INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **39** (2006) L127–L131 doi:10.1088/0953-4075/39/6/L04

LETTER TO THE EDITOR

Electron-impact double ionization of H^-

M S Pindzola[1], F Robicheaux[1] and J Colgan[2]

[1] Department of Physics, Auburn University, Auburn, AL 36849, USA
[2] Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Received 30 January 2006, in final form 10 February 2006
Published 27 February 2006

Abstract
Electron-impact double ionization cross sections for H^- are calculated using a non-perturbative time-dependent close-coupling theory. The total wavefunction for the three-electron system is represented by a coupled channels expansion involving simple products of three-dimensional radial lattices and six-dimensional coupled spherical harmonics. Following time evolution of the total wavefunction according to the Schrödinger equation, collision probabilities are found by projection of the total wavefunction onto fully antisymmetric products of spatial and spin functions representing three outgoing Coulomb waves. The completely *ab initio* double ionization cross section results for H^- are found to be more than a factor of 5 below the experimental measurements of Peart *et al* (1971 *J. Phys. B: At. Mol. Phys.* **4** 88) and in excellent agreement with the experimental measurements of Yu *et al* (1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 4593).

In the last couple of years, a time-dependent close-coupling method has been developed to treat three continuum electrons moving in the field of a charged core, that is Coulomb four-body breakup. This non-perturbative method has produced *ab initio* cross sections for the triple photoionization of Li [1] that are in excellent agreement with synchrotron light source experiments [2] and for the electron-impact double ionization of He [3] that are in excellent agreement with crossed-beams experiments [4]. The time-dependent close-coupling method has also been used to predict double photoionization with excitation and triple photoionization cross sections for Li and Be [5], as well as to investigate the double autoionization of triply excited hollow atom states of Li [6].

In this letter, we apply the time-dependent close-coupling method developed for Coulomb four-body breakup to the electron-impact double ionization of H^- in an attempt to resolve a long-standing disagreement between experimental measurements. The early crossed-beams experimental measurements of Peart *et al* [7] for the double ionization cross section of H^- peaked at 50 Mb (1.0 Mb = 1.0×10^{-18} cm^2) around 50 eV incident electron energy. Subsequent perturbative Born calculations [8] found a peak cross section of about 35 Mb. Two decades later the crossed-beams experimental measurements of Yu *et al* [9] for the double ionization of H^- found a peak cross section of about 10 Mb. More recent perturbative Born calculations [10] report peak cross sections substantially below the Yu *et al* [9] experimental measurements. Depending on the description of the final state, the recent Born results vary from 0.01 Mb to 0.50 Mb at the peak of the cross section.

In the ensuing paragraphs, we first review the time-dependent close-coupling (TDCC) theory, then compare the theoretical cross sections with the experiments and then conclude with a brief summary. Unless otherwise stated, all quantities are given in atomic units.

The fully correlated wavefunction, Φ^L, for the ground state of a two-electron target atom is obtained by relaxation of the time-dependent Schrödinger equation in imaginary time ($\tau = \mathrm{i}t$):

$$-\frac{\partial \Phi^L(\vec{r}_1, \vec{r}_2, \tau)}{\partial \tau} = H_{\mathrm{target}} \Phi^L(\vec{r}_1, \vec{r}_2, \tau), \tag{1}$$

where the non-relativistic Hamiltonian is given by

$$H_{\mathrm{target}} = \sum_i^2 \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \tag{2}$$

and Z is the atomic number. The fully correlated wavefunction, $\Psi^{\mathcal{L}}$, for electron scattering from a two-electron target atom is obtained by evolution of the time-dependent Schrödinger equation in real time:

$$\mathrm{i}\frac{\partial \Psi^{\mathcal{L}}(\vec{r}_1, \vec{r}_2, \vec{r}_3, t)}{\partial t} = H_{\mathrm{system}} \Psi^{\mathcal{L}}(\vec{r}_1, \vec{r}_2, \vec{r}_3, t), \tag{3}$$

where the non-relativistic Hamiltonian is given by

$$H_{\mathrm{system}} = \sum_i^3 \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j}^3 \frac{1}{|\vec{r}_i - \vec{r}_j|}. \tag{4}$$

