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Nonperturbative theory of double photoionization of the hydrogen molecule

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We present completely *ab initio* nonperturbative calculations of the integral and single differential cross sections for double photoionization of H_2 for photon energies from 53.9 to 75.7 eV. The method of exterior complex scaling, implemented with B-splines, is used to solve the Schrödinger equation for a correlated continuum wave function corresponding to a single photon having been absorbed by a correlated initial state. The results are in good agreement with experimental integral cross sections.

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Double photoionization of an atom or molecule is a phenomenon directly associated with electron correlation. The dipole operator corresponding to the absorption of a single photon cannot excite more than one electron if the dynamics and description of the target are restricted to the independent particle model. For atomic double photoionization, it has been demonstrated that accurate, correlated initial and final states are required for the quantitative description of the cross sections, and particularly for the description of the angular dependence of the ejected electrons [1–5]. Thus, detailed experimental measurements of the cross sections for atomic double photoionization are a powerful probe of electron correlation and provide a challenge to *ab initio* theory.

In the case of a molecular target, the challenge is greater and potentially more interesting. Even in the simple case of the H_2 molecule, double photoionization experiments can reveal the effects of electron correlation associated with a chemical bond. Also, because the process is rapid on the time scale of nuclear motion, except for energies very near threshold, these cross sections can show the effects of the correlation between two outgoing electrons in the nonspherical field of the molecular ion.

This study reports a completely *ab initio* treatment of the double photoionization of H_2 with fully correlated initial and final states. 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 the united-atom limit [6,7]. In contrast, we treat both initial and final states on an equal footing and take a completely nonperturbative approach.

The key difficulty in such a calculation is the imposition of the correct outgoing scattering boundary conditions on the final state, because it corresponds to a nonspherical version of the notoriously difficult Coulomb three-body breakup problem. We surmount that difficulty here by the application of exterior complex scaling (ECS) of the electronic coordinates, a method which has been shown to provide a complete theory of the two-electron Coulomb breakup problem and to "reduce it to computation" as discussed in a recent review [8] and many references therein.

Measurements of the total cross section for double photoionization of H_2 were made in 1987 by Dujardin *et al.* [9], who noted that the threshold energy for this process is well below the vertical energy at the equilibrium bond distance. Kossman *et al.* [10] later made measurements with an improved uncertainty (32%), revising the earlier values of the total cross section generally downward, and noting that the angular distributions they observed suggested the importance of high asymptotic orbital angular momenta in the final state.

Recent coincidence measurements [11] of the angular distributions of outgoing electrons *and* nuclei have effectively measured the double photoionization process for molecules oriented relative to the direction of polarization. These studies, using the Cold Target Recoil Ion Momentum Spectroscopy, (COLTRIMS) method, demonstrated that the most detailed cross sections measurable can reveal angular dependences that are sensitive to molecular orientation. Further experiments [7] also show a marked dependence of the angular distribution of electron ejection with internuclear distance, suggesting a sensitivity to changes in electron correlation and dynamics with varying bond distance.

In this study, we focus on the integral and single differential cross sections (SDCS) and present the initial results of the exterior complex scaling treatment of double photoionization of a molecule. These calculations represent an important step forward for nonperturbative methods into the realm of multiple ionization of molecular targets, and most significantly demonstrate that the ECS method can overcome the difficult problem of how to implement the correct scattering boundary conditions for a molecular system.

Formal equations. We begin by noting that the formal definitions of the amplitudes and cross sections are essentially the same as those for the case of atomic double photoionization. However, in the molecular case there are *four* vectors that characterize the triple differential cross section (TDCS) at a given photon energy: the polarization vector $\boldsymbol{\epsilon}$, the momenta of the exiting electrons $\mathbf{k}_1$, $\mathbf{k}_2$, and the molecular axis, $\hat{\mathbf{A}}$. The 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

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$$\frac{d\sigma}{dE_1 d\Omega_1 d\Omega_2} = \frac{4\pi^2}{\omega c} k_1 k_2 |f(\mathbf{k}_1,\mathbf{k}_2)|^2. \quad (1)$$

