

Lattice Calculations of the Photoionization of Li

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Calculations are presented for the double photoionization (with excitation) and triple photoionization of the Li atom. The motion of all three electrons is treated equally by solving the time-dependent Schrödinger equation in nine dimensions. A radial lattice is used to represent three of the nine dimensions, while a coupled channel expansion is used to represent the other six dimensions. Probabilities for photoionization are obtained by $t \rightarrow \infty$ projection onto fully antisymmetric spatial and spin functions. Double photoionization cross sections for lithium leaving the ion in the $1s$, $2s$, and $2p$ states are presented. Good agreement is found with the measurements of Huang *et al.* [Phys. Rev. A **59**, 3397 (1999)] for the total double photoionization cross section and with the measurements of Wehlitz *et al.* [Phys. Rev. Lett. **81**, 1813 (1998)] for the triple photoionization cross section.

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The last decade has seen the development of several nonperturbative theoretical methods that have successfully treated two continuum electrons moving in the field of a charged core, that is, Coulomb three-body breakup. The converged 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 have all obtained total cross sections for the electron-impact ionization of hydrogen that are in excellent agreement with the crossed-beams experiment of Shah *et al.* [6]. To date these nonperturbative methods [7–9] have also successfully calculated the wide range of energy and angle differential cross sections found in the electron induced breakup of the hydrogen atom. In addition, the converged close-coupling [10], the hyperspherical close-coupling [11], and the time-dependent close-coupling [12] methods have all obtained energy and angle differential cross sections for the double photoionization of helium that are in excellent agreement with the recent synchrotron experiment of Bräuning *et al.* [13].

In this Letter we develop a nonperturbative theoretical method to study the double photoionization (with excitation) and triple photoionization of Li. There have been several theoretical studies of these multiple ionization processes in Li. The first such calculation by van der Hart and Greene [14] investigated the double photoionization and triple photoionization of Li in the high-energy limit. Ratios of double-to-single ionization

were in good agreement with the experimental measurements of Wehlitz *et al.* [15]. The contribution of doubly excited states to the double photoionization cross section was found to be significant (over 40%) demonstrating that one must go beyond a “frozen-core” model of double photoionization of Li to obtain accurate results. Pattard and Burgdörfer [16] used a half-collision model to study the triple ionization and related cross section ratios. Good agreement was found with the triple photoionization cross section measurements of Wehlitz *et al.* [15].

In contrast to these previous theoretical approaches, we treat all three electrons of Li equally by propagating in time a nine-dimensional wave function according to the Schrödinger equation, with the three radial dimensions represented on a numerical lattice and the six angular dimensions represented by a coupled channels expansion. Double photoionization with excitation, and triple photoionization probabilities are obtained by $t \rightarrow \infty$ projection onto fully antisymmetric spatial and spin functions, with care as to orthogonality of different representations. We compare our results with the measurements of Huang *et al.* [17] for double photoionization, and with the recent synchrotron experiments of Wehlitz *et al.* [15] for triple photoionization. Unless otherwise stated, we use atomic units.

For multiple photoionization of a three-electron target atom, the angular reduction of a weak-field form of the time-dependent Schrödinger equation yields a single set of time-dependent close-coupled partial differential equations:

$$i \frac{\partial P_{l_1 l_2 l_3}^{\mathcal{L}}(r_1, r_2, r_3, t)}{\partial t} = T_{l_1 l_2 l_3}(r_1, r_2, r_3) P_{l_1 l_2 l_3}^{\mathcal{L}}(r_1, r_2, r_3, t) + \sum_{l'_1, l'_2, l'_3} \sum_{i < j}^3 V_{l_1 l_2 l_3, l'_1 l'_2 l'_3}^{\mathcal{L}}(r_i, r_j) P_{l'_1 l'_2 l'_3}^{\mathcal{L}}(r_1, r_2, r_3, t) + \sum_{l'_1, l'_2, l'_3} \sum_i^3 W_{l_1 l_2 l_3, l'_1 l'_2 l'_3}^{\mathcal{L} \mathcal{L}_0}(r_i, t) \bar{P}_{l'_1 l'_2 l'_3}^{\mathcal{L}_0}(r_1, r_2, r_3) e^{-iE_0 t}, \quad (1)$$

