. A. LUDLOW¹, F. ROBICHEAUX¹ AND J. COLGAN²

¹Department of Physics, Auburn University, Auburn, AL

²Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM

ABSTRACT: A core-orthogonalization method is developed so that time-dependent close-coupling calculations can be carried out for the electron-impact ionization of many-electron atoms and molecules. Calculations using both the pseudopotential and core-orthogonalization methods are found to be in reasonable agreement for the electron-impact ionization of the Li atom. Calculations using the core-orthogonalization method are also carried out for the electron-impact ionization of the Li₂ diatomic molecule. The time-dependent close-coupling calculations are found to be lower at the Li₂ cross section peak than distorted-wave calculations.

I. INTRODUCTION

Studies of the electron-impact ionization of diatomic molecules at low incident energies probe the quantal dynamics of two continuum electrons moving in the non-spherical Coulomb field of the molecular core. To date, non-perturbative theoretical methods which treat correlation effects for the two slow moving continuum electrons have been limited to the ionization of H₂⁺ and H₂. The R-matrix with pseudostates method has produced total cross sections for the electron-impact ionization of H₂ [1] that are in good agreement with H₂ experiments [2, 3] in the near threshold region. The time-dependent close-coupling method has produced total cross sections for the electron-impact ionization of H₂⁺ [4] and H₂ [5] that are in good agreement with H₂⁺ experiments [6] and H₂ experiments [2, 3] over a wide energy range. More recently [7, 8], the time-dependent close-coupling method has been used to calculate energy and angle differential cross sections for the electron-impact ionization of H₂ and compared with three-body distorted-wave calculations and experiment.

To make time-dependent close-coupling calculations for the electron-impact ionization of diatomic molecules beyond H₂⁺ and H₂, we need a method that prevents excitation of filled subshells during the time evolution of the close-coupled equations. For the electron-impact ionization of atoms beyond H and He, we developed a pseudopotential method and used it to make successful time-dependent close-coupling calculations for the electron-impact ionization of the 2s subshell of Be⁺(1s²2s) [9]. Since then the pseudopotential method has made possible time-dependent close-coupling calculations of electron-impact single and double ionization cross sections for a wide variety of neutral atoms and atomic ions [10].

In this article we develop a core-orthogonalization method for time-dependent close-coupling calculations of the electron-impact ionization of atoms and molecules. Our first application is to the electron-impact ionization of the 2s subshell of Li(1s²2s), where we compare with previous pseudopotential method results [11, 12]. Our second application is to the electron-impact ionization of the 2sσ subshell of Li₂(1sσ²2pσ²2sσ²). To check the time-dependent close-coupling results for Li₂, we adapt a previously developed configuration-average distorted-wave method [13] to make calculations using the same ionized subshell orbital and core scattering potential as used in the time-dependent close-coupling calculations.

The rest of the article is organized as follows: formulation of the core-orthogonalization time-dependent close-coupling method for atoms is given in Section IIA, formulation of the core-orthogonalization time-dependent close-coupling method for molecules is given in Section IIB, electron-impact ionization cross sections for Li are presented in Section IIIA, electron-impact ionization cross sections for Li_2 are presented in Section IIIB, and a brief summary is given in Section IV. Unless otherwise stated, all quantities are given in atomic units.

II. THEORY

(A) Time-Dependent Close-Coupling Method for Atoms

The Hamiltonian for electron scattering from an atom with one active electron is given

$$H(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^2 \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + V_{HX}(r_i) \right) + \frac{1}{|\vec{r}_1 - \vec{r}_2|}, \quad (1)$$

where Z is the atomic number and $V_{HX}(r)$ is a Hartree with local exchange potential. The total wavefunction is expanded in coupled spherical harmonics for each LS total symmetry:

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \sum_{l_1, l_2} \frac{P_{l_1 l_2}^{LS}(r_1, r_2, t)}{r_1 r_2} \sum_{m_1, m_2} C_{m_1 m_2 0}^{l_1 l_2 L} Y_{l_1 m_1}(\hat{r}_1) Y_{l_2 m_2}(\hat{r}_2), \quad (2)$$

where $C_{m_1 m_2 m_3}^{l_1 l_2 l_3}$ is a Clebsch-Gordan coefficient and $Y_{lm}(\hat{r})$ is a spherical harmonic. Upon substitution into the time-dependent Schrodinger equation, we obtain the following set of time-dependent close-coupled equations [10]:

$$i \frac{\partial P_{l_1 l_2}^{LS}(r_1, r_2, t)}{\partial t} = T_{l_1 l_2}(r_1, r_2) P_{l_1 l_2}^{LS}(r_1, r_2, t) + \sum_{l'_1, l'_2} V_{l_1 l_2, l'_1 l'_2}^L(r_1, r_2) P_{l'_1 l'_2}^{LS}(r_1, r_2, t) \quad (3)$$

