Computational Atomic and Molecular Physics

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A consortium has been formed to study the many-body quantal dynamics of atoms and molecules utilizing the most advanced computing platforms. Advances in understanding are applied to many general science areas: including controlled fusion, atmospheric chemistry, cold atom condensate dynamics, laser interactions with matter, and observational astrophysics. Beginning Fall of 2003, several of our AMO research computer codes have been tested on the Cray X1 at the ORNL/CCS. For example: 3D time-dependent close-coupling calculations have been completed for electron double ionization of He and triple photoionization of Li, while 4D time-dependent close-coupling calculations are in progress for electron single ionization of H_2^+ and double photoionization of H_2.

I. INTRODUCTION

The oldest and still one of the largest divisions of the American Physical Society is the Division of Atomic, Molecular, and Optical (AMO) Physics. In the Division, basic research studies are carried out in the areas of quantum information, atomic and molecular structure and collisional dynamics, clusters, atomic and molecular processes in external fields, and matter waves and condensation. Due to the pervasive nature of atoms and molecules, applications of these basic research studies are legion: from nanoscale fabrication to observations of the large scale structure of the universe. Theoretical physicists at ORNL, LANL, and several US and UK research universities have formed a consortium to study the many-body quantal dynamics of atoms and molecules utilizing the most advanced computing platforms. Advances in understanding are applied to many general science areas, including controlled fusion, atmospheric chemistry, cold atom condensate dynamics, laser interactions with matter, and observational astrophysics.

Beginning Fall of 2003, several of our AMO research computer codes have been tested in full production mode on the Cray X1 at the ORNL/CCS. In this paper, we will report on completed 3D time-dependent close-coupling calculations for electron double ionization of He and triple photoionization of Li, and planned 4D time-dependent close-coupling calculations for electron single ionization of H_2^+ and double photoionization of H_2. We will also briefly summarize future plans involving other AMO research computer codes. Unless otherwise stated, we will use atomic units (1 a.u. = 27.212 eV).

II. TIME-DEPENDENT CLOSE-COUPLING CALCULATIONS FOR ATOMS AND MOLECULES

For electron ionization of the H atom, the angular reduction of the time-dependent Schrodinger equation for a two electron wavefunction yields a set of time-dependent close-coupled partial differential equations for each L symmetry:

$$i\frac{\partial P^L_{l_1 l_2}(r_1,r_2,t)}{\partial t} = T_{l_1 l_2}(r_1,r_2)P^L_{l_1 l_2}(r_1,r_2,t)$$

$$+\sum_{l_1',l_2'} V^L_{l_1 l_2, l_1' l_2'}(r_1,r_2) P^L_{l_1' l_2'}(r_1,r_2,t) \ , \tag{1}$$

where

$$T_{l_1 l_2}(r_1,r_2) = \sum_i^2 (-\frac{1}{2}\frac{\partial^2}{\partial r_i^2} + \frac{l_i(l_i+1)}{2r_i^2} - \frac{1}{r_i}) \ , \tag{2}$$

and the coupling operators are found by reduction of:

$$V^L_{l_1 l_2, l_1' l_2'}(r_1,r_2) = < (l_1,l_2)L|(r_{12})^{-1}|(l_1',l_2')L > \ , \tag{3}$$

to expressions involving standard 3j and 6j symbols. The initial condition for the solution of the time-dependent close-coupling equations is given by:

$$P^L_{l_1 l_2}(r_1,r_2,t=0) = P_{1s}(r_1) G_{k_0 L}(r_2) \delta_{l_1,0} \delta_{l_2,L} \ , \tag{4}$$

where $P_{1s}(r_1)$ is the ground state wavefunction for the H atom, and the Gaussian wavepacket, $G_{k_0 L}(r_2)$, has a propagation energy of $\frac{k_0^2}{2}$.

For electron ionization of the He atom, the angular reduction of the time-dependent Schrodinger equation for a three electron wavefunction yields a set of time-dependent close-coupled partial differential equations for each $\mathcal{L}$ symmetry:

$$\begin{aligned} i\frac{\partial P^{\mathcal{L}}_{l_1 l_2 L l_3}(r_1,r_2,r_3,t)}{\partial t} &= T_{l_1 l_2 l_3}(r_1,r_2,r_3) P^{\mathcal{L}}_{l_1 l_2 L l_3}(r_1,r_2,r_3,t) \\ &+ \sum_{l_1',l_2',L',l_3'} \sum_{i<j}^3 V^{\mathcal{L}}_{l_1 l_2 L l_3, l_1' l_2' L' l_3'}(r_i,r_j) P^{\mathcal{L}}_{l_1' l_2' L' l_3'}(r_1,r_2,r_3,t) \ , \end{aligned} \tag{5}$$

