

LETTER TO THE EDITOR

Time-dependent close-coupling calculations for the double photoionization of He and H₂

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Abstract

Photoionization cross sections for both atomic helium and molecular hydrogen are calculated using a time-dependent close-coupling method. The total electronic wavefunction for the two-electron system is expanded in six dimensions, where four dimensions are represented on a radial and angular lattice and a coupled channels expansion is used to represent the other two dimensions. Double photoionization cross sections are obtained for both He and H₂ for a range of photon energies above the complete fragmentation threshold. Comparisons are made with absolute experimental measurements.

In recent years much progress has been made in the solution of the three-body Coulomb problem by several theoretical techniques. The double screened Coulomb [1, 2], convergent close-coupling [3, 4], hyperspherical *R*-matrix with semi-classical outgoing waves [5, 6], time-dependent close-coupling (TDCC) [7, 8], and exterior complex-scaling [9] methods have all calculated total, single and triple differential cross sections for the double photoionization of helium, the simplest Coulomb three-body system. This theoretical effort has been matched by important experimental advances in the last 10–15 years. Accurate measurements of the total cross section for double photoionization of helium [10] have been obtained and many measurements have now been made of the triple differential cross sections arising from the double photoionization of helium [11–14].

These experimental measurements of the triple differential cross sections have also been extended to examine the differential cross sections arising from the double photoionization of H₂ (or, equivalently, D₂) [15–17], i.e. the four-body Coulomb problem. Total cross section measurements for the double photoionization of H₂ were measured in the 1980s first by Dujardin *et al* [18] and subsequently by Kossman *et al* [19]. However, it is notable that these experimental efforts have not really been matched by corresponding theoretical work. Early calculations on the double photoionization of H₂ were made by Le Rouzo [20, 21]

and the high-energy asymptotic limit of the ratio of double-to-single photoionization of H_2 was calculated by Sadeghpour and Dalgarno [22]. However, apart from some qualitative studies of the angular distribution of the electrons arising from double photoionization of H_2 by Walter and Briggs [23, 24], using a shape amplitude representation of the photoionization process and a 3C final-state wavefunction, there has been little theoretical work to match the experimental measurements. This is no doubt due to the increased complexity of the molecular system, where the non-spherical nature of the potential removes an important symmetry from the problem. Also, there are dynamics in molecular photoionization that do not exist in the atomic case, such as the possible vibrational and rotational motion of the nuclei.

In this letter, we present a time-dependent close-coupling method which is capable of calculating the double photoionization cross section for both He and H_2 . We build on our previous time-dependent studies of the photoionization of the one-electron system H_2^+ [25], by expanding the electronic wavefunction on a numerical lattice in both radius and angle. In our calculations for H_2 we employ the Born–Oppenheimer approximation, so that the nuclei are assumed fixed in space. For photoionization processes well above the complete fragmentation threshold, this should be a good approximation, since the double photoionization process is typically rapid on the nuclear motion time scale, especially at higher photon energies. We do note however a recent study [26] which indicates the possible breakdown of this approximation and of the importance of the nuclear motion. Studies to include the nuclear motion are currently being considered. Unless otherwise stated, all quantities are given in atomic units.

In the weak-field perturbative limit, the photoionization of the He atom or the H_2 molecule may be found by solving the time-dependent Schrödinger equation [7]:

$$i \frac{\partial \psi(\vec{r}_1, \vec{r}_2, t)}{\partial t} = H \psi(\vec{r}_1, \vec{r}_2, t) + V \psi_0(\vec{r}_1, \vec{r}_2) e^{-iE_0 t}, \quad (1)$$

where H is the atomic or molecular Hamiltonian, V is the time-dependent radiation field Hamiltonian, and ψ_0 and E_0 are the exact eigenfunction and eigenenergy of the atomic or molecular ground state. Due to the reduced symmetry of the molecular case, the time-dependent wavefunction for a given MS symmetry is expanded in products of rotation functions:

$$\psi(\vec{r}_1, \vec{r}_2, t) = \sum_{m_1, m_2} \frac{P_{m_1 m_2}^M(r_1, \theta_1, r_2, \theta_2, t)}{r_1 r_2 \sqrt{\sin \theta_1} \sqrt{\sin \theta_2}} \Phi_{m_1}(\phi_1) \Phi_{m_2}(\phi_2), \quad (2)$$

