

# Fourier transform method of calculating total cross sections using the time-dependent close-coupling theory

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A formulation of the time-dependent close-coupling theory is described which allows efficient calculation of the total ionization cross section for many electron energies. The Fourier transform method is applied to the electron-impact ionization of  $\text{Li}^{2+}$  and excellent agreement is found with experiment and a distorted-wave method.

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## I. INTRODUCTION

The calculation of total integral cross sections for electron-impact ionization of atoms and atomic ions has, in the last 8 years, greatly benefited from the development of several nonperturbative methods, which generally show very good agreement with each other and with experiment. For the electron-impact ionization of hydrogen, the convergent close-coupling [1], the hyperspherical close-coupling [2], the  $R$ -matrix with pseudostates [3], the time-dependent close-coupling [4], and the exterior complex scaling [5] methods yield results over a wide range of incident energies that are all within the error bars of the total cross section measurements of Shah *et al.* [6]. The convergent close-coupling, the  $R$  matrix with pseudostates, and the time-dependent close-coupling methods have been successfully used to calculate electron-impact direct ionization cross sections for many other atoms and their ions.

The  $R$ -matrix with pseudostates method uses analytic functions and/or pseudo-orbitals obtained through diagonalization of the target Hamiltonian to represent the bound orbitals. The  $(N+1)$ -electron Hamiltonian is then diagonalized and a total ionization cross section can be extracted via a simple analytic function involving the  $K$  matrix and the surface amplitudes. It is this diagonalization that forms the main computational aspect of this calculation. The resulting total ionization cross section contains unphysical pseudoresonances that oscillate about the true direct total cross section. This is due to the finite nature of the pseudostate expansion. Of course, since we know that the direct cross section must be smooth (since it generally does not contain any resonance structure), this oscillating function can be easily averaged to give the correct answer, which, in practice, works extremely well.

The time-dependent close-coupling method usually only calculates the total cross section, at three or four points, since each energy point must be calculated separately. Again, this is satisfactory since, as the total cross section is a smooth function, one can easily draw a line through these points to obtain the cross section as a function of energy. The main requirement is to map out the peak of the cross section which then falls off asymptotically with incident electron energy. In this paper we describe a method that allows us to use the time-dependent close-coupling formalism to calculate total

integral cross sections over a range of energies for only one time propagation. We thus eliminate the need for multiple time-dependent calculations to obtain the cross section for more than one energy. Our technique is based on a simple Fourier transform involving the initial wave packet that describes the incoming electron.

Wave-packet descriptions of quantal atomic physics phenomena have been used extensively in computational chemistry [7]. For example, they have been used to study reaction probabilities for atom-atom and atom-molecule collisions [8]. Transition probabilities and rate constants were initially calculated using broad wave packets in radial space, to obtain probabilities at a single energy [9]. This was subsequently generalized to allow probabilities to be obtained for many energies in a single propagation using a highly localized spatial wave function [10]. Wave-packet techniques have also been used in the study of atoms subjected to strong electric fields [11].

Our proposed method is found to take almost the same computational resources as previous calculations and can now give total cross sections over a wide range of electron energies. This is an improvement in the calculation of total integral cross sections, since the computer time necessary is now much less. It could also prove very beneficial in calculations of asymmetry parameters, where partial-wave total integral cross sections are necessary over a range of energies and for which many angular momenta are needed to achieve convergence. We note that our method also allows calculation of angular differential cross sections at many incident electron energies, although this may not be as important since experimental measurements of these quantities tend to be made at only a single incident electron energy. We apply our technique to calculations of total cross sections for electron scattering from  $\text{Li}^{2+}$ . Good agreement is found with existing experimental measurements and distorted-wave calculations. We note that this completes a set of time-dependent calculations for total ionization cross sections for the lithium isonuclear sequence [12,13], which is necessary for collisional radiative modeling of fusion plasmas where lithium beam spectroscopy remains an important diagnostic.