where

$$T_{l_1 l_2 l_3}(r_1,r_2,r_3) = \sum_i^3 (-\frac{1}{2}\frac{\partial^2}{\partial r_i^2} + \frac{l_i(l_i+1)}{2r_i^2} - \frac{2}{r_i}) \ , \tag{6}$$

and the coupling operators are found by reduction of:

$$V^{\mathcal{L}}_{l_1 l_2 L l_3, l_1' l_2' L' l_3'}(r_i,r_j) = < ((l_1,l_2)L,l_3)\mathcal{L}|(r_{ij})^{-1}|((l_1',l_2')L',l_3')\mathcal{L} > \tag{7}$$

to expressions involving standard 3j and 6j symbols. The initial condition for the solution of the time-dependent close-coupling equations is given by:

$$P^{\mathcal{L}}_{l_1 l_2 L l_3}(r_1,r_2,r_3,t=0) = P^S_{ll}(r_1,r_2) G_{k_0 \mathcal{L}}(r_3) \delta_{l_1,l} \delta_{l_2,l} \delta_{L,0} \delta_{l_3,\mathcal{L}} \ , \tag{8}$$

where $P^S_{ll}(r_1,r_2)$ are the ground state wavefunctions for the He atom.

For electron ionization of the H_2^+ molecule, the angular reduction of the time-dependent Schrodinger equation for a two electron wavefunction yields a set of time-dependent close-coupled partial differential equations for each M symmetry:

$$\begin{aligned} i\frac{\partial P^M_{m_1 m_2}(r_1,\theta_1,r_2,\theta_2,t)}{\partial t} &= T_{m_1 m_2}(r_1,\theta_1,r_2,\theta_2) P^M_{m_1 m_2}(r_1,\theta_1,r_2,\theta_2,t) \\ &+ \sum_{m_1',m_2'} V^M_{m_1 m_2, m_1' m_2'}(r_1,\theta_1,r_2,\theta_2) \\ &\times P^M_{m_1' m_2'}(r_1,\theta_1,r_2,\theta_2,t) \ , \end{aligned} \tag{9}$$

where

$$\begin{aligned} T_{m_1 m_2}(r_1,\theta_1,r_2,\theta_2) = \sum_i^2 (&-\frac{1}{2}\frac{\partial^2}{\partial r_i^2} - \frac{1}{2r_i^2}\frac{\partial^2}{\partial \theta_i^2} + \frac{m_i^2}{2r_i^2 \sin\theta_i^2} \\ &- \frac{1}{\sqrt{r_i^2 + \frac{1}{4}R^2 - r_i R\cos\theta_i}} - \frac{1}{\sqrt{r_i^2 + \frac{1}{4}R^2 + r_i R\cos\theta_i}}) \ , \end{aligned} \tag{10}$$

and the coupling operators are found by reduction of:

$$V^M_{m_1 m_2, m_1' m_2'}(r_1, \theta_1, r_2, \theta_2) = < (m_1, m_2) M | (r_{12})^{-1} | (m_1', m_2') M > \ . \tag{11}$$

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

$$P^M_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, t = 0) = P_{1\sigma}(r_1, \theta_1) G_{k_0 M}(r_2, \theta_2) \delta_{m_1, 0} \delta_{m_2, M} \ , \tag{12}$$

where $P_{1\sigma}(r_1, \theta_1)$ is the ground state wavefunction for the H_2^+ molecule.

The time-dependent close-coupling equations (1-12) are solved using standard numerical methods to obtain a discrete representation of the wavefunctions and all operators on a two, three, or four dimensional lattice. Our implementation on massively parallel computers is to partition the coordinates over the many processors, so called domain decomposition. At each time step of the solution only those parts of the wavefunctions on the domain boundaries needed to calculate the second derivatives found in Eqs.(2), (6), and (10) are passed to neighboring processors. Probabilities for all the many collision processes possible are obtained by $t \to \infty$ projection onto final-state fully antisymmetric spatial and spin wavefunctions.

For electron single ionization of the H atom, the solution of the time-dependent close-coupling equations (1-4) has yielded [1] total cross sections in excellent agreement with absolute experimental measurements [2], as shown in Figure 1. Many of the calculational runs were performed on the Cray T3E supercomputer at LBNL/NERSC. The electron single ionization of the H atom is an example of the so-called "Coulomb three-body problem", which until quite recently had remained unsolved for quantal systems [3]. In the last few years, solution of the time-dependent close-coupling equations (1-4) has yielded electron single ionization total cross sections for many atoms and their ions, for example, electron ionization of Li [4]. Electron single ionization differential cross sections, in both energy and angle, may also be obtained [5] by solution of Eqs.(1-4). A related "Coulomb three-body problem" is the photon double ionization of helium. Solution of the time-dependent close-coupling equations (1-4), modified to include radiation field operators, has yielded total [6] and differential [7,8] cross sections in excellent agreement with experimental measurements.