The total one-body operator is given by:

$$T_{l_1 l_2}(r_1, r_2) = \sum_{i=1}^2 \left(-\frac{1}{2} \frac{\partial^2}{\partial r_i^2} + \frac{l_i(l_i+1)}{2r_i^2} - \frac{Z}{r_i} + V_{HX}(r_i) \right) \quad (4)$$

and the two-body operator is given by:

$$V_{l_1 l_2, l'_1 l'_2}^L(r_1, r_2) = (-1)^{L+l_2+l'_2} \sqrt{(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)} \\ \times \sum_{\lambda} \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \begin{pmatrix} l_1 & \lambda & l'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & \lambda & l'_2 \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} L & l'_2 & l'_1 \\ \lambda & l_1 & l_2 \end{matrix} \right\} \quad (5)$$

where $r_{<} = \min(r_1, r_2)$, $r_{>} = \max(r_1, r_2)$, and standard $3j$ and $6j$ symbols are used.

The initial condition for the solution of the time-dependent close-coupling equations is given by:

$$P_{l_1 l_2}^{LS}(r_1, r_2, t=0) = P_{nl}(r_1) G_{k_0 l'}(r_2) \delta_{l_1, l} \delta_{l_2, l'} \quad (6)$$

where $P_{nl}(r)$ is a bound radial orbital and the Gaussian radial wavepacket, $G_{k_0 l'}(r)$, has a incident energy of $\frac{k_0^2}{2}$. The bound radial orbitals are obtained by diagonalization of the Hamiltonian:

$$H(r) = -\frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_{HX}(r). \quad (7)$$

A Hartree-Fock atomic structure code [14] is used to calculate the bound radial orbitals of the next higher ion stage needed to construct the $V_{HX}(r)$ potential.

In the past, to prevent collapse of the radial wavefunctions, $P_{l_1 l_2}^{LS}(r_1, r_2, t)$, into closed inner subshells during time propagation of the close-coupled equations, we have replaced the Hartree with local exchange potential, $V_{HX}(r)$, with a pseudopotential, $V_{pp}(r)$ [9]. For example, for electron-impact ionization of the $2s$ subshell of $Li(1s^2 2s)$, a pseudopotential is needed for $l = 0$ to prevent collapse into the $1s$ core orbitals.

Alternatively, the radial wavefunctions, $P_{l_1 l_2}^{LS}(r_1, r_2, t)$, may be orthogonalized to the core orbitals at each time step. For example, for electron-impact ionization of the $2s$ subshell of $Li(1s^2 2s)$, the $P_{00}^{1S}(r_1, r_2, t)$ radial wavefunction is orthogonalized at each time step according to:

$$\begin{aligned} \bar{P}_{00}^{1S}(r_1, r_2, t) &= P_{00}^{1S}(r_1, r_2, t) \\ &\quad - P_{1s}(r_1) \int dr'_1 P_{1s}(r'_1) P_{00}^{1S}(r'_1, r_2, t) \\ &\quad - P_{1s}(r_2) \int dr'_2 P_{1s}(r'_2) P_{00}^{1S}(r_1, r'_2, t) \\ &\quad + P_{1s}(r_1) P_{1s}(r_2) \int dr'_1 \int dr'_2 P_{1s}(r'_1) P_{1s}(r'_2) P_{00}^{1S}(r'_1, r'_2, t). \end{aligned} \quad (8)$$

On the other hand, the $P_{01}^{1P}(r_1, r_2, t)$ radial wavefunction is orthogonalized at each time step according to:

$$\begin{aligned} \bar{P}_{01}^{1P}(r_1, r_2, t) &= P_{01}^{1P}(r_1, r_2, t) \\ &\quad - P_{1s}(r_1) \int dr'_1 P_{1s}(r'_1) P_{01}^{1P}(r'_1, r_2, t). \end{aligned} \quad (9)$$

We note that $P_{l_1 l_2}^{LS}(r_1, r_2, t)$ radial wavefunctions with $l_1 \neq 0$ and $l_2 \neq 0$ do not need to be orthogonalized.