where $\Phi_m(\phi) = \frac{e^{im\phi}}{\sqrt{2\pi}}$ and $M = m_1 + m_2$. For the spherically symmetric atomic case, the time-dependent wavefunction may also be expanded in products of coupled spherical harmonics, as has been used previously with great success [7]. Upon substitution of equation (2) into equation (1) and application of the variational principle, the time-dependent close-coupled partial differential equations are given by

$$i \frac{\partial P_{m_1 m_2}^M(r_1, \theta_1, r_2, \theta_2, t)}{\partial t} = T_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2) P_{m_1 m_2}^M(r_1, \theta_1, r_2, \theta_2, t) + \sum_{m'_1, m'_2} V_{m_1 m_2, m'_1 m'_2}^M(r_1, \theta_1, r_2, \theta_2) P_{m'_1 m'_2}^M(r_1, \theta_1, r_2, \theta_2, t) + \sum_{m''_1, m''_2} W_{m_1 m_2, m''_1 m''_2}^{MM_0}(r_1, \theta_1, r_2, \theta_2, t) \bar{P}_{m''_1 m''_2}^{M_0}(r_1, \theta_1, r_2, \theta_2) e^{-iE_0 t}, \quad (3)$$

where

$$T_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2) = \sum_i^2 \left(K(r_i, \theta_i) + \frac{m_i^2}{2r_i^2 \sin^2 \theta_i} - \frac{1}{\sqrt{r_i^2 + \frac{1}{4}R^2 - r_i R \cos \theta_i}} - \frac{1}{\sqrt{r_i^2 + \frac{1}{4}R^2 + r_i R \cos \theta_i}} \right), \quad (4)$$

$K(r, \theta)$ is the kinetic energy operator, and R is the internuclear separation. For the He atom we set $R = 0.0$, while for the H_2 molecule we set $R = 1.4$. In equation (3) $P_{m_1 m_2}^M(r_1, \theta_1, r_2, \theta_2, t)$ are the reduced wavefunctions for $\psi(\vec{r}_1, \vec{r}_2, t)$ and $\bar{P}_{m_1' m_2'}^{M_0}(r_1, \theta_1, r_2, \theta_2)$ are the reduced wavefunctions for $\psi_0(\vec{r}_1, \vec{r}_2)$. The Coulomb interaction coupling operator is found by the reduction of

$$\begin{aligned} V_{m_1 m_2, m_1' m_2'}^M(r_1, \theta_1, r_2, \theta_2) &= \langle (m_1, m_2)M | (r_{12})^{-1} | (m_1', m_2')M \rangle \\ &= \sum_{\lambda} \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \sum_q \frac{(\lambda - |q|)!}{(\lambda + |q|)!} P_{\lambda}^{|q|}(\cos \theta_1) P_{\lambda}^{|q|}(\cos \theta_2) \\ &\quad \times \langle (m_1, m_2)M | e^{iq(\phi_2 - \phi_1)} | (m_1', m_2')M \rangle, \end{aligned} \quad (5)$$

where $P_{\lambda}^{|q|}(\cos \theta)$ is an associated Legendre function. The radiation field coupling operator, for linear polarization with respect to the internuclear axis, is found by the reduction of

$$W_{m_1 m_2, m_1' m_2'}^{MM_0}(r_1, \theta_1, r_2, \theta_2, t) = E(t) \cos \omega t \langle (m_1, m_2)M | \sum_i^2 r_i \cos \theta_i | (m_1', m_2')M_0 \rangle, \quad (6)$$

while, for circular polarization with respect to the internuclear axis, is found by the reduction of

$$W_{m_1 m_2, m_1' m_2'}^{MM_0}(r_1, \theta_1, r_2, \theta_2, t) = \frac{E(t)}{\sqrt{2}} \cos \omega t \langle (m_1, m_2)M | \sum_i^2 r_i \sin \theta_i e^{i\phi_i} | (m_1', m_2')M_0 \rangle, \quad (7)$$

where ω is the radiation field frequency. We note that for linear polarization $M = M_0$, while for circular polarization $M = M_0 + 1$. The electric field amplitude, $E(t)$, is slowly ramped on to its final value to avoid ringing effects in the time evolution of equation (3). Since exact wavefunctions are employed in the time evolution, we expect our cross section results to be radiation field gauge invariant, as found in previous time-dependent close-coupling studies of the photoionization of the He atom [7]. Finally, the exact eigenfunction for the He or H_2 ground state is obtained by relaxation of the Schrödinger equation in imaginary time ($\tau = it$):

$$-\frac{\partial \psi_0(\vec{r}_1, \vec{r}_2, \tau)}{\partial \tau} = H \psi_0(\vec{r}_1, \vec{r}_2, \tau). \quad (8)$$

The total wavefunction is again expanded in products of rotation functions and substituted into equation (8), yielding a set of close-coupled partial differential equations in space and imaginary time.