where

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

and the coupling operators are found by reduction of

$$V_{l_1 l_2 l_3, l'_1 l'_2 l'_3}^{\mathcal{L}}(r_i, r_j) = \langle \langle (l_1, l_2)L, l_3 \rangle \mathcal{L} | (r_{ij})^{-1} \times | \langle (l'_1, l'_2)L', l'_3 \rangle \mathcal{L} \rangle \quad (3)$$

to expressions involving standard $3j$ and $6j$ symbols. The dipole radiation field coupling operators are also found by reduction of

$$W_{l_1 l_2 l_3, l'_1 l'_2 l'_3}^{\mathcal{L} \mathcal{L}_0}(r_i, t) = g(r_i) F(t) \langle \langle (l_1, l_2)L, l_3 \rangle \mathcal{L} | \tilde{\mathcal{C}}^1(i) \times | \langle (l'_1, l'_2)L', l'_3 \rangle \mathcal{L}_0 \rangle \quad (4)$$

to expressions involving standard $3j$ and $6j$ symbols. In Eq. (1) the function $\tilde{P}_{l'_1 l'_2 l'_3}^{\mathcal{L}_0}(r_1, r_2, r_3)$ represents the radial part of the fully correlated initial $^2S^e$ ground state, and $P_{l_1 l_2 l_3}^{\mathcal{L}}(r_1, r_2, r_3, t)$ represents the radial part of the fully correlated final state. The radial wave functions $\tilde{P}_{l'_1 l'_2 l'_3}^{\mathcal{L}_0}(r_1, r_2, r_3)$ are obtained by relaxation of the Schrödinger equation in imaginary time for a three-electron target atom. It was found that long relaxation times (up to 20 a.u.) were required to fully complete the relaxation to the ground state. The time dependence of the linearly polarized electric field amplitude, $F(t)$, is proportional to $\cos \omega t$, where ω is the radiation field frequency, while in the length gauge $g(r) = r$. The initial condition for the solution of the time-dependent close-coupling equations of Eq. (1) is given by

$$P_{l_1 l_2 l_3}^{\mathcal{L}}(r_1, r_2, r_3, t = 0) = 0. \quad (5)$$

The three-electron close-coupling equations of Eq. (1) are a generalization of two-electron close-coupling equations used before for photon double ionization of two-electron target atoms [18,19].

The time-dependent close-coupled equations of Eq. (1) are solved using standard numerical methods to obtain a discrete representation of the radial wave functions and all operators on a three dimensional lattice. Our specific implementation on massively parallel computers is to partition both the r_2 and r_3 coordinates over the many processors, so-called domain decomposition.

The probabilities for double or triple photoionization are obtained by $t \rightarrow \infty$ projection of the radial wave function onto fully antisymmetric spatial and spin functions, within double or triple summations over electron momenta (for double and triple photoionization, respectively), including the appropriate angular factors. For double photoionization (with excitation) the radial part of the projections is onto products of one bound nl state and two continuum states, where the continuum radial wave functions are obtained by diagonalization of

$$h(r) = -\frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{2r^2} + V(r), \quad (6)$$

where $V(r)$ is a Hartree-Slater potential that screens the Coulomb field. For triple photoionization the radial part of the projections are made onto products of three continuum radial wave functions which are obtained by diagonalization of Eq. (6) where now $V(r) = -\frac{Z}{r}$. Care must be taken in the sums over the electron momenta k_2, k_3 (double photoionization) or k_1, k_2, k_3 (triple photoionization) found in the photoionization probability expression. When the associated angular momenta are equal, for example, $l_1 = l_2$, the sums must be restricted to avoid double counting of distinct continuum states. More subtle is the unwanted contribution to the probability from the continuum correlation part of two-electron bound wave functions. This point has been discussed in detail by McCurdy *et al.* [20] in a study of the electron double ionization of an s -wave model He atom. We found that a simple restriction of the sums over the electron momenta, so that the conservation of energy

$$E_{\text{atom}} + E_{\text{projectile}} - E_{nl} = \frac{k_2^2}{2} + \frac{k_3^2}{2} \quad (7)$$

for double ionization leaving the ion in an nl state, and

$$E_{\text{atom}} + E_{\text{projectile}} = \frac{k_1^2}{2} + \frac{k_2^2}{2} + \frac{k_3^2}{2} \quad (8)$$

for triple ionization, was approximately conserved, greatly reduced contamination from the continuum piece of the two-electron bound state wave functions. In addition, this method of restricted momenta sums should become more accurate as the lattice size increases.