Probabilities for the electron-impact excitation and ionization processes are obtained by time propagating the close-coupled equations and then projecting the $P_{l_1 l_2}^{LS}(r_1, r_2, t \rightarrow \infty)$ radial wavefunctions onto fully antisymmetric spatial and spin wavefunctions constructed from bound, $P_{nl}(r)$, and continuum, $P_{kl}(r)$, radial orbitals. The probabilities are then used to obtain total, energy differential, and energy and angle differential cross sections as a function of incident electron energy [10].

(B) Time-Dependent Close-Coupling Method for Molecules

The Hamiltonian for electron scattering from a homonuclear diatomic molecule with one active electron is given by:

$$H(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^2 \left(-\frac{1}{2} \nabla_i^2 - \sum_{\pm} \frac{Z}{\sqrt{r_i^2 + \frac{1}{2} R^2 \pm r_i R \cos \theta_i}} + V_{HX}(r_i, \theta_i) \right) + \frac{1}{|\vec{r}_1 - \vec{r}_2|}, \quad (10)$$

where Z is the charge on each nucleus, R is the internuclear distance, and $V_{HX}(r, \theta)$ is a Hartree with local exchange potential. The total wavefunction is expanded in rotational functions for each MS total symmetry:

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \sum_{m_1, m_2} \frac{P_{m_1 m_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t)}{r_1 r_2 \sqrt{\sin \theta_1} \sqrt{\sin \theta_2}} \Phi_{m_1}(\phi_1) \Phi_{m_2}(\phi_2), \quad (11)$$

where $\Phi(\phi) = \frac{e^{im\phi}}{\sqrt{2\pi}}$ and $M = m_1 + m_2$. Upon substitution into the time-dependent Schrodinger equation, we obtain the following set of time-dependent close-coupled equations [10]:

$$i \frac{\partial P_{l_1 l_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t)}{\partial t} = T_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2) P_{m_1 m_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t) + \sum_{m'_1, m'_2} V_{m_1 m_2, m'_1 m'_2}^M(r_1, \theta_1, r_2, \theta_2) P_{m'_1 m'_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t) \quad (12)$$

The total one-body operator is given by:

$$T_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2) = \sum_{i=1}^2 \left(K(r_i) + \bar{K}(r_i, \theta_i) + \frac{m_i^2}{2r_i^2 \sin^2 \theta_i} \right) + \sum_{i=1}^2 \left(- \sum_{\pm} \frac{Z}{\sqrt{r_i^2 + \frac{1}{4}R^2 \pm r_i R \cos \theta_i}} + V_{HX}(r_i, \theta_i) \right) \quad (13)$$

where $K(r)$ and $\bar{K}(r, \theta)$ are kinetic energy operations. The two-body operator is given by:

$$V_{m_1 m_2, m'_1 m'_2}^M(r_1, \theta_1, r_2, \theta_2) = \sum_{\lambda} \frac{(r_1, r_2)_{<}^{\lambda}}{(r_1, r_2)_{>}^{\lambda+1}} \sum_q \frac{(\lambda - |q|)!}{(\lambda + |q|)!} P_{\lambda}^{|q|}(\cos \theta_1) P_{\lambda}^{|q|}(\cos \theta_2) \times \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \Phi_{m_1}(\phi_1) \Phi_{m_2}(\phi_2) e^{iq(\phi_2 - \phi_1)} \Phi_{m'_1}(\phi_1) \Phi_{m'_2}(\phi_2), \quad (14)$$

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

The initial condition for the solution of the time-dependent close-coupling equations is given by:

$$P_{m_1 m_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t=0) = P_{nlm}(r_1, \theta_1) G_{k_0 l_0 m'}(r_2, \theta_2) \delta_{m_1, m} \delta_{m_2, m'}, \quad (15)$$

where $P_{nlm}(r, \theta)$ is a bound radial and angular orbital and $G_{k_0 l_0 m'}(r, \theta)$ is a Gaussian radial and angular wavepacket with incident energy $\frac{k_0^2}{2}$ and incident angular momentum l_0 . The bound radial and angular orbitals are obtained by diagonalization of the Hamiltonian:

$$H(r, \theta) = K(r) + \bar{K}(r, \theta) + \frac{m^2}{2r^2 \sin^2 \theta} - \sum_{\pm} \frac{Z}{\sqrt{r^2 + \frac{1}{4}R^2 \pm rR \cos \theta}} + V_{HX}(r, \theta). \quad (16)$$

A self-consistent field molecular structure code [15, 16] is used to calculate the bound radial and angular orbitals of the next higher ion stage needed to construct the $V_{HX}(r, \theta)$ potential.