## II. THEORY

For electron scattering from a one-electron target atom the Hamiltonian in atomic units is given by

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

where  $r_1$  and  $r_2$  are the coordinates of the two electrons and  $Z$  is the atomic number. The total wave function can be expanded in coupled spherical harmonics as

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

where  $L$  and  $S$  are the total orbital and spin angular momentum of the system,  $Y_{lm}(\hat{r})$  is a spherical harmonic, and  $C_{m_1 m_2 0}^{l_1 l_2 L}$  is a Clebsch-Gordan coefficient. From projection onto the time-dependent Schrödinger equation we obtain a set of time-dependent close-coupled partial differential equations for each  $LS$  symmetry

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

where  $T_{l_1 l_2}(r_1, r_2)$  contains kinetic energy, centrifugal barrier, nuclear, direct Hartree and local exchange operators, and  $V_{l_1 l_2, l'_1 l'_2}^L(r_1, r_2)$  couples the various  $(l_1 l_2)$  scattering channels. Explicit expressions for these quantities may be found in Ref. [4].

We note here that our time-dependent radial wave function may also be written, for a time-independent Hamiltonian, in the form

$$P_{l_1 l_2}^{LS}(r_1, r_2, t) = \int A(E) P_{1s}(r_1) \phi_{kl}(r_2) e^{-iEt} dE, \quad (4)$$

where  $\phi_{kl}(r)$  are energy normalized radial continuum functions, product functions are used for simplicity, and the time-independent quantity  $A(E)$  may be defined as

$$A(E) = \int P_{1s}(r_1) \phi_{kl}(r_2) P_{l_1 l_2}^{LS}(r_1, r_2, t=0) dr_1 dr_2, \quad (5)$$

where  $E = \epsilon_{1s} + k^2/2$ .

We now choose a ‘‘parent’’ time-dependent wave function  $P_{\alpha}^{LS}(r_1, r_2, t)$ , and a family of ‘‘children’’ wave functions  $P_{\beta}^{LS}(r_1, r_2, t)$  (where we have dropped the  $l_1 l_2$  subscript on the radial wave functions for clarity), where we choose the

energy width of each  $P_{\beta}^{LS}$  to be smaller than that of  $P_{\alpha}^{LS}$ . By applying a Fourier transform to Eq. (4) we can write

$$\frac{1}{2\pi} \int e^{iEt} P_{\alpha}^{LS}(r_1, r_2, t) dt = A_{\alpha}(E) P_{1s}(r_1) \phi_{kl}(r_2), \quad (6)$$

so that

$$\begin{aligned} P_{\beta}^{LS}(r_1, r_2, \tau) &= \int \frac{A_{\beta}(E)}{A_{\alpha}(E)} A_{\alpha}(E) P_{1s}(r_1) \phi_{kl}(r_2) e^{-iE\tau} dE \\ &= \frac{1}{2\pi} \int \int \frac{A_{\beta}(E)}{A_{\alpha}(E)} e^{iE(t-\tau)} P_{\alpha}^{LS}(r_1, r_2, t) dE dt \\ &= \int P_{\alpha}^{LS}(r_1, r_2, t) \\ &\times \left\{ \frac{1}{2\pi} \int \frac{A_{\beta}(E)}{A_{\alpha}(E)} e^{iE(t-\tau)} dE \right\} dt. \quad (7) \end{aligned}$$

The ratios  $A_{\beta}(E)/A_{\alpha}(E)$  can be calculated numerically from Eq. (5) once we have defined our initial ( $t=0$ ) wave function and need only be computed once, since they are time independent. The widths of the wave packets must be chosen such that  $A_{\beta}(E)/A_{\alpha}(E) \rightarrow 0$  as  $E \rightarrow \pm\infty$ . Also, since we are only concerned with the ratios, the normalization of the continuum functions need not be computed. Thus the children wave functions  $P_{\beta}^{LS}$  may be calculated from the parent  $P_{\alpha}^{LS}$  in a straightforward manner. Also, the number of time steps  $\tau$  necessary for computation of  $P_{\beta}^{LS}$  is much less than the number required in the main time propagation of  $P_{\alpha}^{LS}$ . This is because the computation of  $P_{\beta}^{LS}$  in Eq. (7) is an integral over a smoothly varying function, whereas  $P_{\alpha}^{LS}$  is obtained via an explicit time propagation that depends on the radial grid spacing.

