

## Classical Two-Slit Interference Effects in Double Photoionization of Molecular Hydrogen at High Energies

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Recent experiments on double photoionization of H<sub>2</sub> with photon energies between 160 and 240 eV have revealed body-frame angular distributions that suggest classical two-slit interference effects may be present when one electron carries most of the available energy and the second electron is not observed. We report precise quantum mechanical calculations that reproduce the experimental findings. They reveal that the interpretation in terms of classical diffraction is only appropriate at substantially higher photon energies. At the energies considered in the experiment we offer an alternative explanation based on the mixing of two nondiffractive contributions by circularly polarized light.

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The angular and energy dependence of single ionization of diatomic molecules at high energies exhibit aspects of classical two-slit diffraction that are now well understood, having first been suggested by Cohen and Fano [1] in 1966, then modeled by Walter and Briggs [2] in 1999, and recently studied by accurate theoretical methods [3,4] and experiments [5,6]. In particular, Fernández *et al.* [3] have shown, by explicit inclusion of electron correlation and nuclear motion, that the observed interferences in H<sub>2</sub> can indeed be interpreted as resulting from diffraction of a single electron by the two nuclei, the second electron being a mere spectator. Surprisingly, in one-photon double ionization of H<sub>2</sub>, a process that is only possible through electron correlation [7], very recent experimental results by Akoury *et al.* [8] and Kreidi *et al.* [9] have suggested that a similar interpretation is still appropriate when one electron is much faster than the other. On the theoretical front, over the past four years new computational developments have made it possible to solve the Schrödinger equation numerically for double ionization of two-electron molecules to produce effectively exact wave functions and cross sections [7,10–14]. In this Letter we report such calculations at the photon energies used in the experiments [8,9], and show that at these energies there is almost no trace of double slit diffraction patterns and that the apparent interference patterns arise from the use of circularly polarized light. However, we are able to predict that the effects sought in these experiments can indeed be observed at higher photon energies.

In the experiments of Akoury *et al.* [8], the central observation was a four-lobed angular distribution seen for the faster of the two ejected electrons when it carries most of the available kinetic energy and when the other electron is not detected. These experiments use the cold

target recoil ion momentum spectroscopy (COLTRIMS) method of coincident detection of the electrons and the protons released by the Coulomb explosion that follows complete ionization of the H<sub>2</sub> molecule. For that reason the experiment is able to give kinematically complete information about double photoionization of molecules whose orientation is known. Of course, it is the knowledge of that orientation that makes the discussion of angular diffraction effects possible, and this is one of the unique qualities of this powerful momentum imaging technique. The photon energies used were 160 and 240 eV, corresponding to maximum available energies (from a vertical transition to the doubly ionized state) to be shared by the two outgoing electrons of 109 and 189 eV, respectively. The observed angular distributions, shown in Fig. 1, were described as a “strong interference pattern” and were reproduced qualitatively by model one-electron calculations, even though the asymptotic wavelengths associated with the kinetic energies of ejection, 2.2 bohr for 160 eV photons or 1.7 bohr for 240 eV photons, in the limit that one electron is ejected with all of the available energy, were larger than the equilibrium internuclear distance of the molecule, which is  $1.4a_0$ .

Calculations at these energies using the exterior complex scaling (ECS) method [15] implemented with the discrete variable representation (DVR) in finite elements for the radial variables of each of the two electrons require considerably denser grids and more partial waves than any calculations on molecular double photoionization previously reported using these methods. The details of the theoretical and computational methods can be found in Refs. [11,15]. To converge the calculations at the two energies considered in the experiment, 160 and 240 eV, we used radial grids with a maximum value of the elec-