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,

$$(E_0 + \omega - H)|\Psi_{sc}^{+}\rangle = \boldsymbol{\epsilon}\cdot(\boldsymbol{\nabla}_1 + \boldsymbol{\nabla}_2)|\Psi_0\rangle, \quad (2)$$

where $\boldsymbol{\epsilon}$ is the polarization unit vector, $\boldsymbol{\nabla}_1$ and $\boldsymbol{\nabla}_2$ 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 [1,8], from the integral expression,

$$f(\mathbf{k}_1,\mathbf{k}_2) = \langle \Phi^{(-)}(\mathbf{k}_1,\mathbf{r}_1)\Phi^{(-)}(\mathbf{k}_2,\mathbf{r}_2)|[E - T - v(r_1) - v(r_2)] \times |\Psi_{sc}^{+}(\mathbf{r}_1,\mathbf{r}_2)\rangle, \quad (3)$$

where E is the excess energy above the double ionization threshold (51.3 eV vertical electronic energy at the equilibrium internuclear distance), 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 the molecular case, even the one-electron testing functions in Eq. (3) pose a challenge. For an 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. Thus the one-electron testing functions $\Phi^{(-)}$ are solutions of

$$\left[\frac{k^2}{2} + \frac{\nabla^2}{2} + \frac{1}{|\mathbf{r}-\mathbf{A}|} + \frac{1}{|\mathbf{r}+\mathbf{A}|}\right]\Phi^{(-)}(\mathbf{k},\mathbf{r}) = 0, \quad (4)$$

and satisfy the usual relation, $\Phi^{(-)}(\mathbf{k},\mathbf{r}) = [\Phi^{(+)}(-\mathbf{k},\mathbf{r})]^*$. We will later convert Eq. (4) into a driven equation for the scattered wave part of $\Phi^{(+)}$.

The problem of molecular double photoionization is stated in Eqs. (1)–(4). We must solve Eq. (2) with pure outgoing boundary conditions and Eq. (4) with proper molecular scattering boundary conditions.

A central result of this study is the demonstration that these problems, in the molecular context, can be solved with exterior complex scaling of the radial coordinates of the electrons. To the radial coordinate of each electron we apply the ECS transformation, $r \to R_0 + (r - R_0)e^{i\gamma}$, beyond some point R_0 using a nonzero scaling angle, γ. After this transformation, we apply the boundary condition that the solution vanishes as $r \to \infty$ for any electron along the exterior scaling contour. This condition is formally equivalent to outgoing scattering boundary conditions (for producing the solution for $r < R_0$), even in the presence of long-range potentials, as has been discussed at length elsewhere [8]. In an exact or converged calculation the solutions of the Schrödinger equation for $r < R_0$ do not depend on γ.

One-electron test functions. The incoming wave part of the solution of Eq. (4) is determined by the long-range behavior of the potential and thus is the same as that of the atomic Coulomb problem with $Z=2$. So we can write $\Phi^{(+)}(\mathbf{k},\mathbf{r}) = \chi(\mathbf{k},\mathbf{r}) + \psi_c^{(+)}(\mathbf{k},\mathbf{r})$ with the "unperturbed" portion being the standard ($Z=2$) Coulomb function, $\psi_c^{(+)}(\mathbf{k},\mathbf{r})$, whose incoming momentum specifies the direction of $\mathbf{k}$. The scattered wave portion, $\chi(\mathbf{k},\mathbf{r})$, of the exact H_2^{+} continuum function then satisfies the driven Schrödinger equation

$$\left(\frac{k^2}{2} - h\right)\chi(\mathbf{k},\mathbf{r}) = \left(\frac{2}{r} - \frac{1}{|\mathbf{r}-\mathbf{A}|} - \frac{1}{|\mathbf{r}+\mathbf{A}|}\right)\psi_c^{(+)}(\mathbf{k},\mathbf{r}), \quad (5)$$

with h being the one-electron Hamiltonian in Eq. (4). Since χ is an outgoing wave, the correct boundary conditions can be imposed using the ECS transformation as described above.

To solve Eq. (5) we make use of a single center expansion about the middle of the molecule, $r=0$, and express it in the body-fixed frame in which incoming Coulomb waves, $\phi_{l,k}^{c}(r)$, are associated with a single partial wave at a time, but outgoing waves, $R_{l'}^{lm}$, appear in all symmetry allowed partial waves. In terms of these quantities, we can then construct the solution of Eq. (4) in the form

$$\Phi^{(+)}(\mathbf{k},\mathbf{r}) = \left(\frac{2}{\pi}\right)^{1/2}\sum_{l,m} i^l e^{i\eta_l(k)} Y_{lm}^{*}(\hat{\mathbf{k}})\sum_{l'}\Delta_{l,l'}\left(\frac{\phi_{l,k}^{(c)}(r)}{kr}\delta_{l,l'} + \frac{R_{l'}^{lm}(r)}{r}\right)Y_{l'm}(\hat{\mathbf{r}}). \quad (6)$$