The total wavefunction, Φ^L, for the two-electron target is represented by a coupled channels expansion involving simple products of two-dimensional radial functions, $P^L_{l_1 l_2}(r_1, r_2, \tau)$, and four-dimensional coupled spherical harmonics, while the total wavefunction, $\Psi^{\mathcal{L}}$, for the three-electron scattering system is represented by a coupled channels expansion involving simple products of three-dimensional radial functions, $P^{\mathcal{L}}_{l_1 l_2 L l_3}(r_1, r_2, r_3, t)$, and six-dimensional coupled spherical harmonics. Angular reduction of the time-dependent Schrödinger equations, equations (1) and (3), results in a coupled set of partial differential equations for the radial expansion functions, $P^L_{l_1 l_2}(r_1, r_2, \tau)$ and $P^{\mathcal{L}}_{l_1 l_2 L l_3}(r_1, r_2, r_3, t)$ (see [3] for more details). The resulting time-dependent close-coupled (TDCC) equations are solved by standard numerical methods to obtain a discrete representation of the radial functions and all operators on either two- or three-dimensional lattices. Our implementation on massively parallel computers is complete domain decomposition by partition over all r_i coordinates.

At time $\tau = 0$, the two-dimensional radial functions for an $L = 0$ target are given by

$$P^S_{l_1 l_2}(r_1, r_2, \tau = 0) = \sum_{l_1, l_2} P_{1s}(r_1) P_{1s}(r_2) \delta_{l_1,0} \delta_{l_2,0}, \tag{5}$$

where $P_{1s}(r)$ is a radial solution of a Z hydrogenic one-electron target. At the end of the relaxation of equation (1), the radial expansion coefficients for the fully correlated target wavefunction are given by

$$\bar{P}^S_{ll}(r_1, r_2) = P^S_{ll}(r_1, r_2, \tau \to \infty), \tag{6}$$

where $l \geqslant 0$. At time $t = 0$, the radial expansion coefficients for the fully correlated initial wavefunction of the scattering system are given by

$$P^{\mathcal{L}}_{l_1 l_2 L l_3}(r_1, r_2, r_3, t = 0) = \sum_{l} \bar{P}^{S}_{ll}(r_1, r_2) G_{k_0 \mathcal{L}}(r_3) \delta_{l_1,l} \delta_{l_2,l} \delta_{L,0} \delta_{l_3,\mathcal{L}}, \tag{7}$$

where the Gaussian radial wave packet, $G_{k_0\mathcal{L}}(r)$, has a propagation energy of $\frac{k_0^2}{2}$. At the end of the evolution of equation (3), the probabilities for electron-impact double ionization of a two-electron target are obtained by projection of a simple product of $\Psi^{\mathcal{L}}(\vec{r}_1, \vec{r}_2, \vec{r}_3, t)$ and a total doublet spin function onto fully antisymmetric products of spatial and spin functions representing three outgoing Z hydrogenic Coulomb waves. The partial-wave double ionization probability is given by

$$\mathcal{P}^{2\mathcal{L}}_{\text{double}} = \sum_{l_1,l_2,L,l_3} \sum_{s_1,s_2,S,s_3} \int_0^\infty \mathrm{d}k_1 \int_0^\infty \mathrm{d}k_2 \int_0^\infty \mathrm{d}k_3 \left| \mathcal{P}^{2\mathcal{L}}_{l_1 l_2 L l_3, s_1 s_2 S s_3}(k_1, k_2, k_3) \right|^2. \tag{8}$$

The partial-wave momentum space probabilities, $\mathcal{P}^{2\mathcal{L}}_{l_1 l_2 L l_3, s_1 s_2 S s_3}(k_1, k_2, k_3)$, are given in terms of angular and spin factor combinations of the six possible permutations of the momentum space function:

$$R(ijk) = \int_0^\infty \mathrm{d}r_1 \int_0^\infty \mathrm{d}r_2 \int_0^\infty \mathrm{d}r_3 \, P_{k_1 l_1}(r_i) P_{k_2 l_2}(r_j) P_{k_3 l_3}(r_k) P^{\mathcal{L}}_{l_1 l_2 L l_3}(r_i, r_j, r_k, t \to \infty), \tag{9}$$

where $P_{kl}(r)$ are radial Z hydrogenic Coulomb waves and $s_1 = s_2 = s_3 = \frac{1}{2}$ (see [3] for more details). We note that the coupled channel expansion over quantum numbers $l_1 l_2 L l_3$ for $\Psi^{\mathcal{L}}(\vec{r}_1, \vec{r}_2, \vec{r}_3, t)$ is different from the summation over projection quantum numbers $l_1 l_2 L l_3, s_1 s_2 S s_3$ for $\mathcal{P}^{2\mathcal{L}}_{\text{double}}$. In addition, a simple restriction of the sums over the electron momenta, k_i, so that the conservation of energy,