Finally, the photon double and triple ionization cross section is given by

$$\sigma_{\omega} = \frac{\omega}{I} \sum_{l_1, l_2, l_3, L, S} \frac{\partial \mathcal{P}_{l_1 l_2 l_3 L, (1/2)(1/2)S(1/2)}(t)}{\partial t} \Big|_{t \rightarrow \infty}, \quad (9)$$

where I is the intensity of the radiation field and \mathcal{P} is the total photoionization probability for either double or triple photoionization obtained previously. Care must also be taken in the sums over the quantum numbers associated with the fully antisymmetric spatial and spin wave functions to avoid double counting.

We first examined the photodouble and phototriple ionization of the $^2S^e$ ground state of lithium at various incident photon energies. A $(192)^3$ lattice was employed with each radial direction from $0.0 \rightarrow 19.2$ spanned by a uniform mesh with spacing $\Delta r = 0.10$ a.u. For the calculations presented here, 11 channels (up to and including $l = 2$) were used in the relaxation of the ground state, yielding a lattice energy of -198.35 eV. A list of channels for a given maximum l is in Table I. Our lattice energy is within 2% of the exact ground state Li energy. Including 23 channels (up to and including $l = 3$)

TABLE I. List of channels used in the relaxation of the $2S^e$ ground state of lithium.

max l	Channels	Total number of channels
1	$(ss)Ss, (sp)Pp, (ps)Pp, (pp)Ss$	4
2	$(sd)Dd, (ds)Dd, (dd)Ss, (pp)Dp, (pd)Pp, (dp)Pp, (dd)Dd$	11
3	$(sf)Ff, (fs)Ff, (ff)Ss, (pd)Ff, (dp)Ff, (pf)Dd, (fp)Dd, (df)Pp, (fd)Pp, (df)Ff, (fd)Ff, (ff)Dd$	23

changed the lattice energy to -198.45 eV, showing that our ground state energy is converged to around 0.1% of the exact ground state energy on the lattice. This shows that, due to our long relaxation times, all of the correlation in this system is very well represented. The difference with the exact Li ground state energy is almost entirely due to the kinetic energy terms in Eq. (1), which are determined largely by the lattice spacing.

Once a fully correlated ground state is obtained, the time-dependent close-coupling equations of Eq. (1) are propagated in real time for 5700 time steps or ten radiation field periods. Twenty-one channels (up to and including $l = 2$) were used to represent the final $2P^o$ state. Convergence checks were made on our calculations at selected energies by including up to 51 channels in the final state representation (up to and including $l = 3$). Projections onto as many as 16 fully antisymmetric spatial and spin states were then made to obtain the desired probabilities for double and triple photoionization.

The double ionization cross sections are plotted in Fig. 1. In (a) we compare the summed double ionization cross sections to the $1s$, $2s$, and $2p$ states of Li^{2+} with experimental synchrotron measurements [17] of Huang *et al.* It is clear that the time-dependent calculations are in excellent agreement with the measurements.

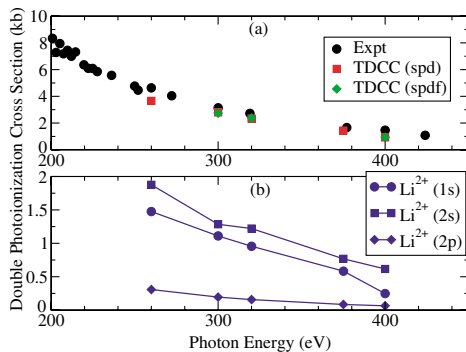


FIG. 1 (color online). Double photoionization cross sections for Li as a function of incident photon energy. (a) Two time-dependent calculations are shown: the first (squares) include all angular momentum channels $l \leq 2$ and the second (diamonds) include all angular momentum channels $l \leq 3$. The calculations are compared with the experimental measurements of Huang *et al.* [17]. The experimental measurements quote an uncertainty of 10%. (b) Partial double photoionization cross sections, leaving the Li^{2+} ion in one of three states as shown. ($1.0 \text{ kb} = 1.0 \times 10^{-21} \text{ cm}^2$).