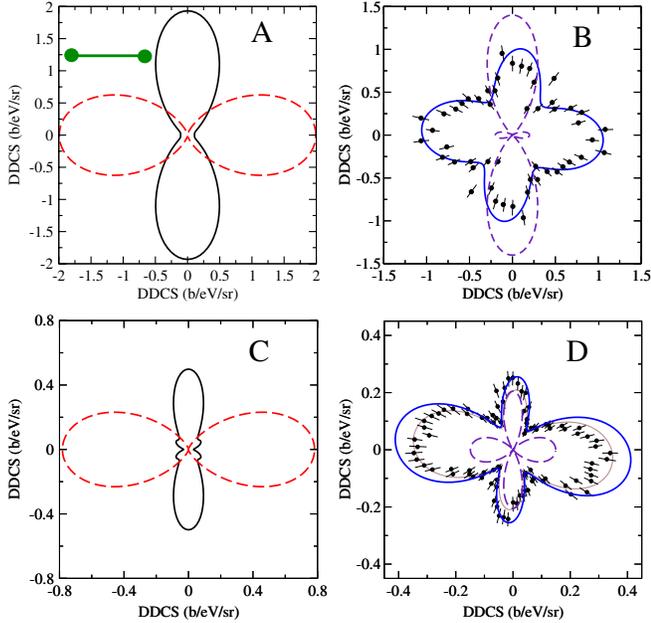


FIG. 1 (color online). DDCCS for linearly and circularly polarized radiation. Top row: Photon energy of 160 eV. Bottom row: Photon energy of 240 eV. Left column: Parallel polarization (dashed line) and perpendicular polarization (solid line) for ejected electron energy of 108 eV. Right column: (top) Relative measurements of [8] normalized to calculated DDCCS (solid line) for circularly polarized radiation at 160 eV and ejected electron at 108 eV, and (bottom) at 240 eV to calculated DDCCS for energy sharing 97%–100% (light solid line). Heavy solid line: Ejected electron at 187 eV; dashed lines: simple diffraction model (see text).

tronic coordinate of  $90a_0$  and exterior scaling radius of  $50a_0$ . The densest grids contained 209 DVR polynomial basis functions for each electron. Our calculations involve a single center expansion of the two-electron wave function around the center of the molecule in terms of products of spherical harmonics,  $Y_{\ell_1, m_1}(\Omega_1)Y_{\ell_2, m_2}(\Omega_2)$ , and we included all such products with angular momenta up to and including  $\ell = 9$ . Varying the parameters of the grid and angular momentum expansion showed these large scale calculations to be converged to graphical accuracy for all the results presented here.

Our calculations produce the triple differential cross section (TDCS),  $d\sigma/dE_1 d\Omega_1 d\Omega_2$ , which when integrated over the angles of one of the electrons produces the doubly differential cross section (DDCCS),  $d\sigma/dE_1 d\Omega_1$ , differential in energy sharing (specified by the energy of one electron  $E_1$ ) and the ejection angles of that electron. The results for extreme energy sharing at the two energies of the experiments are shown in Fig. 1. The DDCCS in all four panels is plotted as a cut of the three-dimensional cross section in the plane containing the molecule and perpendicular to the photon wave vector.

Turning our attention first to Fig. 1(a) we see that the DDCCSs for parallel and perpendicular polarization show simple dipolelike patterns with two lobes when the elec-

tron whose angular distribution is plotted is ejected with 108 eV of kinetic energy, or 99% energy sharing. There is no hint of a diffraction pattern in those cross sections. However, when the amplitudes for parallel and perpendicular polarization are combined to correspond to the dipole operator for circularly polarized radiation,  $(x + iz)/\sqrt{2}$ , they add to form the four lobes shown in Fig. 1(b) and observed in the experiment. A key point to notice, however, is that the simple diffraction formula used in [8] for circular polarization,  $\cos^2[k_e R \cos(\theta_{e\text{-mol}})/2]$ , and also discussed further below, fails to reproduce the observed patterns. Another significant point is that while at lower energies the amplitudes for double ionization by perpendicular or parallel polarization are different by as much as a factor of 5 [12,14], they are of roughly equal magnitude at 160 eV. Since one is large at angles where the other is small, the resulting angular distribution is not very sensitive to their relative phases when they are mixed by circular polarization.

At a photon energy of 240 eV we see a similar effect. In Fig. 1(c) we see a simple dipolelike pattern for parallel polarization, but for perpendicular polarization we can see just the hint of the beginning of additional lobes developing as the wavelength of the ejected electron is lowered. It is in perpendicular polarization where we expect the simple effects of diffraction to appear as the energy is raised, as has been demonstrated conclusively in the single photoionization case by accurate calculations [3]. The small lobes for perpendicular polarization in this case are completely obscured, however, in circularly polarized light as shown in Fig. 1(d), where the origin of the four lobes is again the mixing of  $\Sigma$  and  $\Pi$  contributions corresponding to parallel and perpendicular polarization.