$$E_{\text{atom}} + \frac{k_0^2}{2} = \frac{k_1^2}{2} + \frac{k_2^2}{2} + \frac{k_3^2}{2}, \tag{10}$$

is approximately conserved, greatly reduces the contamination from the continuum piece of the two-electron bound state wavefunctions. Finally, the electron-impact double ionization cross section is given by

$$\sigma_{\text{double}} = \frac{\pi}{2k_0^2} \sum_{\mathcal{L}} 2(2\mathcal{L} + 1) \mathcal{P}^{2\mathcal{L}}_{\text{double}}. \tag{11}$$

The electron-impact double ionization cross sections for the ^{1}S ground state of H$^-$ were calculated at three incident electron energies near the peak of the cross section, as indicated by experimental measurements. Bound and continuum radial wavefunctions of a $Z = 1$ hydrogenic one-electron atom were obtained by matrix diagonalization of the Hamiltonian:

$$h(r) = -\frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r}. \tag{12}$$

The ground-state energy for a mesh spacing of $\Delta r = 0.2$ is found to be -13.47 eV, as compared to the analytic value of -13.61 eV. Relaxation of the time-dependent Schrödinger equation of equation (1) employed a $(192)^2$ point lattice with each radial direction from $0.0 \to 38.4$ spanned by a uniform mesh with spacing of $\Delta r = 0.2$. The ground-state energy of H$^-$ on the lattice is found to be -14.18 eV, using three coupled channels (ss, pp and dd). Thus, the ionization potential on the lattice is 0.71 eV, which compares well to the experimental value of 0.75 eV. Evolution of the time-dependent Schrödinger equation of equation (3) employed a $(192)^3$ point lattice with again a mesh spacing in all directions of $\Delta r = 0.2$. Initially, the radial wave packets of equation (7) were centred at $r_3 = 19.2$ with a coordinate space spread

Table 1. Electron-impact double ionization partial-wave and total cross sections for H^-, as calculated by the time-dependent close-coupling (TDCC) method, at various incident electron energies. All cross sections are in Mb (1.0 Mb = 1.0×10^{-18} cm^2).

$\mathcal{L}$	Close-coupling channels	Projection functions	TDCC 40 eV	TDCC 50 eV	TDCC 60 eV
0	11	10	0.23	0.27	0.28
1	21	16	0.62	0.62	0.59
2	23	22	0.97	0.98	0.92
3	49	30	1.30	1.40	1.34
4	63	38	1.45	1.57	1.51
5	87	46	1.04	1.30	1.35
Sub-total			5.61	6.14	5.99
Top-up			1.36	1.81	1.93
Total			6.97	7.95	7.92

of 4.8. Depending on the incident energies and total angular momenta, $\mathcal{L}$, the evolution of the time-dependent Schrödinger equation of equation (3) involved up to a maximum of 7600 time steps.

Partial-wave double ionization cross sections for H^- are presented in table 1. The number of coupled channels and projection functions are indicated in columns 2 and 3, respectively, for each total angular momentum. For example, for $\mathcal{L} = 0$, we used 11 coupled channels ((ss)Ss, (sp)Pp, (ps)Pp, (pp)Ss, (sd)Dd, (ds)Dd, (dd)Ss, (pp)Dd, (pd)Pp, (dp)Pp, and (dd)Dd) and 10 projection functions ((ss)^{1}Ss, (ss)^{3}Ss, (sp)^{1}Pp, (sp)^{3}Pp, (sd)^{1}Dd (sd)^{3}Dd, (pp)^{1}Dd, (pp)^{3}Dd, (dd)^{1}Dd, and (dd)^{3}Dd). The number of coupled channels and projection functions for $\mathcal{L} = 0$ to $\mathcal{L} = 5$ are identical to those used in earlier TDCC calculations for the electron-impact double ionization of He [3]. We note that the partial-wave double ionization cross sections for H^- are approximately 50 times larger than the partial-wave double ionization cross sections for He at incident energies near the peak of the cross section.