In Eq. (6), $\phi_{l,k}^{(c)}(r)$ is the standard radial Coulomb function which goes asymptotically as $\sin[kr + (Z/k)\ln 2kr - \pi l/2 + \eta_l(k)]$ with the Coulomb phase shift $\eta_l(k)$. The factor $\Delta_{l,l'}$ equals 1 if $l+l'$ is even and zero otherwise. Finally, we expand the radial solutions, $R_{l'}^{lm}(r)$, in B-splines and substitute them back in Eq. (5) to obtain linear equations for their coefficients, using the standard methods and technology described previously [12,13], and modified appropriately to make use of the B-spline implementation of ECS in previous applications [1,14].

Two-electron scattered wave. With the one-electron continuum states of H_2^{+} in hand, we turn to the calculation of the two-electron continuum function, Ψ_{sc}^{+}, in Eq. (2). We can write that wave function, for a fixed value of the projection, M, of the electronic angular momentum along the molecular axis and for singlet spin coupling, as a sum of products of two-dimensional radial wave functions and spherical harmonics

$$\Psi_{sc}^{+(M)} = \sum_{j_1\mu_1,j_2\mu_2}\left(\frac{\psi_{j_1\mu_1,j_2\mu_2}^{dir}(r_1,r_2)}{r_1 r_2}Y_{j_1\mu_1}(\hat{\mathbf{r}}_1)Y_{j_2\mu_2}(\hat{\mathbf{r}}_2) + \frac{\psi_{j_1\mu_1,j_2\mu_2}^{exch}(r_1,r_2)}{r_1 r_2}Y_{j_2\mu_2}(\hat{\mathbf{r}}_1)Y_{j_1\mu_1}(\hat{\mathbf{r}}_2)\right). \quad (7)$$

For double photoionization of the $^1\Sigma_g^{+}$ ground state of H_2, the state Ψ_{sc}^{+} can have only $^1\Sigma_u^{+}$ ($M=0$) or $^1\Pi_u$ ($M=\pm 1$) symmetry. The radial functions, $\psi_{j_1\mu_1,j_2\mu_2}^{dir}(r_1,r_2)$ and $\psi_{j_1\mu_1,j_2\mu_2}^{exch}(r_1,r_2)$, are then expanded in products of B-splines so that the Hamiltonian matrix elements corresponding to the left-hand side of Eq. (2) are the same as those in a "complete

configuration interaction" calculation in that basis [15]. To solve Eq. (2) with the proper outgoing scattering boundary conditions, we again use the ECS version of the B-spline basis. The calculations reported here made use of 60 eighth-order B-splines in each angular momentum, 50 on the interval $r=(0,45)a_0$ and the remaining 10 on the interval $(45,70)a_0$. Exterior complex scaling beginning at $r=40a_0$ with a scaling angle of $\gamma=30°$ was used throughout. We included molecular symmetries σ_g, σ_u, π_g, π_u and δ_g in Ψ_{sc}^{+}, restricted to contributions with values of $j\leqslant 3$. For Π_u symmetry with $M=1$, for example, there are then eight "double continua" labeled by j_1, μ_1, j_2, μ_2 with a total of 28 800 configurations.

What remains to implement Eq. (2) as a set of linear equations is a correlated initial state, Ψ_0. That state was constructed in the present calculations using B-splines in the standard fashion [15]. In a calculation including 524 configurations with angular momentum components up to $l=5$ we obtained a ground state energy of −1.166 379 hartrees to be compared with the accurate value of Kolos *et al.* [16] of −1.171 304 hartrees for the equilibrium bond distance of $1.4a_0$.

Calculating the amplitudes. To construct the amplitudes for double photoionization corresponding to a continuum with a particular value of M, we substitute $\Psi_{sc}^{(+)}$, and $\Phi^{+}(\mathbf{k},\mathbf{r})$ for the values of $\mathbf{k}_1$ and $\mathbf{k}_2$ in question, into Eq. (3) for the ionization amplitude. The amplitude is an integral over angular and radial coordinates on a finite volume bounded by R_0 in both coordinates. Performing the angular integrations over $\hat{\mathbf{r}}_i$ yields to a sum over l_1, l_2, j_1, μ_1, j_2, and μ_2 of two-dimensional radial integrals where the components $\psi_{j_1\mu_1,j_2\mu_2}^{dir/exch}$ of Eq. (7) are integrated with corresponding radial components of the H_2^{+} continuum functions of Eq. (6). Each term is associated with a product of spherical harmonics $Y_{l_1\mu_1}(\hat{\mathbf{k}}_1)Y_{l_2\mu_2}(\hat{\mathbf{k}}_2)$ in the angles of the outgoing momenta.