Calculations with larger box sizes of 28.8 and 38.4 a.u. at a single energy point gave very similar cross sections, demonstrating good convergence with respect to box size. The results of the calculations which included all angular momenta channels up to and including $l = 3$ are represented in Fig. 1(a) by the diamonds. It is clear that the summed cross section changes only very slightly with the inclusion of these many extra channels. In Fig. 1(b) we show the partial double ionization cross section leaving the Li^{2+} ion in any one of the ($1s$), ($2s$), or ($2p$) states. We note that the time-dependent close-coupling calculations predict that double ionization to $\text{Li}^{2+}(1s)$ and to $\text{Li}^{2+}(2s)$ are roughly similar at around 1.5 to 2 times the complete fragmentation threshold of lithium. This allows us to draw some conclusions as to the nature of the mechanisms leading to the multiple ionization processes in Li.

Recent studies of multiple ionization processes in Li [15,21] have discussed a “shakeoff” model, in which the dominant mechanism is the double photoionization of the $1s^2$ core of Li, followed by the ionization of the remaining $2s$ electron via shakeoff for triple photoionization. If this were indeed the case, in the region of interest of 300–400 eV, one would expect the double ionization leaving the Li^{2+} ion in its $2s$ state to be much more probable than double ionization leaving the Li^{2+} ion in its $1s$ state. Our calculations, presented in Fig. 1(b), show clearly that the magnitudes of the cross sections leaving the ion in either the $1s$ or $2s$ state are almost equal. Therefore, another mechanism must also contribute strongly to the double (and triple) ionization process. An alternative mechanism may be based on internal scattering by the fast electron following photoabsorption, where the photon initially ionizes a $1s$ or $2s$ electron, which then collides with the remaining two electrons and ionizes one (or both) electrons for double (or triple) ionization. This double ionization mechanism would account for some of the Li^{2+} ions remaining in the $1s$ state. Of course these two quantum-mechanical processes may also interfere and this can also contribute to the double and triple ionization cross sections. Thus it is essential to have both processes included explicitly in any calculation.

Finally, in Fig. 2 we present the triple ionization cross section of Li and compare it with experimental synchrotron measurements [15]. In this case, we find that our larger time-dependent calculations (diamonds), which included channels with $l \leq 3$, are significantly higher than the time-dependent calculations (squares) which include channels up to and including $l \leq 2$. This is unlike

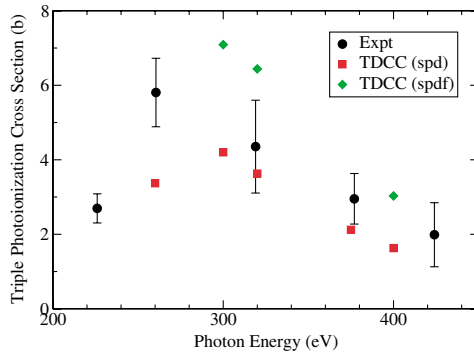


FIG. 2 (color online). Triple photoionization cross sections for Li as a function of incident photon energy. Again, two time-dependent calculations are shown; the first (squares) include all angular momentum channels $l \leq 2$ and the second (diamonds) include all angular momentum channels $l \leq 3$. The calculations are compared with the experimental measurements of Wehlitz *et al.* [15]. ($1.0 b = 1.0 \times 10^{-24} \text{ cm}^2$.)

the double ionization calculations, which were well converged with respect to the number of channels. This shows that the triple ionization quantity is much more difficult to converge, chiefly because of the very small nature of the absolute cross section (in barns). It can often be more difficult to obtain numerical convergence in calculations of very small quantities. It is possible that larger radial meshes may increase the level of convergence of these calculations. We await larger computational resources to confirm these calculations. Our calculations are supported by the experimental measurements, which in general fall between our two sets of time-dependent calculations. We note that the measurements themselves show large error bars, reflecting also the difficulty in measuring these extremely small quantities. However, it is significant that our theoretical calculations and the experimental measurements are in very good agreement as to the magnitude of the triple photoionization cross section for Li. We also note that our calculations are in good agreement with the theoretical calculations presented by [16] based on a “half-collision” model for multiple photoionization.

In conclusion we find that a nonperturbative lattice solution of the time-dependent Schrödinger equation appears capable of yielding accurate cross sections for Coulomb four-body breakup. For double photoionization of Li, our calculations are in very good agreement with

the measurements of Huang *et al.* [17]. We have also, for the first time, given values of the partial double ionization cross section leaving the Li^{2+} ion in selected states. Our calculations of triple photoionization cross sections are in good agreement with experimental measurements [15]. We are also continuing our complementary calculations on electron-He ionization, where again all three electrons are treated on an equal footing.

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