We solve the time-dependent close-coupling equations using lattice techniques to obtain a discrete representation of the reduced wavefunctions and all operators on a four-dimensional radial and angular grid. For example, a low-order finite difference representation of the kinetic energy operator is given by [25]:

$$\begin{aligned} (K(r, \theta)P(r, \theta, r', \theta', t))_{i,j,i',j'} &= -\frac{1}{2} \left(\frac{c_i P_{i+1,j,i',j'}(t) + c_{i-1} P_{i-1,j,i',j'}(t) - \bar{c}_i P_{i,j,i',j'}(t)}{\Delta r^2} \right) \\ &\quad - \frac{1}{2r_i^2} \left(\frac{d_j P_{i,j+1,i',j'}(t) + d_{j-1} P_{i,j-1,i',j'}(t) - \bar{d}_j P_{i,j,i',j'}(t)}{\Delta \theta^2} \right), \end{aligned} \quad (9)$$

where the variationally derived coefficients are given by $c_i = \frac{r_{i+1/2}^2}{r_i r_{i+1}}$, $\bar{c}_i = \frac{(r_{i+1/2}^2 + r_{i-1/2}^2)}{r_i^2}$, $d_j = \frac{\sin \theta_{j+1/2}}{\sqrt{\sin \theta_j \sin \theta_{j+1}}}$ and $\bar{d}_j = \frac{(\sin \theta_{j+1/2} + \sin \theta_{j-1/2})}{\sin \theta_j}$. Our implementation on massively parallel computers is to partition the radial coordinates (r_1, r_2) over the many processors, so-called domain decomposition. Both explicit and implicit algorithms are used to time propagate the close-coupled equations.

The total cross section for single photoionization leaving the atom or molecule in a specific bound state is given by

$$\sigma_{nlm} = \frac{\omega}{I} \frac{\partial \mathcal{P}_{nlm}}{\partial t}, \quad (10)$$

where I is the intensity of the radiation field. The single ionization probability is given by

$$\begin{aligned} \mathcal{P}_{nlm} = & \sum_{m'} \int_0^\infty dr_1 \int_0^\pi d\theta_1 \left[\int_0^\infty dr_2 \int_0^\pi d\theta_2 P_{m'm}^M(r_1, \theta_1, r_2, \theta_2, T) P_{nl|m|}(r_2, \theta_2) \right]^2 \\ & - \sum_{n', l', m'} \left[\int_0^\infty dr_1 \int_0^\pi d\theta_1 \int_0^\infty dr_2 \int_0^\pi d\theta_2 \right. \\ & \times \left. P_{m'm}^M(r_1, \theta_1, r_2, \theta_2, T) P_{n'l'|m'|}(r_1, \theta_1) P_{nl|m|}(r_2, \theta_2) \right]^2 \\ & + \sum_{m'} \int_0^\infty dr_2 \int_0^\pi d\theta_2 \left[\int_0^\infty dr_1 \int_0^\pi d\theta_1 P_{m'm}^M(r_1, \theta_1, r_2, \theta_2, T) P_{nl|m|}(r_1, \theta_1) \right]^2 \\ & - \sum_{n', l', m'} \left[\int_0^\infty dr_1 \int_0^\pi d\theta_1 \int_0^\infty dr_2 \int_0^\pi d\theta_2 \right. \\ & \times \left. P_{m'm}^M(r_1, \theta_1, r_2, \theta_2, T) P_{nl|m|}(r_1, \theta_1) P_{n'l'|m'|}(r_2, \theta_2) \right]^2, \quad (11) \end{aligned}$$

where the two-electron reduced wavefunctions, $P_{mm'}^M(r_1, \theta_1, r_2, \theta_2, T)$, are evaluated at an asymptotic time T following the collision, and the one-electron reduced wavefunctions, $P_{nl|m|}(r, \theta)$, are obtained by direct diagonalization of the one electron atomic or molecular Hamiltonian. The total cross section for double photoionization is given by

$$\sigma_{\text{dion}} = \frac{\omega}{I} \frac{\partial \mathcal{P}_{\text{dion}}}{\partial t}. \quad (12)$$

