

First principles calculations of the double photoionization of atoms and molecules using B-splines and Exterior Complex Scaling

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Abstract. We report a fully ab initio implementation of exterior complex scaling in B-splines to evaluate total, singly and triply differential cross sections in double photoionization problems. Results for He and H₂ double photoionization are presented and compared with experiment.

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INTRODUCTION

Exterior complex scaling (ECS) has been shown to be a powerful method to solve atomic and molecular scattering problems, because it allows the correct imposition of continuum boundary conditions without their explicit analytic application [1]. In ECS, the coordinates are scaled outside a fixed radius,

$$r \rightarrow \begin{cases} r & r \leq R_0 \\ R_0 + (r - R_0)e^{i\eta} & r > R_0 \end{cases} \quad (1)$$

where R_0 defines the radius within which the wave function will be the usual function of real-valued coordinates, and η is a scaling angle. In an exact or converged calculation the solutions of the Schrödinger equation for $r < R_0$ do not depend on η , because exterior complex scaling provides the exact solution with the coordinates taken on a particular complex contour [2]. Setting $\eta \neq 0$ while imposing the boundary condition that *on the ECS contour* the wave function vanishes as $r \rightarrow \infty$ effectively imposes outgoing scattering boundary conditions on the exact solution, and that is why the ECS approach provides a path to compute collision amplitudes. It is this property that makes ECS particularly useful in cases where the asymptotic boundary conditions make traditional methods difficult to apply.

The B-spline method has been extensively applied to atomic and molecular photoionization problems [3, 4, 5]. An important property of B-splines is that they are able to span a large volume to any degree of accuracy without encountering the numerical problems that prevent the use of exponentially decreasing basis functions. This is crucial for the description of continuum states, especially when the asymptotic region is needed. In

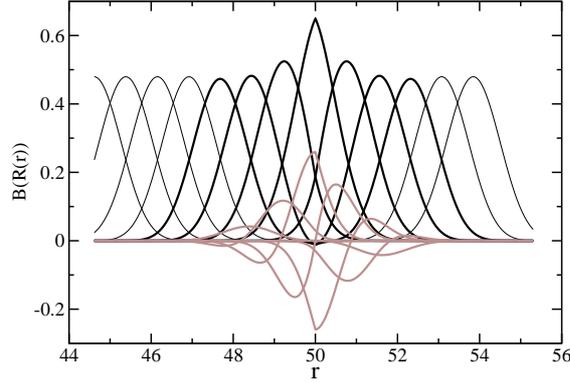


FIGURE 1. 8th order B-splines on the complex exterior scaling contour with $R_0 = 50$ and $\eta = 40^0$. Heavy black lines are the real parts of the only complex splines. Grey lines are the imaginary parts.

addition, B-spline basis sets are effectively complete, which is an ideal property in those problems where the entire spectrum is needed [3]. The double ionization continuum lies in this category.

In this paper we report an implementation of ECS with B-splines [6] to evaluate total, singly and triply differential cross sections in double photoionization problems. The method has been successfully applied to study double photoionization of He and H₂ [7, 8, 9]. A few results are presented and compared with experiment.

THEORY

A complex B-spline basis. B-splines that scale according to the ECS transformation are defined by setting a series of knots $t_i \leq t_{i+1}$ on the complex contour and by using the usual recursion relation [10] for B-splines of order k ,

$$B_i^k(r) = \frac{r - t_i}{t_{i+k-1} - t_i} B_i^{k-1}(r) + \frac{t_{i+k} - r}{t_{i+k} - t_{i+1}} B_{i+1}^{k-1}(r) \quad (2)$$

together with the definition of B-splines of order $k = 1$

$$B_i^1(r) = \begin{cases} 1 & \text{for } t_i \leq r < t_{i+1} \\ 0 & \text{otherwise} \end{cases} \quad (3)$$

A basis of B-splines is defined by a grid of breakpoints, ξ_i , coinciding with the knots, t_i (which may be multiple), that appear in the recursion relation above. The breakpoints can be placed arbitrarily on this contour but one of them and its corresponding knot must be placed at $t_i = R_0$. In this way, B_i^k has a discontinuous first derivative with respect to r at $r = R_0$, because the derivative of the contour itself is discontinuous at that point. The discontinuity in the first derivative of all the B-splines that span the point R_0 is essential to reproduce that of the exact wave function. Figure 1 shows a typical B-spline basis of order $k = 8$ and the discontinuities of the first derivatives at $r = R_0$. Only B-splines that straddle the point R_0 have both real and imaginary components. All other B-splines are real, whether they are on the complex part of the contour or not.