The theoretical results shown in Fig. 1 were obtained for 99% energy sharing with the exception of the curve in Fig. 1(d) that shows that averaging the calculated cross section over the experimental range of energy sharing (97%–100%) produces a DDCCS that is almost identical in shape to that at 99% energy sharing. This result is the consequence of the fact that, in this interval, the DDCCS mostly changes its magnitude while generally preserving its shape. However, the angular behavior of the circularly polarized results at 160 eV photon energy varies rapidly away from extreme energy sharing. Thus, when the energy acceptance interval contains a sizable range of energy sharings, the resulting peaks and valleys largely average out of the observation. This fact is seen clearly in the comparison with experiment at 160 eV shown in Fig. 2(a), while Fig. 2(b) shows individual DDCCS curves at discrete values of energy sharing over the range averaged in the experiment. The apparent disappearance of the interference pattern in this experiment was interpreted by Akoury *et al.* as a result of decoherence of the entangled pair of exiting electrons. That interpretation is at odds with the results of Fig. 2(c), in which the DDCCS for exactly 50% energy sharing is plotted in the same manner, demonstrat-

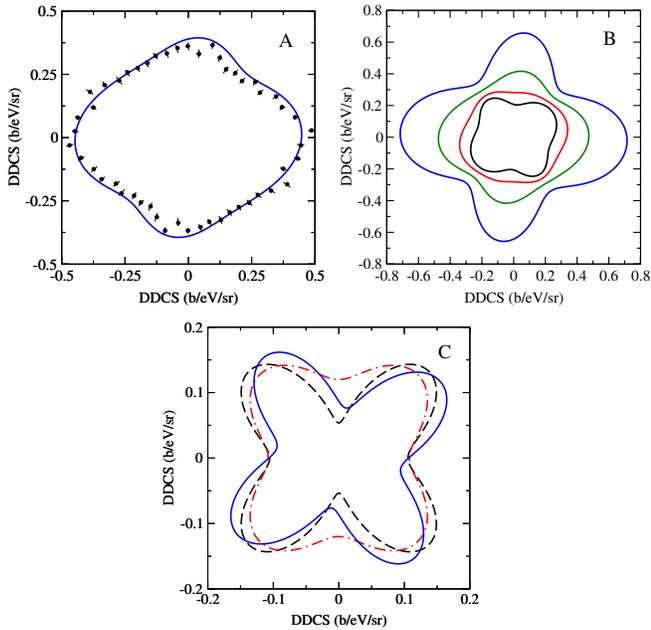


FIG. 2 (color online). (a) DDCS for photon energy of 160 eV for energy sharing 78%–96% compared with the results of Ref. [8]. (b) DDCS for (inner to outer curves) 80%, 85%, 90%, and 95% energy sharing. (c) DDCS for photon energy of 160 eV at 50% energy sharing. Long-dashed line: Perpendicular polarization; dash-dotted line: parallel polarization; solid line: circular polarization, molecule horizontal.

ing that circularly polarized light still produces a four-lobed cross section. A detailed analysis of the underlying TDCS shows that the reason is that at this energy sharing a combination of electron repulsion in the final state and the effects of selection rules [16] for particular directions of the outgoing electrons gives rise to the four lobes in the DDCS for linear polarizations.

The effects of electron correlation can be seen most directly when the TDCS is plotted as a function of the angle between the directions of the two ejected electrons, as Akoury *et al.* pointed out [8] when displaying their coincidence measurements of the angular distributions. In Fig. 3 we show experimental measurements and our converged calculations of the TDCS. The TDCS is shown in contour plots as a function of the angle between the faster electron and the molecular axis and the angle between the two electrons. Figure 3(a) shows the experimental results—which use circularly polarized light and are integrated over energy sharings between 78% and 96%—plotted with both electrons near the plane perpendicular to the direction of light propagation that contains the molecule. That is the range of energy sharing that produces the nearly featureless DDCS in Fig. 2(a).