For electron double ionization of the He atom, the solution of the time-dependent close-coupling equations (5-8) has yielded [9] total cross sections in excellent agreement with absolute experimental measurements [10], as shown in Figure 2. Many of the calculational runs were performed on the Cray X1 supercomputer at ORNL/CCS. The electron double ionization of the He atom is an example of the so-called "Coulomb four-body problem", which until now had remained unsolved for quantal systems. A related "Coulomb four-body problem" is the photon triple ionization of lithium. Solution of the time-dependent close-coupling equations (5-8), modified to include radiation field operators, has yielded [11] total cross sections in good agreement with experimental measurements.

Work is in progress for electron single ionization of the H_2^+ molecule by solution of the time-dependent close-coupling equations (9-12) on the Cray X1 supercomputer at ORNL/CCS. The electron single ionization of the H_2^+ molecule, and the photon double ionization of the H_2 molecule, are examples of a Coulomb three-body problem for fixed nuclei and a Coulomb four-body problem for moving nuclei.

III. FUTURE PLANS

Several other of our AMO research computer codes have been tested on the Cray X1 at the ORNL/CCS. The R-matrix with pseudo-states method has been adapted for use on massively parallel machines and provides accurate electron-impact excitation and ionization cross sections for many atoms and their ions, for example, electron excitation of C^{2+} [12]. Work has recently been completed for electron-impact excitation of the Ne atom [13], involving repeated diagonalizations of 50,000 $\times$ 50,000 dense matrices in which all eigenvalues and eigenvectors are needed. The time-dependent semi-classical lattice method has been adapted for use on massively parallel machines and provides accurate excitation and charge-transfer cross sections for many ion-atom collisions, for example, p + Li collisions [14]. Work is in progress for charge transfer cross sections involving He^{2+} and Be^{4+} collisions with H atoms [15], in which the time propagated Cartesian lattice has dimensions of up to 150 $\times$ 10^6.

IV. ACKNOWLEDGMENTS

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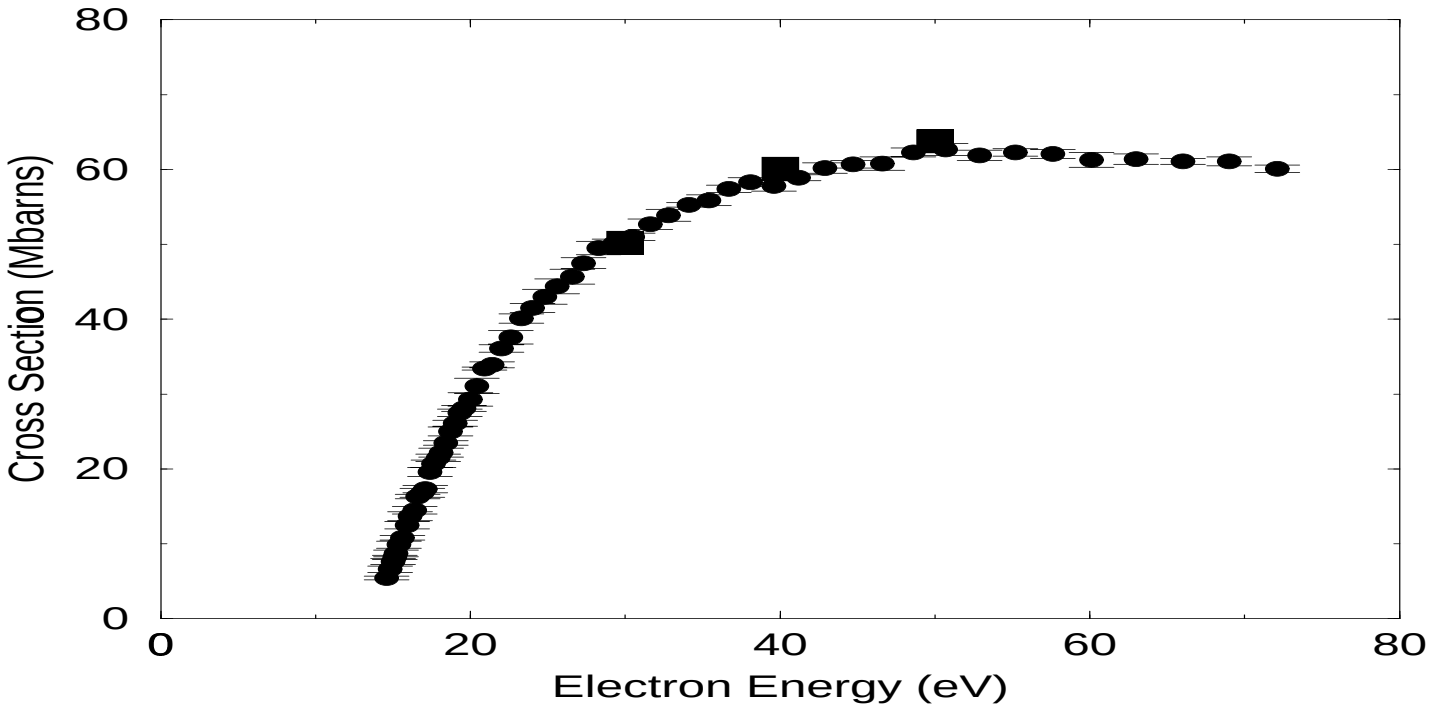