To prevent collapse of the radial and angular wavefunctions, $P_{m_1 m_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t)$, into closed inner subshells during time propagation of the close-coupled equations, we use the core-orthogonalization method. For example, for electron-impact ionization of the $2s\sigma$ subshell of $Li_2(1s\sigma^2 2p\sigma^2 2s\sigma^2)$, the $P_{00}^{1\Sigma}(r_1, \theta_1, r_2, \theta_2, t)$ radial and angular wavefunction is orthogonalized at each time step according to:

$$\begin{aligned}
 \bar{P}_{00}^{1\Sigma}(r_1, \theta_1, r_2, \theta_2, t) = & P_{00}^{1\Sigma}(r_1, \theta_1, r_2, \theta_2, t) \\
 & - P_{1s\sigma}(r_1, \theta_1) \int dr'_1 \int d\theta'_1 P_{1s\sigma}(r'_1, \theta'_1) P_{00}^{1\Sigma}(r'_1, \theta'_1, r_2, \theta_2, t) \\
 & - P_{2p\sigma}(r_1, \theta_1) \int dr'_1 \int d\theta'_1 P_{2p\sigma}(r'_1, \theta'_1) P_{00}^{1\Sigma}(r'_1, \theta'_1, r_2, \theta_2, t) \\
 & - P_{1s\sigma}(r_2, \theta_2) \int dr'_2 \int d\theta'_2 P_{1s\sigma}(r'_2, \theta'_2) P_{00}^{1\Sigma}(r_1, \theta_1, r'_2, \theta'_2, t) \\
 & - P_{2p\sigma}(r_2, \theta_2) \int dr'_2 \int d\theta'_2 P_{2p\sigma}(r'_2, \theta'_2) P_{00}^{1\Sigma}(r_1, \theta_1, r'_2, \theta'_2, t) \\
 & + P_{1s\sigma}(r_1, \theta_1) P_{1s\sigma}(r_2, \theta_2) \\
 & \times \int dr'_1 \int d\theta'_1 \int dr'_2 \int d\theta'_2 P_{1s\sigma}(r'_1, \theta'_1) P_{1s\sigma}(r'_2, \theta'_2) P_{00}^{1\Sigma}(r'_1, \theta'_1, r'_2, \theta'_2, t) \\
 & + P_{1s\sigma}(r_1, \theta_1) P_{2p\sigma}(r_2, \theta_2) \\
 & \times \int dr'_1 \int d\theta'_1 \int dr'_2 \int d\theta'_2 P_{1s\sigma}(r'_1, \theta'_1) P_{2p\sigma}(r'_2, \theta'_2) P_{00}^{1\Sigma}(r'_1, \theta'_1, r'_2, \theta'_2, t) \\
 & + P_{2p\sigma}(r_1, \theta_1) P_{2p\sigma}(r_2, \theta_2) \\
 & \times \int dr'_1 \int d\theta'_1 \int dr'_2 \int d\theta'_2 P_{2p\sigma}(r'_1, \theta'_1) P_{1s\sigma}(r'_2, \theta'_2) P_{00}^{1\Sigma}(r'_1, \theta'_1, r'_2, \theta'_2, t) \\
 & + \int P_{2p\sigma}(r_1, \theta_1) P_{1s\sigma}(r_2, \theta_2) \\
 & \times \int dr'_1 \int d\theta'_1 \int dr'_2 \int d\theta'_2 P_{2p\sigma}(r'_1, \theta'_1) P_{1s\sigma}(r'_2, \theta'_2) P_{00}^{1\Sigma}(r'_1, \theta'_1, r'_2, \theta'_2, t)
 \end{aligned} \tag{17}$$

On the other hand, the $P_{01}^{1\Pi}(r_1, \theta_1, r_2, \theta_2, t)$ radial and angular wavefunction is orthogonalized at each time step according to:

$$\begin{aligned}
 \bar{P}_{01}^{1\Pi}(r_1, \theta_1, r_2, \theta_2, t) = & P_{01}^{1\Pi}(r_1, \theta_1, r_2, \theta_2, t) \\
 & - P_{1s\sigma}(r_1, \theta_1) \int dr'_1 \int d\theta'_1 P_{1s\sigma}(r'_1, \theta'_1) P_{01}^{1\Pi}(r'_1, \theta'_1, r_2, \theta_2, t) \\
 & - P_{2p\sigma}(r_1, \theta_1) \int dr'_1 \int d\theta'_1 P_{2p\sigma}(r'_1, \theta'_1) P_{01}^{1\Pi}(r'_1, \theta'_1, r_2, \theta_2, t).
 \end{aligned} \tag{18}$$

We note that $P_{m_1 m_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t)$ radial and angular wavefunctions with $m_1 \neq 0$ and $m_2 \neq 0$ do not need to be orthogonalized.