At a time  $t=0$  before the collision the two-electron radial wave functions  $P_{l_1 l_2}^{LS}(r_1, r_2, t=0)$ , for  $l=L$  are defined by

$$\begin{aligned} P_{l_0}^{LS}(r_1, r_2, t=0) &= \sqrt{\frac{1}{2}} g_{kl}(r_1) P_{1s}(r_2), \\ P_{0l}^{LS}(r_1, r_2, t=0) &= \sqrt{\frac{1}{2}} (-1)^S P_{1s}(r_1) g_{kl}(r_2), \quad (8) \end{aligned}$$

where  $k$  is the linear momentum and  $P_{1s}(r)$  is the bound radial orbital of  $\text{Li}^{2+}$ , and we now use an antisymmetrized product function. The radial wave packet  $g_{kl}^{\alpha}(r)$  that defines  $P_{\alpha}^{LS}$  is given by

$$g_{kl}^{\alpha}(r) = \frac{1}{(w^2 \pi)^{1/4}} e^{-(r-s)^2/2w^2} h_l^{-}(kr), \quad (9)$$

where  $s$  is the localization radius of the wave packet,  $w$  is the width of the wave packet and  $h_l^{-}(kr)$  is an asymptotic Hankel function, i.e.,  $h_l^{-}(kr) = e^{-ikr} e^{i\pi l/2}$ . For the  $P_{\beta}^{LS}$  wave functions we choose a wave packet where