Those direct and exchange amplitudes have a form exactly analogous to the corresponding amplitudes in an ECS calculation of atomic double photoionization [1]. They can be expressed as surface integrals on a surface of radius ρ_0 in hyperspherical coordinates using Green's theorem. Like Eqs. (30)–(33) of Ref. [1] they have the form of matrix elements of the radial flux operator, $(\overleftarrow{\partial}/\partial\rho)\delta(\rho-\rho_0)-\delta(\rho-\rho_0)(\overrightarrow{\partial}/\partial\rho)$ [expressed in hyperspherical coordinates where $\rho=(r_1^2+r_2^2)^{1/2}$] between the radial components of the one-electron testing functions and the two-electron radial functions.

To express the TDCS and SDCS compactly we must collect the terms in the amplitude that multiply particular products of $Y_{l_1\mu_1}(\hat{\mathbf{k}}_1)Y_{l_2\mu_2}(\hat{\mathbf{k}}_2)$. Doing so, and then integrating the TDCS over $d\Omega_1 d\Omega_2$ gives a result for the SDCS in terms of reduced amplitudes, $\mathcal{F}$, that closely resembles the atomic case [1]

$$\frac{d\sigma^{(M)}}{dE_1}=\frac{4\pi^2}{\omega c}k_1k_2\left(\frac{2}{\pi}\right)^2\sum_{l_1>l_2,\mu_1,\mu_2}[|\mathcal{F}_{l_1,l_2,\mu_1,\mu_2}^{dir(M)}(k_1,k_2)|^2+|\mathcal{F}_{l_1,l_2,\mu_1,\mu_2}^{exch(M)}(k_1,k_2)|^2]. \tag{8}$$

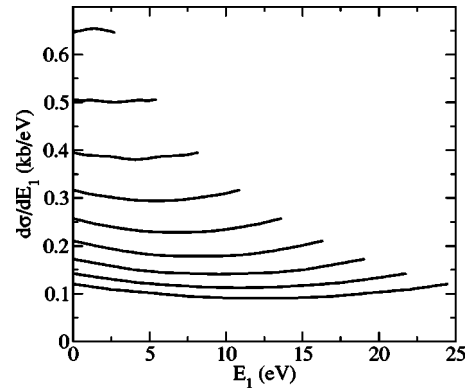

FIG. 1. Calculated SDCS for photon energies 53.90–75.66 eV in steps of 0.1 hartree (top to bottom).

For polarized incident radiation and randomly oriented molecules the physical SDCS has contributions from all three M values, and we can write it in the form

$$\frac{d\sigma}{dE_1}=\frac{1}{3}\left(\frac{d\sigma^{(\Sigma)}}{dE_1}+2\frac{d\sigma^{(\Pi)}}{dE_1}\right). \tag{9}$$

The integral cross section is the integral of this SDCS from 0 to E, the energy of the photon above the double photoionization threshold.

Comparison of results with experiment. Figure 1 shows the SDCS from calculations in the velocity form for photon energies from 53.90 to 75.66 eV. The same characteristic variation in the shape of the SDCS with increasing photon energy is seen here as in the atomic case, namely that the cross section shows an increasing tendency for one electron to exit with more energy than the other. The corresponding integral cross sections are shown in Fig. 2. We see that the total cross sections have the same shape as those of Kossmann *et al.* [10], but they show a very different threshold than the Dujardin *et al.* [9] measurements, because the integral cross sections we present are all calculated at the equi-