Transition amplitudes. The triply differential cross section (TDCS) for an atom or molecule to absorb one photon, of frequency ω and for two electrons, one having energy E_1 , to emerge into solid angles $d\Omega_1$ and $d\Omega_2$ is

$$\frac{d\sigma}{dE_1 d\Omega_1 d\Omega_2} = \frac{4\pi^2}{\omega c} k_1 k_2 |f(\mathbf{k}_1, \mathbf{k}_2)|^2. \quad (4)$$

The amplitude, $f(\mathbf{k}_1, \mathbf{k}_2)$, is associated with the purely outgoing wave function Ψ_{sc}^+ that is the solution of the driven Schrödinger equation for the “first order wave function,” which we can write in the velocity form as,

$$(E_0 + \omega - H)|\Psi_{sc}^+\rangle = \boldsymbol{\varepsilon} \cdot (\nabla_1 + \nabla_2)|\Psi_0\rangle, \quad (5)$$

where $\boldsymbol{\varepsilon}$ is the polarization unit vector, ∇_1 and ∇_2 are the gradient operators for the electronic coordinates, and Ψ_0 is the initial bound state of the system. The amplitude for double ionization corresponding to Ψ_{sc}^+ can be evaluated, aside from an irrelevant overall phase discussed elsewhere [1, 7], from the integral expression,

$$f(\mathbf{k}_1, \mathbf{k}_2) = \langle \Phi^{(-)}(\mathbf{k}_1, \mathbf{r}_1) \Phi^{(-)}(\mathbf{k}_2, \mathbf{r}_2) | [E - T - v(r_1) - v(r_2)] | \Psi_{sc}^+(\mathbf{r}_1, \mathbf{r}_2) \rangle, \quad (6)$$

where E is the excess energy above the double ionization threshold, T is the two-electron kinetic energy operator, and $v(r)$ is the nuclear attraction potential seen by one electron in the field of the bare nuclei.

For a He atom, the functions $\Phi^{(-)}(\mathbf{k}, \mathbf{r})$ would be the standard atomic Coulomb wave functions, but in the case of H_2 , in the Born-Oppenheimer approximation where the two electrons leave behind two bare protons, positioned at $\pm \mathbf{A}$, they are the continuum states of the H_2^+ ion. In the latter case, they are the solutions of

$$\left[\frac{k^2}{2} + \frac{\nabla^2}{2} + \frac{1}{|\mathbf{r} - \mathbf{A}|} + \frac{1}{|\mathbf{r} + \mathbf{A}|} \right] \Phi^{(-)}(\mathbf{k}, \mathbf{r}) = 0, \quad (7)$$

and satisfy the usual relation, $\Phi^{(-)}(\mathbf{k}, \mathbf{r}) = (\Phi^{(+)}(-\mathbf{k}, \mathbf{r}))^*$.

Wave functions. To solve Eq. (5) with the proper outgoing scattering boundary conditions, we use the ECS version of the B-spline basis. The two-electron continuum function, Ψ_{sc}^+ , in Eq. (5) is written, for a fixed value of L (atomic case) or M (molecular case) as a sum of products of two-dimensional radial wave functions and spherical harmonics. The radial functions are made of B-splines. The ground state is also constructed using B-splines in the standard fashion [5]. This transforms Eq. (5) in a set of linear equations.