Akoury *et al.* argued that the two rows of four maxima in Fig. 3(a) arise from two-slit-like interference of one of the entangled pair of electrons which also has a binary collision with the other electron, ejecting it at characteristic values of  $\theta_{12}$  near  $90^\circ$ . In this interpretation, integrating the

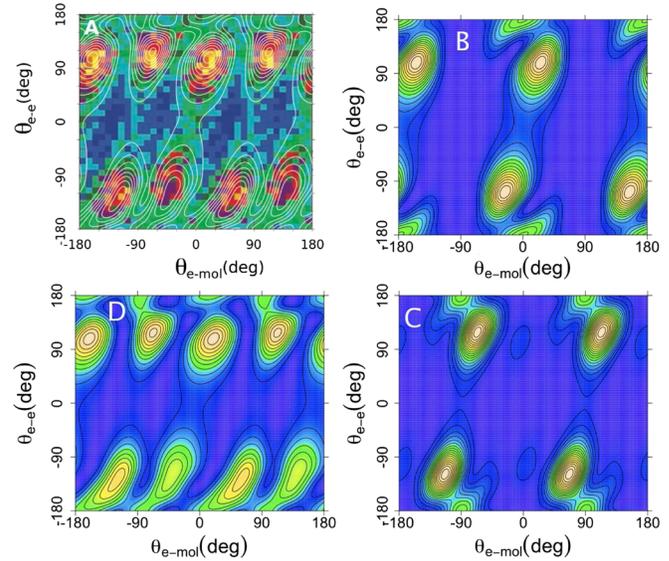


FIG. 3 (color online). TDCS at photon energy of 160 eV plotted as function of angle of faster electron with molecular axis and angle between electrons. (a) Experiments with circular polarization of Ref. [8] with ECS calculations superimposed as white contours. Data include all energy sharings between 78% and 96%. (b) ECS calculations for parallel polarization for ejection energy of 108 eV (99% energy sharing). (c) Corresponding calculations for perpendicular polarization. (d) Calculations for circular polarization.

data of Fig. 3(a) over all  $\Theta_{e-e}$  destroys the four-lobed interference pattern, because doing so obscures the electrons' quantum entanglement. The interference pattern is only recovered when one integrates over particular ranges of  $\Theta_{e-e}$ . However, our essentially exact calculations for extreme energy sharing shown in Figs. 3(b) and 3(c) indicate that the perpendicular and parallel polarizations show only a simple dipole pattern in  $\theta_{e-mol}$  superimposed on the typical “binary peak” that is generally interpreted in atomic double photoionization as arising from a collision of the electrons during the ejection process. Circular polarization, which is a combination of parallel and perpendicular amplitudes, produces Fig. 3(d), which is nearly identical to the experiment in Fig. 3(a). Moreover, by averaging such calculated cross sections over the energy sharing range in the experiment in Fig. 3(a) we are able to reproduce it almost exactly. Those calculations are also shown in Fig. 3(a) superimposed as contours on the original data of Akoury *et al.* Thus we conclude that the experiments at photon energies of 160 and 240 eV have not in fact demonstrated the expected physical effects of quantum interference and entanglement but rather only the superposition of the contributions of parallel and perpendicular polarization.

So do those fundamental quantum effects sought by the authors of Refs. [8,9] not exist in molecular double photoionization? To answer that question we also converged ECS calculations of the TDCS for a photon energy of 375 eV. In these calculations we have used a denser grid

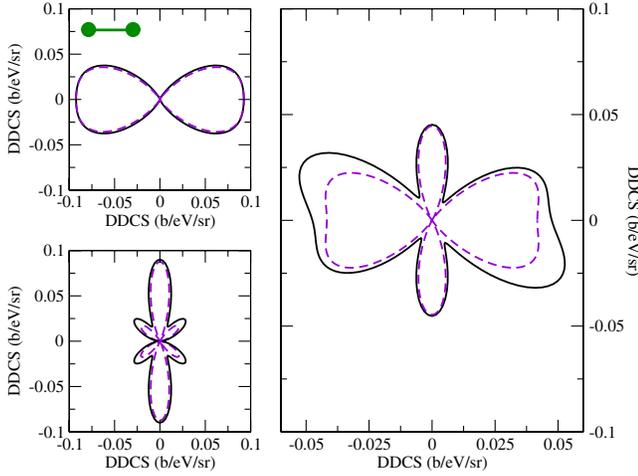


FIG. 4 (color online). DDCS for photon energy of 375 eV and 99% energy sharing. Left: Parallel (upper panel) and perpendicular (lower panel) polarization. Right: Circular polarization. Dashed curves: Simple diffraction model (see text).