Probabilities for the electron-impact excitation and ionization processes are obtained by time propagating the close-coupled equations and then projecting the $P_{m_1 m_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t \rightarrow \infty)$ radial and angular wavefunctions onto fully antisymmetric spatial and spin wavefunctions constructed from bound, $P_{nlm}(r, \theta)$, and continuum, $P_{klm}(r, \theta)$, radial and angular orbitals. The probabilities are then used to obtain total, energy differential, and energy and angle differential cross sections as a function of incident electron energy and internuclear distance [10].

III. RESULTS

(A) Electron-Impact Ionization of Li

Time-dependent close-coupling (TDCC) calculations, using the core-orthogonalization method outlined in Section IIA, were carried out for the electron-impact ionization of the $2s$ subshell of $\text{Li}(1s^2 2s)$ at an incident energy of 15.0 eV. The Hartree with local exchange potential is given by:

$$V_{HX}(r) = \int \frac{dr'}{r'_>} 2P_{1s}^2(r') - \frac{\alpha_l}{2} \left(\frac{24\rho(r)}{\pi} \right)^{\frac{1}{3}}, \quad (19)$$

where

$$\rho(r) = \frac{2P_{1s}^2(r)}{4\pi r^2} \quad (20)$$

and the $P_{1s}(r)$ bound radial orbital is found from an atomic structure calculation [14] for $\text{Li}^+(1s^2)$. Diagonalization of the $l = 0$ Hamiltonian of Eq. (7) with $\alpha_0 = 0.58$, on a 512 point radial mesh with a mesh spacing of $\Delta r = 0.10$, yields an ionization potential for the $2s$ subshell of $\text{Li}(1s^2 2s)$ of 5.39 eV, in agreement with experimental results [17]. Diagonalization of the $l = 1$ Hamiltonian of Eq. (7) with $\alpha_1 = 0.22$ yields an ionization potential for the $2p$ subshell of $\text{Li}(1s^2 2p)$ of 3.54 eV, again in agreement with experimental results [17]. For $l \geq 2$ the Hamiltonian of Eq.(7) is diagonalized with $\alpha_l = 0.0$.

Partial cross section results obtained by propagating the $P_{l_1 l_2}^{LS}(r_1, r_2, t)$ radial wavefunctions using Eq. (3), on a $(512)^2$ point numerical lattice with $\Delta r_1 = \Delta r_2 = 0.10$, are presented in column 3 of Table I. The number of $l_1 l_2$ coupled channels ranged from 4 for $L = 0$ to 20 for $L = 5$.

The TDCC results using the core-orthogonalization method are found to be in reasonable agreement with previous TDCC results using the pseudopotential method [12], as presented in column 4 of Table I. Using an LS distorted-wave method [12] for $L = 6$ to $L = 50$ we “topped up” both TDCC calculations. The TDCC orthogonalization total cross section is 322 Mb, while the TDCC pseudopotential total cross section is 337 Mb. We note that the previous TDCC pseudopotential calculations [12] used a 300 point radial mesh with $\Delta r = 0.30$.

(B) Electron-Impact Ionization of Li_2

Time-dependent close-coupling calculations, using the core-orthogonalization method outlined in Section IIB, were carried out for the electron-impact ionization of the $2s\sigma$ subshell of $\text{Li}_2(1s\sigma^2 2p\sigma^2 2s\sigma^2)$ at an incident energy of 10.0 eV. The Hartree with local exchange potential is given by:

$$V_{HX}(r, \theta) = \sum_{k=0,2,4} \int dr' \int d\theta' \frac{r_{<}^k}{r_{>}^{k+1}} P_0^k(\cos \theta) P_0^k(\cos \theta') \\ \times \left(2P_{1s\sigma}^2(r', \theta') + 2P_{2p\sigma}^2(r', \theta') + P_{2s\sigma}^2(r', \theta') \right) \quad (21)$$

$$-\frac{\alpha}{2} \left(\frac{24\rho(r, \theta)}{\pi} \right)^{\frac{1}{3}},$$

where

$$\rho(r, \theta) = \frac{(2P_{1s\sigma}^2(r, \theta) + 2P_{2p\sigma}^2(r, \theta) + P_{2s\sigma}^2(r, \theta))}{2\pi r^2 \sin \theta} \quad (22)$$