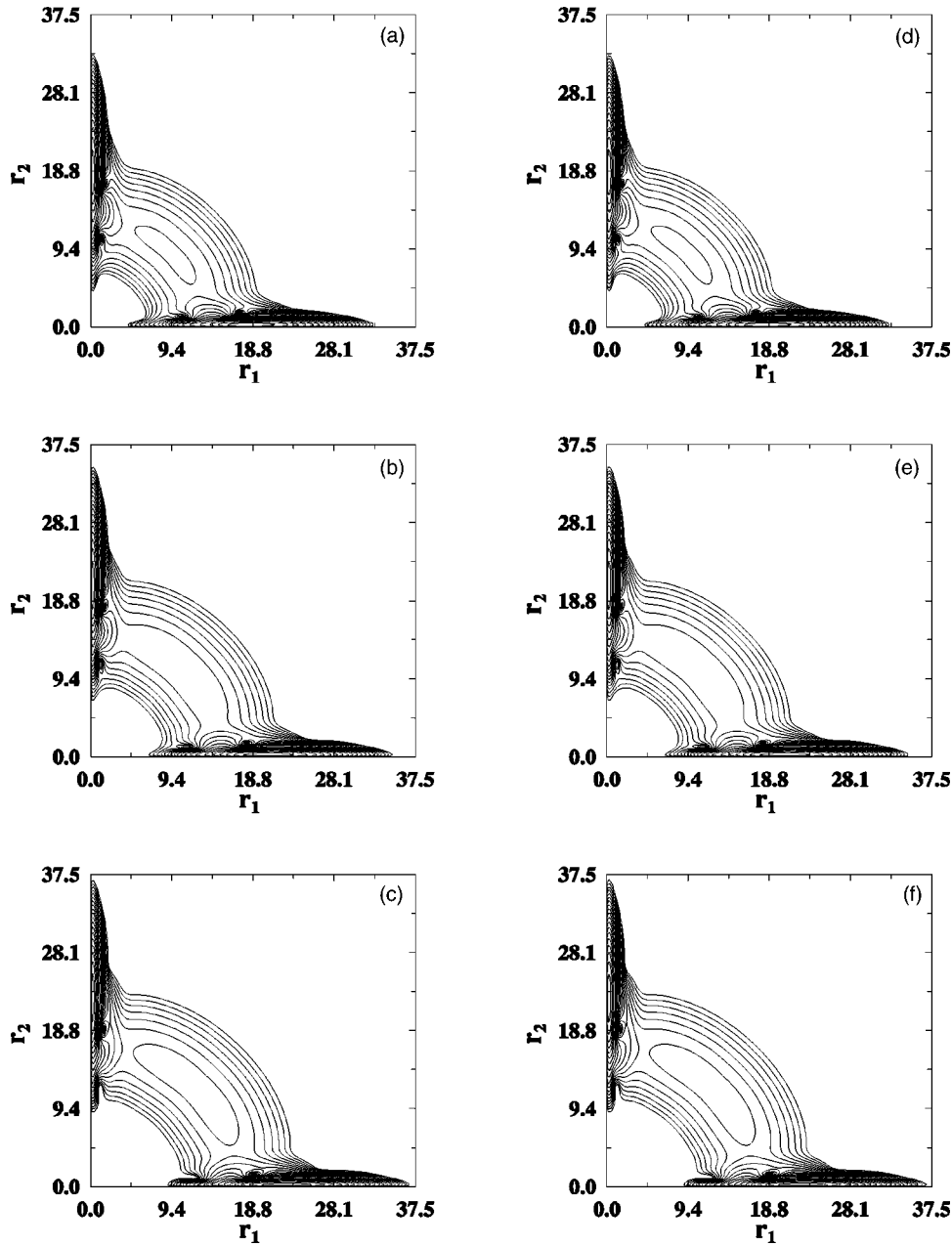


FIG. 1. Contour plot of the probability density for the  $^1S l_1=l_2=0$  channel for electron scattering from  $\text{Li}^{2+}$ . For (a), (b), and (c) the plots were made with separate runs using the older version of our time-dependent programs. For (d), (e), and (f) the plots were made using one run of our proposed program, with the initial energy centered at 200 eV. For (a) and (d) the electron energy is 180 eV, for (b) and (e) the electron energy is 200 eV, and for (c) and (f) the electron energy is 220 eV.

$$g_{kl}^\beta(r) = \frac{1}{[(4w)^2\pi]^{1/4}} e^{-(r-s)^2/2(4w)^2} h_l^-(kr), \quad (10)$$

i.e., we have taken a much narrower width in momentum space (and so broader in radial space). This allows the children  $P_\beta^{LS}$  wave functions to cover a wide range of energies and Eq. (7) ensures that these wave functions may be extracted efficiently from a normal time propagation of  $P_\alpha^{LS}$ . The same bound orbitals  $P_{1s}(r)$  are used for both the  $P_\alpha^{LS}$  and  $P_\beta^{LS}$  wave functions.

As in our previous time-dependent calculations, the close-coupled equations are solved on a lattice of uniform mesh spacing, in this case  $\Delta r=0.1$  a.u., with 500 points. This gives an ionization threshold of 119.8 eV, within 2% of the experimental value. We propagate the  $P_\alpha^{LS}$  wave function as

normal and extract the  $P_\beta^{LS}$  wave functions from it using Eq. (7), using the stored values of the ratios  $A_\beta(E)/A_\alpha(E)$ . We note that the  $P_\alpha^{LS}$  wave function is propagated for longer than would usually be necessary, in order to allow the transformed wave functions associated with the lowest energies stored in  $P_\beta^{LS}$  sufficient time to converge. After the time propagation the probabilities and cross sections for both excitation and ionization may be extracted by the usual projection onto products of bound and continuum radial orbitals.

In Fig. 1 we show contour plots of the probability density for the  $^1S l_1=l_2=0$  channel for electron scattering from  $\text{Li}^{2+}$ , for three different initial electron energies. Figures 1(a) and 1(d) show the probability density for an initial electron energy of 180 eV, 1(b) and 1(e) show the probability density for an energy of 200 eV, and 1(c) and 1(f) show the probability density for an energy of 220 eV. The probabilities in

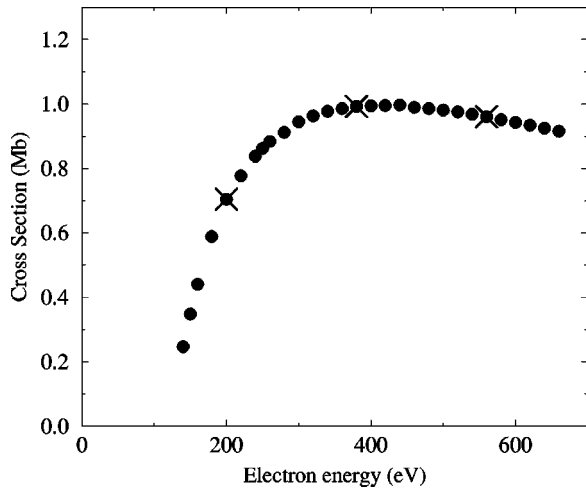


FIG. 2. Electron-impact ionization cross sections for  $\text{Li}^{2+}$  calculated using the time-dependent close-coupling method. The crosses are the results at the energies of the three parent calculations and the circles are the results of the children calculations as described in the text. ( $1.0 \text{ Mb} = 1.0 \times 10^{-18} \text{ cm}^2$ ).

Figs. 1(a)–1(c) were generated using three separate runs of our computer programs used in all our previous calculations. For Figs. 1(d)–1(f) the probabilities were generated using a single run of our computer program, which generates the wave functions from a single propagation of the  $P_{\alpha}^{LS}$  wave function (at 200 eV initial electron energy) and which then extracts the  $P_{\beta}^{LS}$  wave functions as described previously. The runs used to generate the probabilities in Figs. 1(d)–1(f) took only slightly longer than a single run of Figs. 1(a)–1(c). In practice, we used our method to generate the transformed wave functions for typically ten energies, for one propagation of the parent  $P_{\alpha}^{LS}$  wave function. The saving in computer time is then easily an order of magnitude over our previous time-dependent calculations and shows how cross sections may now be efficiently generated over a wide range of energies.