that contains 220 DVR polynomial basis functions for each electron. At this energy the minimum asymptotic wavelength of the ejected electrons is 1.3 bohr, and is comparable to the internuclear distance of ground state  $H_2$ . Results analogous to those in Fig. 1 for this case are shown in Fig. 4. Here one sees that in perpendicular polarization the DDCS shows a pronounced six-lobed shape, while in parallel polarization it shows a typical dipolelike shape. Both DDCSs are qualitatively reproduced by the simple formula,  $(\epsilon \cdot \mathbf{k})^2 \cos^2[k_e R \cos(\theta_{e-mol})/2]$  [2], which is nothing other than the intensity distribution resulting from two dipole radiating antennas [3]. In particular, the angle  $\theta$  between the main and the secondary lobes in the perpendicular case approximately satisfies  $R \sin\theta = \lambda_e$ , which is the condition for constructive interferences for an electron of wavelength  $\lambda_e$  diffracted by two slits separated a distance  $R$ . The coherent combination of perpendicular and parallel amplitudes that represents circular polarization produces the DDCS shown in Fig. 4(c) that, in contrast with the DDCSs shown in Figs. 1(b) and 1(d), shows a reminiscence of the six lobes associated with double slit interferences in the perpendicular amplitude. The simple diffraction formula used in [8] for circular polarization,  $\cos^2[k_e R \cos(\theta_{e-mol})/2]$ , nearly reproduces this result, but not the slight twist that arises from the distinction between right- and left-handed polarization. It must be stressed, however, that the same formula leads to a much poorer description of the DDCS at photon energies of 160 and 240 eV [8] (see Fig. 1): as in the experiment, four lobes are predicted by the formula; however, the relative intensity of these lobes is not correct. This gives additional support to the conclusion that the observed angular patterns at 160 and 240 eV (especially the former) are not due to classical interferences produced by two diffractive centers.

The present results at 375 eV confirm the insightful observation of Akoury *et al.* that to see two-slit interference effects in double ionization one should look at the DDCSs at extreme energy sharing. Nonetheless, we have demonstrated here in calculations in excellent agreement with the experiment that such effects are not seen at lower photon energies. New experiments with linear polarization would check the correctness of the present interpretation and our predictions at the lower photon energies and would be able to see the diffractive effects we predict at higher energies.

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- [1] H. D. Cohen and U. Fano, *Phys. Rev.* **150**, 30 (1966).
  - [2] M. Walter and J. S. Briggs, *J. Phys. B* **32**, 2487 (1999).
  - [3] J. Fernandez, O. Fojón, A. Palacios, and F. Martín, *Phys. Rev. Lett.* **98**, 043005 (2007).
  - [4] M. Foster, J. Colgan, O. Al-Hagan, J. L. Peacher, D. H. Madison, and M. S. Pindzola, *Phys. Rev. A* **75**, 062707 (2007).
  - [5] D. Rolles *et al.*, *Nature (London)* **437**, 711 (2005).
  - [6] X. J. Liu *et al.*, *J. Phys. B* **39**, 4801 (2006).
  - [7] W. Vanroose, F. Martín, T. N. Rescigno, and C. W. McCurdy, *Science* **310**, 1787 (2005).
  - [8] D. Akoury *et al.*, *Science* **318**, 949 (2007).
  - [9] K. Kreidish *et al.*, *Phys. Rev. Lett.* **100**, 133005 (2008).
  - [10] W. Vanroose, F. Martín, T. N. Rescigno, and C. W. McCurdy, *Phys. Rev. A* **70**, 050703(R) (2004).
  - [11] W. Vanroose, D. A. Horner, F. Martín, T. N. Rescigno, and C. W. McCurdy, *Phys. Rev. A* **74**, 052702 (2006).
  - [12] D. A. Horner, W. Vanroose, T. N. Rescigno, F. Martín, and C. W. McCurdy, *Phys. Rev. Lett.* **98**, 073001 (2007).
  - [13] J. Colgan, M. S. Pindzola, and F. Robicheaux, *Phys. Rev. Lett.* **98**, 153001 (2007).
  - [14] T. J. Reddish, J. Colgan, P. Bolognesi, L. Avaldi, M. Gisselbrecht, M. Lavollée, M. S. Pindzola, and A. Huetz, *Phys. Rev. Lett.* **100**, 193001 (2008).
  - [15] C. W. McCurdy, M. Baertschy, and T. N. Rescigno, *J. Phys. B* **37**, R137 (2004).
  - [16] M. Walter and J. S. Briggs, *Phys. Rev. Lett.* **85**, 1630 (2000).