and the $P_{1s\sigma}(r, \theta)$, $P_{2p\sigma}(r, \theta)$, and $P_{2s\sigma}(r, \theta)$ bound radial and angular orbitals are found from a molecular structure calculation [15, 16] for $Li_2^+(1s\sigma^2 2p\sigma^2 2s\sigma)$ at the equilibrium internuclear distance of $R = 5.0$ for $Li_2(1s\sigma^2 2p\sigma^2 2s\sigma^2)$. Diagonalization of the $m = 0$ Hamiltonian of Eq. (16) with $\alpha = 1.10$, on a 240 point radial mesh with $\Delta r = 0.20$ and a 32 point angular mesh with $\Delta\theta = \pi/32$, yields an ionization potential for the $2s\sigma$ subshell of $Li_2(1s\sigma^2 2p\sigma^2 2s\sigma^2)$ of 5.11 eV, in agreement with experimental results [17].

Partial cross section results obtained by propagating the $P_{m_1 m_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t)$ radial and angular wavefunctions using Eq.(12), on a $(240 \times 32)^2$ numerical lattice with $\Delta r_1 = \Delta r_2 = 0.20$ and $\Delta\theta_1 = \Delta\theta_2 = \pi/32$, are presented in column 3 of Table II. The number of $m_1 m_2$ coupled channels was 5 for $M = 0$, 6 for $M = 1$, and 5 for $M = 2$. The results presented in Table II sum over the cross sections for $S = 0$ and $S = 1$. Separate calculations are required for each incident angular momentum l_0 as found in Eq.(15). Since partial cross sections for $-M$ are assumed equal to those for $+M$, the results presented in Table II for $M \neq 0$ are twice the individual M result.

Configuration-average distorted-wave (CADW) calculations [13] were carried out for the electron-impact ionization of the $2s\sigma$ subshell of $Li_2(1s\sigma^2 2p\sigma^2 2s\sigma^2)$ at an incident energy of 10.0 eV. We used the same Hartree with local exchange potential found in Eq. (21) on the same $\Delta r = 0.20$ radial and $\Delta\theta = \pi/32$ angular mesh to generate the $P_{2s\sigma}(r, \theta)$ bound orbital and all the $P_{klm}(r, \theta)$ distorted waves. CADW partial cross sections are presented in column 4 of Table II.

As found in Table II, all of the TDCC partial cross section results are lower than the CADW partial cross section results. To obtain total cross sections for both the TDCC and CADW methods a constant extrapolation of the partial cross sections was made for $M \geq 3$, while a fitting function of the form: $F(l) = al^b e^{-\frac{2I_p}{E}}$ was used to extrapolate the partial cross sections for $l_0 \geq 6$. The TDCC cross section is estimated at 730 Mb, while the CADW cross section is estimated at 890 Mb. The reduction due to electron correlation effects found in the TDCC calculations is in keeping with previous reductions seen in the electron-impact ionization of neutral atoms [10].

CADW calculations were also carried out for the electron-impact ionization of the $2s\sigma$ subshell of $Li_2(1s\sigma^2 2p\sigma^2 2s\sigma^2)$ at an incident energy of 10 eV using a $\Delta r = 0.10$ radial and $\Delta\theta = \pi/64$ angular mesh. Diagonalization of the $m = 0$ Hamiltonian of Eq.(16) with $\alpha = 0.63$ yields an ionization potential for the $2s\sigma$ subshell of $Li_2(1s\sigma^2 2p\sigma^2 2s\sigma^2)$ of again 5.11 eV. CADW partial cross sections for the new radial and angular mesh are presented in column 5 of Table II. Overall the agreement between the CADW partial cross sections on the two different meshes is reasonably good. The largest disagreements are at the larger values of M and l_0 , where the finer radial and angular mesh should better represent the $P_{klm}(r, \theta)$ distorted-waves. An extrapolation for $M \geq 3$ and $l_0 \geq 6$ yields a total CADW cross section estimate of 820 Mb.

Table I
Partial Ionization Cross Sections for the Electron-impact Ionization of the 2s subshell of Li(1s²2s) at an Incident Energy of 15.0 eV (1.0 Mb = 1.0 × 10⁻¹⁸ cm²)

L	S	<i>TDCC</i> <i>orthogonalization</i> <i>(present)</i>	<i>TDCC</i> <i>pseudopotential</i> <i>(reference [12])</i>
0	0	4.2 Mb	3.6 Mb
0	1	1.6 Mb	1.7 Mb
1	0	11.9 Mb	12.7 Mb
1	1	18.1 Mb	18.1 Mb
2	0	30.9 Mb	34.0 Mb
2	1	12.1 Mb	12.2 Mb
3	0	24.0 Mb	27.0 Mb
3	1	14.6 Mb	15.4 Mb
4	0	30.1 Mb	32.8 Mb
4	1	15.1 Mb	16.8 Mb
5	0	24.0 Mb	25.2 Mb
5	1	22.2 Mb	24.2 Mb