FIG. 1. Electron single ionization of the H atom. Solid squares: time-dependent close-coupling calculations[1], solid circles with error bars: experimental measurements[2]. (1.0 Mbarn = 1.0×10^{-18} cm^2)

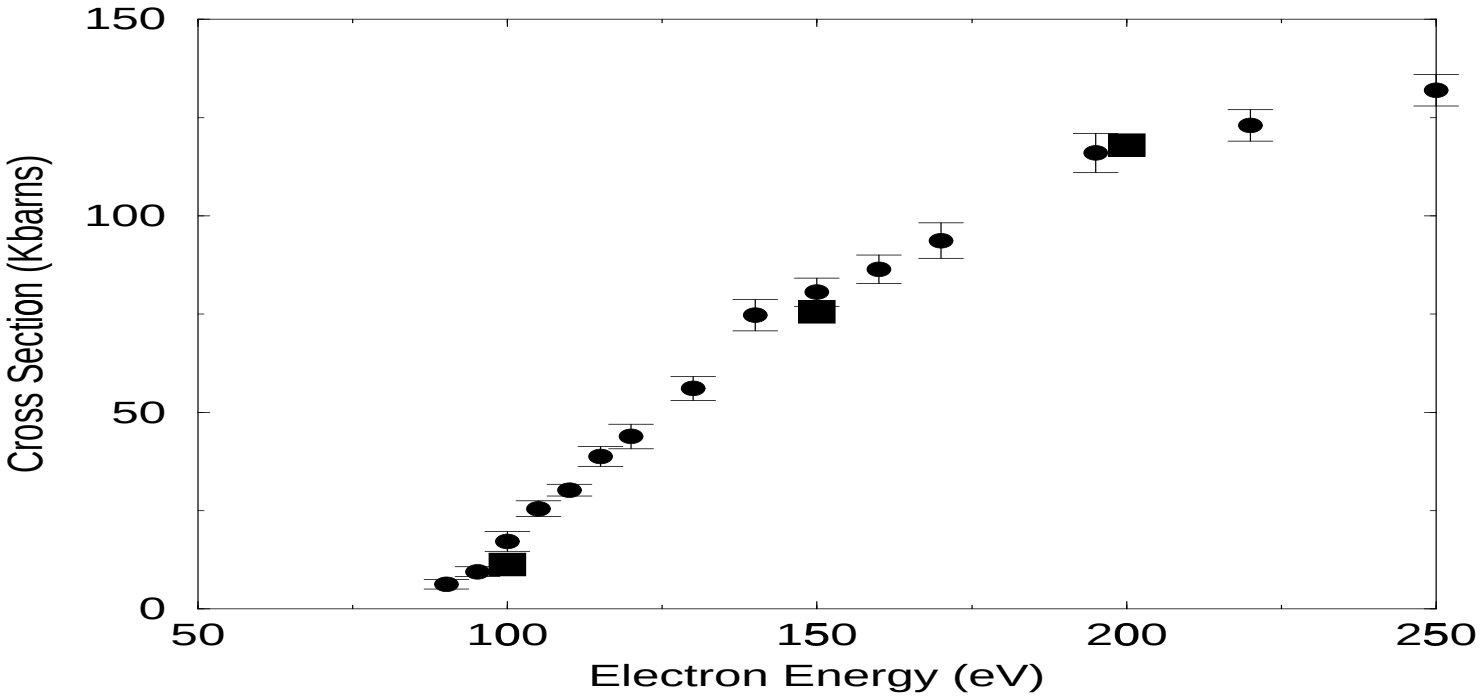

FIG. 2. Electron double ionization of the He atom. Solid squares: time-dependent close-coupling calculations[9], solid circles with error bars: experimental measurements[10]. (1.0 Kbarn = 1.0×10^{-21} cm^2)