DOUBLE PHOTOIONIZATION OF HE

The components of Ψ_{sc}^+ reveal much of the dynamics of the photoionization process at a glance. The first two of them, the *ksp* and *kpkd* contributions, are plotted in Fig. 2 for a photon energy 20eV above the double ionization threshold. These plots show only the direct contribution and are thus not symmetric under interchange of r_1 and

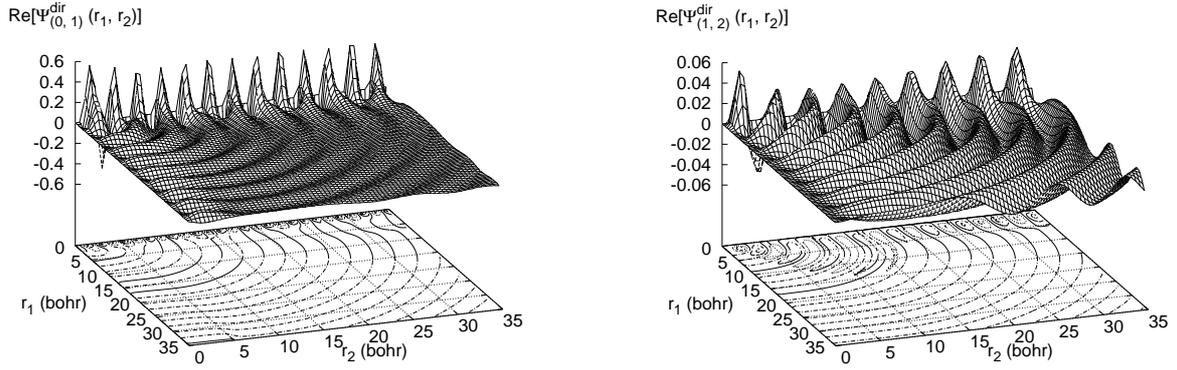


FIGURE 2. Real part of direct contribution to the He wave function at 20 eV. The panels from left to right show the contributions from the $kskp$ and $kpkd$ partial waves.

r_2 . In the first of them we see the single ionization contribution as an outgoing wave parallel to the r_2 axis and confined to small r_1 . The $kskp$ contribution also displays the outgoing waves for double ionization as wave fronts at constant hyperradius. For the higher angular component the relative importance of single ionization decreases since it proceeds through higher ionization thresholds; thus the outgoing double ionization wave fronts are more apparent. As l_1 and l_2 increase the wave function components rapidly decrease in magnitude as can be seen in the $kpkd$ contribution.

Braüning *et al.* [11] have measured absolute TDCS's for a photon energy of 20 eV above threshold. These experiments and essentially all others on this system were performed in “coplanar geometry”, that is, with the polarization vector and both momenta \mathbf{k}_1 and \mathbf{k}_2 lying in the same plane. The measurements provide a rigorous test of the theoretical description of the double photoionization process. In Fig. 3 we compare the ECS results with the experimental ones for the cases in which the first electron exits parallel with an angle of $\theta_1 = 60^\circ$ and $\theta_1 = 90^\circ$ with respect to the polarization axis.

DOUBLE PHOTOIONIZATION OF H₂

In the case of a molecular target, the theoretical challenge is greater and potentially more interesting. Previous treatments have generally made use of a correlated initial state in combination with a final state that is simply an uncorrelated product of Coulomb wave functions or treated only in united-atom limit [12, 13]. Here, we treat both initial and final states on equal footing and take a completely non perturbative approach.

Fig. 4 compares length and velocity forms of the calculated integral cross section, which should be identical in a completely converged calculation, as they are in ECS calculations on double photoionization of helium [7, 8]. The remaining discrepancy here is likely due to an insufficient number of angular momentum values in the final state, Ψ_{sc}^+ , which we treat with fewer partial waves than the initial state. Including higher angular momenta in a molecular calculation increases the size of the calculation faster