The double ionization probability is given by

$$\begin{aligned} \mathcal{P}_{\text{dion}} = & \langle \psi(t) | \psi(t) \rangle - \sum_{nlm} \mathcal{P}_{nlm} - \sum_{n, l, m} \sum_{n', l', m'} \left[\int_0^\infty dr_1 \int_0^\pi d\theta_1 \int_0^\infty dr_2 \int_0^\pi d\theta_2 \right. \\ & \times \left. P_{mm'}^M(r_1, \theta_1, r_2, \theta_2, T) P_{nl|m|}(r_1, \theta_1) P_{n'l'|m'|}(r_2, \theta_2) \right]^2. \quad (13) \end{aligned}$$

We note that this projection is of the final, time-propagated, fully correlated wavefunction onto products of one-electron ionic states. This projection can only be made after the wavefunction has sufficiently evolved in time. We further note that this projection technique has produced total, single and triple differential cross sections for the double photoionization of He which are in excellent agreement with other theoretical work and many experimental measurements. The key to whether this projection technique onto one-electron ionic states is valid lies in the ratio of the potential to kinetic energy of the electrons at large distances from the interaction. At a sufficiently large distance this ratio is small, so that the projection onto ionic states, which

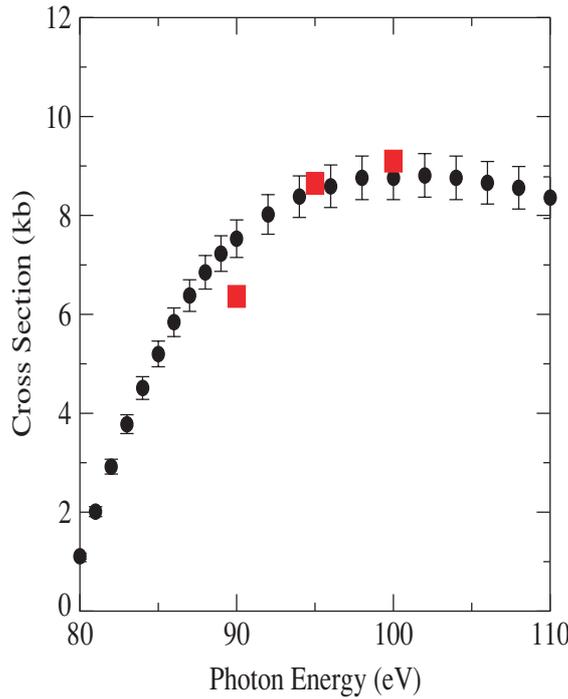


Figure 1. Double photoionization cross sections for He. The new time-dependent close-coupling calculations (squares) are compared with the experimental measurements of Samson *et al* [10]. (1.0 kb = 1.0×10^{-21} cm²).

can be thought of as accessing the kinetic energy portion of the wavefunction, is valid. For lower energies near threshold the kinetic energy is smaller so a larger mesh is necessary.

We use the new time-dependent close-coupling method, outlined above, to calculate the double photoionization cross sections for both He ($R = 0.0$) and H₂ ($R = 1.4$). We employ a $288 \times 288 \times 32 \times 32$ point lattice with a uniform radial mesh spacing of $\Delta r = 0.2$ from 0 to 57.6 in both r_1 and r_2 and a uniform angular mesh spacing of $\Delta\theta = 0.03125\pi$ from 0 to π in both θ_1 and θ_2 . Changing the mesh spacing for the θ coordinates made little difference to our calculations. Also, these calculations were very similar to those made with a smaller lattice of $192 \times 192 \times 16 \times 16$ points. The calculations were made at an intensity of 10^{15} W cm⁻². It was found that changing this intensity did not affect our cross sections significantly. For relaxation of the Schrödinger equation in imaginary time, five coupled channels are employed for the $M = 0$ symmetry of the ground states of He and H₂, resulting in correlated states on the lattice with energies within 2% of the infinite lattice limit. For propagation of the Schrödinger equation in real time, five coupled channels are employed for the $M = 0$ symmetry found in the linear polarized case and six coupled channels are employed for the $M = 1$ symmetry found in the circular polarized case. Increasing the number of coupled channels retained in this expansion made a difference of no more than 2% for the calculations presented here, demonstrating convergence of our calculations. The real-time close-coupled equations are propagated for ten radiation field periods. The time-dependent radial wavefunctions are projected onto one-electron wavefunctions following equations (11) and (13) at each time period. Convergence of collision probabilities is found after eight or nine time periods.