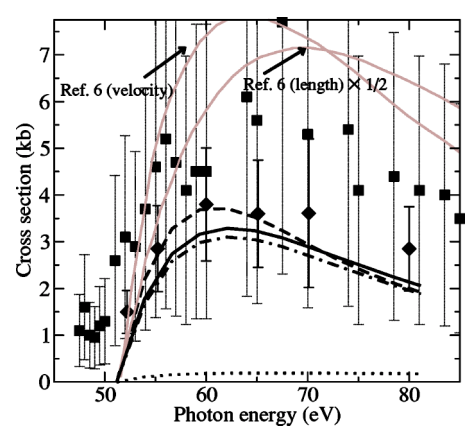

FIG. 2. Integral cross section. Solid curve: velocity form. Dashed: length form. Dotted: $^1\Sigma_u^{+}$ contribution to velocity form. Dot-dashed: $^1\Pi_u$ contribution to velocity form. Gray lines, theory of Ref. [6], length form (lower) times 1/2 and velocity form (upper). Experiments: squares, Dujardin *et al.* of 1987 [9] and diamonds, Kossmann *et al.* of 1989 [10].

librium bond distance of $1.4a_0$. Vibrational motion between the classical turning points in the initial state changes the value of the threshold by more than ±3 eV, because of the variation of the repulsive Coulomb potential in the final state corresponding to different releases of energy into nuclear motion. Also shown in Fig. 2 are the 1986 Coulomb-Born calculations of Le Rouzo [6] using atomic final states, which have a large discrepancy between length and velocity forms and agree poorly with experiment. Later such calculations [6], including zero point nuclear motion, showed marginally better agreement.

Figure 2 compares length and velocity forms of the calculated integral cross section, which should be identical in a completely converged calculation, as they were in ECS calculations on double photoionization of helium [1,2]. 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. We note that although the velocity form generally converges faster in single photoionization calculations on atoms and molecules, no such trend has yet been established for double photoionization. Including higher angular momenta in a molecular calculation increases the size of the calculation faster than in an atomic calculation. The lower symmetry generates a larger number of distinct "double continua" for each pair of j_1, j_2 values since all μ_1, μ_2 adding up to M label distinct double continua. The present calculations are therefore sufficiently well converged to provide useful SDCS and integral cross sections, but not to accurately represent the TDCS which generally requires the small contributions of higher angular momenta ($l=4$ and 5 in the corresponding atomic case of He).

Figure 2 also 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 [7,11] noted the dominance of the Π_u contribution and therefore of polarization perpendicular to the molecular axis. These measurements also suggest that a quantitative description of the complicated TDCS for particular orientations and internuclear distances will require significantly higher angular momenta.

The calculations presented here are an important step towards understanding how molecular double photoionization can probe electron correlation, and how it changes with internuclear distance. It will require accurate theoretical treatments to fully interpret such experiments, particularly in more complicated systems.

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[1] C. W. McCurdy, D. A. Horner, T. N. Rescigno, and F. Martín, Phys. Rev. A **69**, 032707 (2004).
[2] D. A. Horner, J. Colgan, F. Martín, C. W. McCurdy, M. S. Pindzola, and T. N. Rescigno, Phys. Rev. A (to be published).
[3] J. Colgan, M. S. Pindzola, and F. Robicheaux, J. Phys. B **34**, L457 (2001).
[4] A. S. Kheifets and I. Bray, Phys. Rev. A **65**, 022708 (2002).
[5] P. Selles, L. Malegat, and A. K. Kazansky, Phys. Rev. A **65**, 032711 (2002).
[6] H. Le Rouzo, J. Phys. B **19**, L677 (1986); Phys. Rev. A **37**, 1512 (1988).
[7] T. Weber *et al.*, Nature (London) **431**, 437 (2004).
[8] C. W. McCurdy, M. Baertschy, and T. N. Rescigno, J. Phys. B **37**, R137 (2004).
[9] G. Dujardin, M. J. Besnard, L. Hellner, and Y. Malinovitch, Phys. Rev. A **35**, 5012 (1987).
[10] H. Kossmann, O. Schwarzkopf, B. Kämmerling, and V. Schmidt, Phys. Rev. Lett. **63**, 2040 (1989).
[11] Th. Weber *et al.*, Phys. Rev. Lett. **92**, 163001 (2004).
[12] F. Martín, J. Phys. B **32**, R197 (1999).
[13] H. Bachau, E. Cormier, P. Decleva, J. E. Hansen, and F. Martín, Rep. Prog. Phys. **64**, 1815 (2001).
[14] C. W. McCurdy and F. Martín, J. Phys. B **37**, 917 (2004).
[15] I. Sánchez and F. Martín, J. Phys. B **30**, 679 (1997).
[16] W. Kolos, K. Szalewicz, and H. J. Monkhorst, J. Chem. Phys. **84**, 3278 (1986).