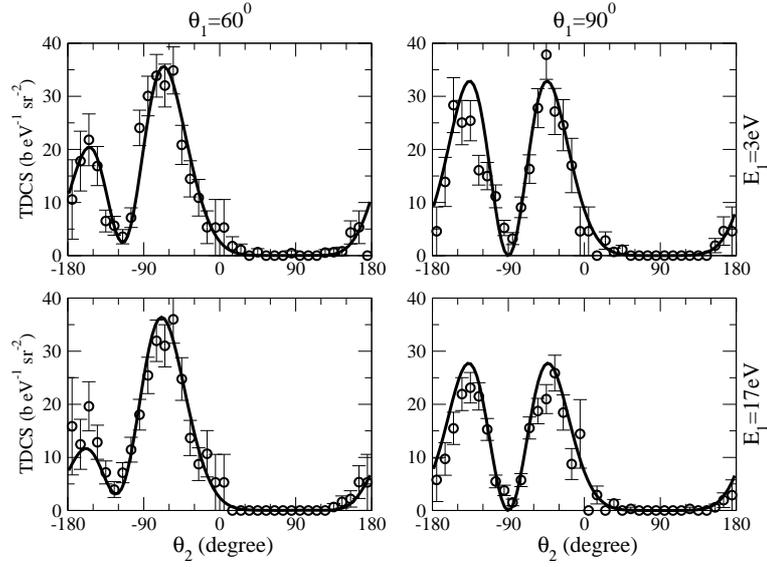


FIGURE 3. He TDCS for photon energy 20 eV above threshold, at energy sharings with $E_1 = 3\text{ eV}$ (upper panels) and 17 eV (lower panels) for $\theta_1 = 60^\circ$ and $\theta_1 = 90^\circ$. Circles: experiment by Braüning *et al.* [11]. Thick solid curve: Present result.

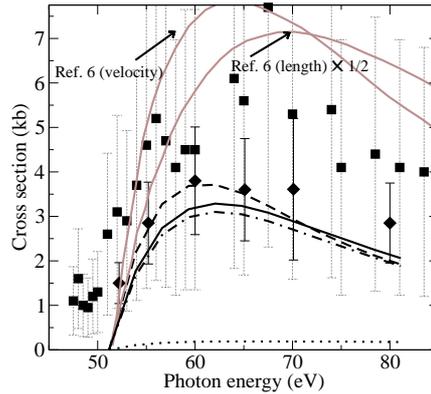


FIGURE 4. Integral cross section of H_2 . Solid curve: velocity form. Dashed: length form. Dotted: $^1\Sigma_u^+$ contribution to velocity form. Dot-dashed: $^1\Pi_u$ contribution to velocity form. Grey lines, theory of ref. [12], length form (lower) times 1/2 and velocity form (upper). Experiments: squares, Dujardin *et al.* of 1987 [14] and diamonds, Kossmann *et al.* of 1989 [15].

than in an atomic calculation. The lower symmetry generates a larger number of distinct “double continua” for each pair of l_1, l_2 angular momenta since all m_1, m_2 adding up to M label distinct double continua. Fig. 4 shows a dramatic difference between double photoionization and either single photoionization of H_2 or double photoionization of He. The $^1\Pi_u$ contribution dominates by about a factor of 10 over that of the $^1\Sigma_u^+$ symmetry. Recent COLTRIMS experiments [13, 16] noted the dominance of the Π_u contribution and therefore of polarization perpendicular to the molecular axis.

In the same COLTRIMS experiments, the TDCS has been measured for *oriented* H_2 molecules. In Fig. 5, we present a comparison of calculated and measured TDCS

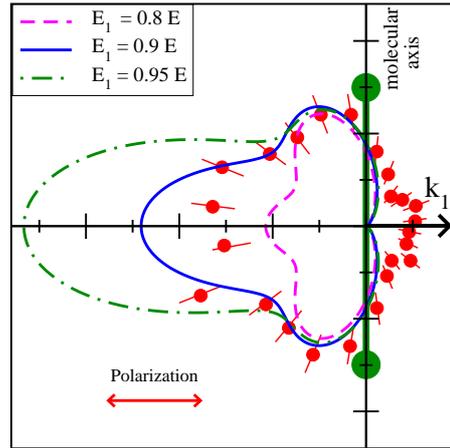


FIGURE 5. Measured and calculated H_2 TDCS for photon energy 75.5 eV in an “in-plane” geometry. Experiment averages all $E_2 > 0.8E$. Circles: experiment by Weber *et al.* [13].

for the case in which two electrons exit in the plane defined by the axis of the H_2 molecule and the polarization direction. Three different energy sharings compatible with the experimental measurements are shown. The TDCS is very sensitive to the energy of each electron as well as to the description of correlation in the ground state of the molecule and the final continuum state. All in all, the figure shows that results of the calculations are compatible with the experimental measurements.

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