Table II
Partial Ionization Cross Sections for the Electron-impact Ionization of the 2s_σ Subshell of Li₂(1sσ²2pσ²2sσ²) at an Incident Energy of 10.0 eV (1.0 Mb = 1.0 × 10⁻¹⁸ cm²)

M	l_n	<i>TDCC</i> $(\Delta r = 0.20, \Delta\theta = \pi/32)$	<i>CADW</i> $(\Delta r = 0.20, \Delta\theta = \pi/32)$	<i>CADW</i> $(\Delta r = 0.10, \Delta\theta = \pi/64)$
0	0	18.7 Mb	24.5 Mb	23.6 Mb
0	1	9.1 Mb	24.2 Mb	24.4 Mb
0	2	11.7 Mb	17.4 Mb	17.7 Mb
0	3	22.3 Mb	31.0 Mb	30.9 Mb
0	4	16.9 Mb	21.4 Mb	19.4 Mb
0	5	11.5 Mb	13.2 Mb	11.1 Mb
1	1	28.5 Mb	41.6 Mb	41.7 Mb
1	2	32.1 Mb	45.8 Mb	49.8 Mb
1	3	32.2 Mb	40.7 Mb	40.1 Mb
1	4	30.6 Mb	39.0 Mb	35.8 Mb
1	5	23.0 Mb	25.5 Mb	22.5 Mb
2	2	26.4 Mb	33.8 Mb	34.5 Mb
2	3	33.4 Mb	48.9 Mb	47.8 Mb
2	4	27.4 Mb	34.0 Mb	30.5 Mb
2	5	22.3 Mb	24.9 Mb	21.7 Mb

We note that the TDCC calculations for the electron-impact ionization of Li_2 are much more computationally intensive than CADW calculations. The CADW calculations on the $\Delta r = 0.2$ radial and $\Delta\theta = \pi/32$ angular mesh took 10 core-hours on an IBM IDataPlex system at NERSC, while the CADW calculations on the $\Delta r = 0.1$ radial

and $\Delta\theta = \pi/64$ angular mesh took 50 core-hours. On the other hand, the TDCC calculations on a $\Delta r_1 = \Delta r_2 = 0.20$ and $\Delta\theta_1 = \Delta\theta_2 = \pi/32$ numerical lattice took 10^5 core-hours on the IBM computer. With a 16 fold increase in the number of lattice points and a factor of 4 reduction in the time step, TDCC calculations on a $\Delta r_1 = \Delta r_2 = 0.10$ and $\Delta\theta_1 = \Delta\theta_2 = \pi/64$ numerical lattice becomes quite a computational challenge.

In previous work [18], we reported CADW calculations for the electron-impact ionization of Li_2 over a wide energy range. The calculations were carried out on a $\Delta r = 0.10 - 0.30$ variable radial and $\Delta\theta_1 = \pi/64$ angular mesh. The $P_{2s\sigma}(r, \theta)$ radial and angular orbital for ionization was found from a molecular structure calculation [15, 16] for $Li_2(1s\sigma^2 2p\sigma^2 2s\sigma^2)$. The $P_{1s\sigma}(r, \theta)$, $P_{2p\sigma}(r, \theta)$, and $P_{2s\sigma}(r, \theta)$ radial and angular orbitals needed for the calculation of the Hartree-local exchange potential of Eq.(21) were found from a molecular structure calculation [15,16] for $Li_2^+(1s\sigma^2 2p\sigma^2 2s\sigma)$. All of the $P_{klm}(r, \theta)$ distorted-waves were generated with the Hartree local exchange potential with $\alpha = 1.0$. A total cross section slightly below 700 Mb was found at an incident energy of 10 eV. We attribute the lower cross section, in comparison to the CADW results of Table II, as due to the use of a different $P_{2s\sigma}(r, \theta)$ radial and angular orbital in the first-order ionization matrix elements. The $P_{2s\sigma}(r, \theta)$ radial and angular orbital from diagonalization of the Hamiltonian of Eq.(16) on a $\Delta r = 0.20$ radial and $\Delta\theta = \pi/32$ angular mesh has a mean radius $\langle r \rangle = 4.26$, while the $P_{2s\sigma}(r, \theta)$ radial and angular orbital from diagonalization of the Hamiltonian of Eq. (16) on a $\Delta r = 0.10$ radial and $\Delta\theta = \pi/64$, angular mesh has a mean radius $\langle r \rangle = 4.29$. On the other hand, the $P_{2s\sigma}(r, \theta)$ radial and angular orbital taken directly from a molecular structure calculation [15, 16] interpolated onto a $\Delta r = 0.10 - 0.30$ variable radial and $\Delta\theta = \pi/64$ angular mesh has a mean radius $\langle r \rangle = 3.89$, making it harder to ionize.