### III. RESULTS

Using our modified time-dependent method, cross sections are calculated for electron scattering from  $\text{Li}^{2+}$  over a wide range of energies. This ion was chosen in order to complete our set of calculations on the lithium isonuclear sequence for both excitation and ionization, following previous work on Li and  $\text{Li}^{+}$  [12–15].

The time-dependent method was used to generate ionization cross sections over a range of energies from 140 to 660 eV in steps of 20 eV. For each angular momentum from  $L = 0 - 6$  three parent time propagations were made at an energy of 200, 380, and 560 eV, and the probabilities and cross sections extracted for children energies from 80 eV below to 80 eV above each parent energy. For the high angular momentum above  $L = 6$  our total cross sections were topped up with distorted-wave calculations following previous work. In Fig. 2 we present the results of two sets of time-dependent calculations. The crosses are three independent calculations

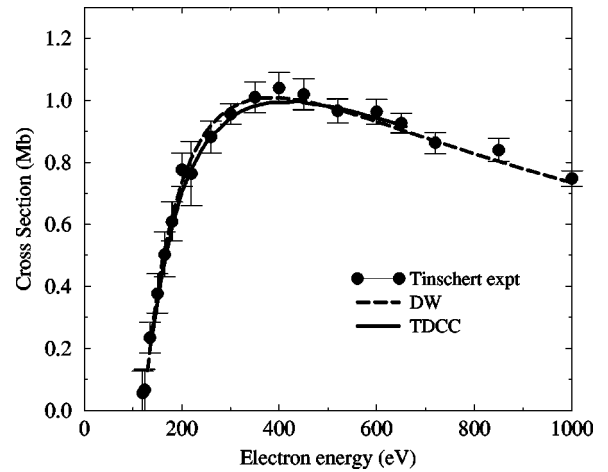


FIG. 3. Electron-impact ionization cross sections for  $\text{Li}^{2+}$ . We show the experimental measurements of Tinschert *et al.* [16] (solid circles), distorted-wave calculations (dashed line) and time-dependent close-coupling calculations (solid line). ( $1.0 \text{ Mb} = 1.0 \times 10^{-18} \text{ cm}^2$ ).

made at the parent energies of 200, 380, and 560 eV and the circles are the calculations made at the children energies as described. It is clear that our Fourier transform method is in excellent agreement with the previous time-dependent method and that the total ionization cross section is a smooth curve as expected.

In Fig. 3 we now present the total ionization cross section and compare the time-dependent calculations (solid line), fully distorted-wave calculations (dashed line), and the experimental measurements of Tinschert *et al.* [16] (circles). The agreement between both sets of theoretical calculations and the experimental measurements is very good over a wide range of energies. It is clear that for a doubly charged ion such as  $\text{Li}^{2+}$ , distorted-wave calculations are reasonably accurate for total ionization cross sections. The time-dependent calculations are slightly lower than the distorted-wave calculations near the peak of the cross section, but both sets are well within the error bars of the experimental measurements. We note that this good agreement between distorted-wave and time-dependent calculations did not extend to the total ionization cross sections for Li, where the distorted-wave calculations overestimated the total ionization cross section by up to 50% at some energies.

### IV. SUMMARY

In this paper we have described a method of extracting total ionization cross sections from time-dependent close-coupling theory using a simple Fourier transform technique. Our method allows time-dependent calculations for many more energy points than in previous calculations for almost no increase in computer time. We have demonstrated the effectiveness of our technique by calculating total ionization cross sections for electron scattering from  $\text{Li}^{2+}$  for many energy points. Although distorted-wave calculations for this

process are also in excellent agreement with available experimental measurements, this set of calculations conveniently illustrates our method.

In the future we expect to apply our method to calculations of total ionization cross sections of other atomic species. We remark that excitation cross sections can also be easily extracted from these time-dependent calculations and work on comparison with other theoretical calculations is underway for  $\text{Li}^{2+}$ . Also, the calculation of single and triple differential cross sections can easily be made at any of the

many initial electron energies at which the total ionization cross section is computed.

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