The double photoionization cross section results for He are shown in figure 1. As expected for the atomic case, the linear and circular polarized cross sections for He are found to be

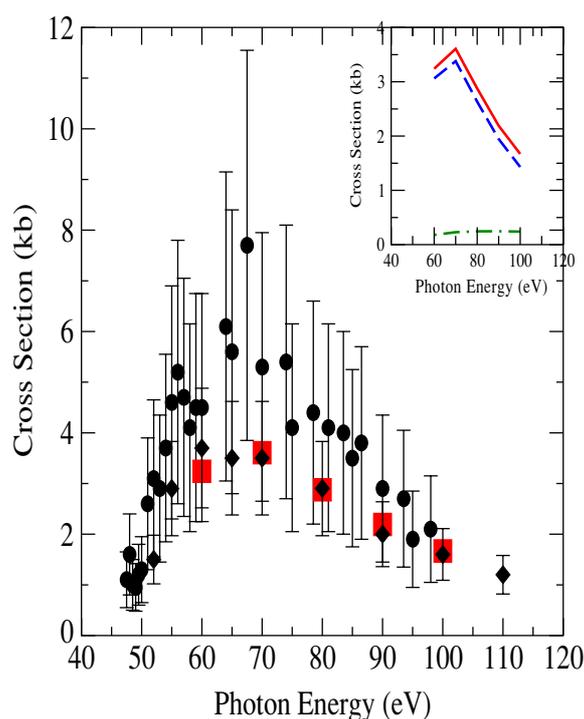


Figure 2. Double photoionization cross sections for H₂. The new time-dependent close-coupling calculations (squares) are compared with the experimental measurements of Dujardin *et al* [18] (circles) and the measurements of Kossman *et al* [19] (diamonds). The inset shows the contribution to the total double photoionization cross section (solid line) from the circular polarized cross section (dashed) and the linear polarized cross section (dot-dashed). (1.0 kb = 1.0×10^{-21} cm²).

approximately the same. In figure 1 we compare our He results with the absolute experimental measurements of Samson *et al* [10] and find good agreement between experiment and the new TDCC calculations. Although there are other experimental measurements for the double photoionization of He, the measurements reported by Samson *et al* have become something of a standard and so we compare only to these results. We note that our current calculations are also in good agreement with our previous TDCC calculations [7, 8], which expanded the wavefunction in coupled spherical harmonics with the radial dimensions represented on a two-dimensional lattice.

The good agreement of the new TDCC calculations for the helium case with both experiment and previous theoretical calculations gives us confidence to perform calculations for $R = 1.4$, the equilibrium internuclear separation of H₂. We propagate the same close-coupled equations on an identical four-dimensional lattice for the same length of time. The double photoionization cross section results for H₂, at its equilibrium internuclear separation, averaged over both circular polarization components and the linear polarization component, are shown in figure 2. The inset shows the contributions from linear and circular polarized light; as expected for the molecular case, the linear and circular polarized cross sections for H₂ are quite different; the circular polarized cross sections being very much larger of the two. Also, the behaviour of both contributions as a function of photon energy is different; in this energy range the contribution from circular polarized light peaks and then falls off, whereas the contribution from linear polarized light increases slightly over all this energy range. This

large difference indicates that the dominant contribution to double ionization is from the $^1\Pi_u$ state, which implies polarization perpendicular to the molecular axis, in agreement with the conclusions of [19]. We compare our H₂ results with the absolute experimental measurements of Dujardin *et al* [18] (circles) and Kossmann *et al* [19] (diamonds) and find good agreement between the new TDCC calculations and experiment. Our cross sections are lower than the measurements of Dujardin *et al*, but well within the large error bars of the experiment. The calculations are also in very good agreement with the later experiment of Kossmann *et al*. We also note that our theoretical calculations are substantially below the early calculations of Le Rouzo [20, 21], which were higher than the experimental measurements. These early calculations, however, showed large differences when carried out in the length and velocity gauge formulations, indicating the approximate nature of the initial and/or final wavefunctions used. We finally note that the exterior complex-scaling method has also started to explore calculations of double photoionization processes in H₂ [27]. We look forward to comparing with these non-perturbative calculations in the near future.

In summary, we have described a new time-dependent close-coupling method which can be used to obtain double photoionization cross sections for two-electron diatomic molecules. We have demonstrated the validity of our theory by comparing calculations made for He with absolute experimental measurements. We have then, for the first time, calculated *ab initio* double photoionization cross sections for H₂ and found that our results agree well with previous absolute experimental measurements. Much work remains to be done on the four-body Coulomb problem. Of great interest are the differential cross sections arising from the two ejected electrons in the double photoionization process. Our method has enormous potential to calculate and examine the interesting dynamics which contribute to the angular differential cross sections. We are currently working on ways to calculate these quantities to compare with the experimental measurements already available.

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