To obtain total cross sections, we must extrapolate our time-dependent close-coupling results to higher angular momentum $\mathcal{L}$. Luckily, the partial-wave cross sections found in table 1, for all incident electron energies, climb to a peak at $\mathcal{L} = 4$ and then fall off for $\mathcal{L} = 5$. In extrapolating the time-dependent results to larger $\mathcal{L}$, we chose a fitting function of the form

$$f(\mathcal{L}) = (A + B\mathcal{L} + C\mathcal{L}^2)\,\mathrm{e}^{-\mathcal{L}}, \tag{13}$$

where A, B and C are varied over an angular momentum range from $\mathcal{L} = 2$ to $\mathcal{L} = 5$. The ratio of the 'top-up' found from the extrapolation to our final 'total' cross section ranges from 20% at 40 eV to 24% at 60 eV. We also used a second fitting function of the form

$$f(\mathcal{L}) = A(\mathcal{L} - \mathcal{L}_0)^n\,\mathrm{e}^{-B\mathcal{L}}, \tag{14}$$

where A, $\mathcal{L}_0$, n and B are varied over an angular momentum range from $\mathcal{L} = 0$ to $\mathcal{L} = 5$. The total cross sections obtained from the second fitting function differed from those reported in table 1 from the first fitting function by around 5%.

Total electron-impact double ionization cross sections for H^- are shown in figure 1. The time-dependent close-coupling results are shown as filled squares, the experimental measurements of Peart *et al* [7] are open circles with error bars and the experimental measurements of Yu *et al* [9] are open diamonds with error bars. The TDCC results are found to be more than a factor of 5 below the Peart *et al* [7] measurements and in excellent

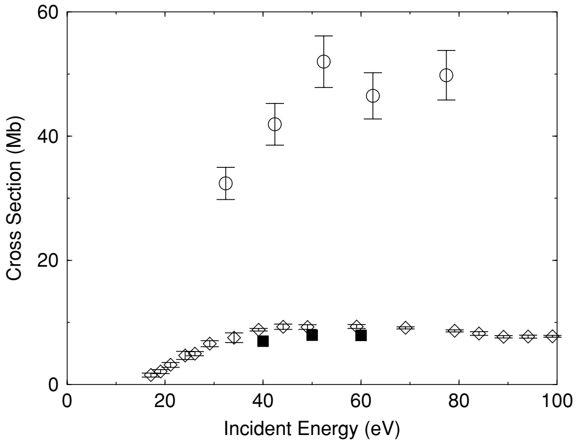

Figure 1. Electron-impact double ionization cross section for H$^-$. Solid squares: time-dependent close-coupling method, open circles: crossed-beams experiment [7], open diamonds: crossed-beams experiment [9] (1 Mb = 10^{-18} cm^2).

agreement with the Yu *et al* [9] measurements. The extension of the TDCC calculations to lower energies will require a larger radial lattice, while an extension to higher energies will require the inclusion of higher $\mathcal{L}$ partial waves with a larger number of coupled channels.

In summary, a time-dependent close-coupling method, formulated to solve Coulomb four-body breakup problems, has been used to calculate the electron-impact double ionization cross section for H$^-$. The non-perturbative TDCC results are found to be in excellent agreement with the most recent crossed-beams experimental measurements of Yu *et al* [9], helping to resolve a long-standing experimental discrepancy. In the future, we plan to continue the development of the TDCC method so that it can be applied to other few-body Coulomb breakup problems.

Acknowledgments

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 and at the National Center for Computational Sciences in Oak Ridge, Tennessee.

References

[1] Colgan J, Pindzola M S and Robicheaux F 2004 *Phys. Rev. Lett.* **93** 053201
[2] Wehlitz R, Huang M-T, DePaola B D, Levin J C, Sellin I A, Nagata T, Cooper J W and Azuma Y 1998 *Phys. Rev. Lett.* **81** 1813
[3] Pindzola M S, Robicheaux F, Colgan J P, Witthoeft M C and Ludlow J A 2004 *Phys. Rev.* A **70** 032705
[4] Shah M B, Elliott D S, McCallion P and Gilbody H B 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 2751
[5] Colgan J, Pindzola M S and Robicheaux F 2005 *Phys. Rev.* A **72** 022727
[6] Pindzola M S, Robicheaux F and Colgan J 2005 *Phys. Rev.* A **72** 022709
[7] Peart B, Walton D S and Dolder K T 1971 *J. Phys. B: At. Mol. Phys.* **4** 88
[8] Tweed R J 1973 *J. Phys. B: At. Mol. Phys.* **6** 270
[9] Yu D J, Rachafi S, Jureta J and Defrance P 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 4593
[10] Defrance P, Kereselidze T M, Machavariani Z S and Noselidze I L 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** 4323