IV. SUMMARY

In conclusion, we have developed a core-orthogonalization method so that nonperturbative time-dependent close-coupling calculations can now be made for the electron-impact ionization of diatomic molecules with interior closed subshells. The core-orthogonalization method, when used in TDCC calculations for the electron-impact ionization of Li, produced cross sections in reasonable agreement with previous pseudostate TDCC results. The core-orthogonalization method, when used in TDCC calculations for the electron-impact ionization of Li_2 , produced cross sections lower than CADW results, in keeping with previous electron correlation effect reductions seen in the electron-impact ionization of atoms.

In the future, we plan to apply the time-dependent close-coupling method to the calculation of the electron-impact ionization of diatomic molecules, including further studies of Li_2 and new studies of C_2 and CO . Besides total cross sections, energy and angle differential cross sections can be extracted using the fully propagated $P_{m_1 m_2}^{MS}(r_1, \theta_1, r_2, \theta_2, t \rightarrow \infty)$ radial and angular wavefunctions. We also note that the core-orthogonalization method now allows the electron-impact ionization of the inner subshells of both atoms and molecules that possess outer closed subshells.

Acknowledgements

This work was supported in part by grants from the US Department of Energy. Computational work was carried out at the National Energy Research Scientific Computing Center in Oakland, California.

References

- [1] J. D. Gorfinkiel and J. Tennyson, *J. Phys. B* **38**, 1607, (2005).
- [2] E. Krishnakumar and S. K. Srivastava, *J. Phys. B* **27**, L251, (1994).

- [3] H. C. Straub, P. Renault, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, *Phys. Rev. A* **54**, 2146, (1996).
- [4] M. S. Pindzola, F. Robicheaux, and J. Colgan, *J. Phys. B* **38**, L285, (2005).
- [5] M. S. Pindzola, F. Robicheaux, S. D. Loch, and J. Colgan, *Phys. Rev. A* **73**, 052706, (2006).
- [6] B. Peart and K. Dolder, *J. Phys. B* **6**, 2409, (1973).
- [7] J. Colgan, M. S. Pindzola, F. Robicheaux, C. Kaiser, A. J. Murray, and D. H. Madison, *Phys. Rev. Letts.* **101**, 233201, (2008).
- [8] J. Colgan, O. Al-Hagan, D. H. Madison, C. Kaiser, A. J. Murray, and M. S. Pindzola, *Phys. Rev. A* **79**, 052704, (2009).
- [9] M. S. Pindzola, F. Robicheaux, N. R. Badnell, and T. W. Gorczyca, *Phys. Rev. A* **56**, 1994 (1997).
- [10] M. S. Pindzola, F. Robicheaux, S. D. Loch, J. C. Berengut, T. Topcu, J. Colgan, M. Foster, D. C. Griffin, C. P. Ballance, D. R. Schultz, T. Minami, N. R. Badnell, M. C. Witthoef, D. R. Plante, D. M. Mitnik, J. A. Ludlow, and U. Kleiman, *J. Phys. B* **40**, R39, (2007).
- [11] J. Colgan, M. S. Pindzola, D. M. Mitnik, D. C. Griffin, and I. Bray, *Phys. Rev. Letts.* **87**, 213201, (2001).
- [12] J. Colgan, M. S. Pindzola, D. M. Mitnik, and D. C. Griffin, *Phys. Rev. A* **63**, 062709, (2001).
- [13] M. S. Pindzola, F. Robicheaux, J. Colgan, and C. P. Ballance, *Phys. Rev. A* **76**, 012714, (2007).
- [14] C. F. Fischer, *Comput. Phys. Commun.* **43**, 355, (1987).
- [15] Theoretical Chemistry Group, Computer code ALCHEMY (IBM Research Laboratory, San Jose, CA, 1970).
- [16] M. A. Morrison, *Comput. Phys. Commun.* **21**, 63, (1980).
- [17] <http://physics.nist.gov/PhysRefData>
- [18] M. S. Pindzola, F. Robicheaux, C. P. Ballance, and J. Colgan, *Phys. Rev. A* **78**, 042703, (2008).

