Single-photon double ionization of H₂ away from equilibrium: A showcase of two-center electron interference

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We demonstrate the effect of two-center interference on single-photon double ionization [double photoionization (DPI)] of the aligned H₂ molecule when it shrinks or expands from the equilibrium internuclear distance. This interference affects the first stage of the DPI process in which the primary photoelectron is ejected predominantly along the polarization axis of light and its geometrical interference factor is most sensitive to the internuclear distance in the parallel (Σ) orientation of the internuclear and polarization axes. This effect is responsible for strong modification of the DPI amplitude in the parallel orientation while the corresponding amplitude for the perpendicular (Π) orientation is rather insensitive to the internuclear distance. The combination of these two factors explains the profound kinetic energy release effect on the fully differential cross sections of DPI of H₂.

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The two-center electron interference in photoionization of diatomic molecules was predicted theoretically as early as in the 1960s [1,2]. However, experimental observations of this seemingly simple effect proved to be elusive. It was not until very recently that this effect was detected in the form of oscillations in the corresponding vibrational ratios of the angle-integrated photoionization cross sections of H₂, N₂, and CO [3,4]. The earlier measurements of the angle differential cross sections of single-photon two-electron ionization (double photoionization or DPI) on H₂ with circular polarized light [5–7] were originally interpreted in terms of the two-center interference. However, these measurements were later explained by mixing of two nondiffractive contributions of circularly polarized light [8]. The two-center interference interpretation of the DPI measurements is only appropriate at substantially higher photon energies that are not yet explored experimentally.

In the meantime, experimental observations of DPI of H₂ in the molecular frame showed a clear dependence on the internuclear separation R accessible in the vibrational ground state [1.1–1.7 a.u. at full width at half maximum (FWHM)]. The authors of the pioneering works [9,10] reported a set of fully differential cross sections (FDCS) resolved with respect to the kinematics of the two ejected electrons and the kinetic energy release (KER) available to the two protons after the molecule breaks up. The corresponding internuclear distance is simply $R = 1/\text{KER}$. The original experimental data were later revised [11] and subsequently found in fair agreement with numerical calculations using the exterior complex scaling (ECS) [12] and the time-dependent close-coupling (TDCC) [13] methods performed at the corresponding R values.

The KER effect on the FDCS was attributed to pronounced differences in the R dependence of the parallel $\mathbf{e} \parallel \mathbf{R}$ (Σ) and perpendicular $\mathbf{e} \perp \mathbf{R}$ (Π) components of the DPI amplitude [12]. Here, $\mathbf{e}$ and $\mathbf{R}$ are the polarization and internuclear axes, respectively. The contribution of the parallel (Σ) component had a minimum in the range of internuclear distances being sampled by the experiment, while the perpendicular (Π) component decreased monotonically as R increased. Another

set of measurements and calculations of KER specific FDCS was reported in Refs. [14,15]. As in previous theoretical work [12], the KER effect on the FDCS was ascribed to the Σ amplitude, which displayed an appreciable dependence on R , while the Π amplitude, being strongly dominant, showed little variation with R .

In their search for explanation of this peculiar dependence of the Σ and Π ionization amplitudes on the internuclear distance, the authors of Refs. [14,15] turned their attention to a related, but much simpler, process of single photoionization of H₂⁺ [16]. They noted that the σ electronic states, which showed the strong sensitivity to changes in R , lie on or near the internuclear axis, while the π states, which are less sensitive to changes in R , are concentrated in the plane between the nuclei. It was plausible to suggest that similar effects were at play in DPI of H₂. However, this analogy is not straightforward since the DPI process is strongly driven by the electron correlations between the outgoing electrons that are absent in single photoionization of H₂⁺. So the KER effect in DPI is still not explained on a simple qualitative level.

In this Brief Report, we give such an explanation in terms of the two-center interference. To do so, we focus our analysis on the knockout (KO) mechanism of DPI which is the dominant channel for photon energies not far above the double ionization threshold. In this mechanism, the primary photoelectron, that is produced by single photoionization (SPI) of the H₂ molecule, knocks out the secondary photoelectron by means of ionizing collision or ($e, 2e$) reaction on the singly charged H₂⁺ ion. In the approximation of the two separated H atoms, the single photoionization amplitude of H₂ is governed by a simple interference factor [17]:

$$f_{\text{SPI}}(\mathbf{k}_e) \sim (\mathbf{e} \cdot \mathbf{k}_e) \cos(\mathbf{k}_e \cdot \mathbf{R}/2). \quad (1)$$

Here $\mathbf{k}_e$ is the momentum of the ejected electron and the factor $\cos(\mathbf{k}_e \cdot \mathbf{R}/2)$ appears due to the two-center interference. In the case of the parallel orientation of the molecular and polarization axes $\mathbf{R} \parallel \mathbf{e}$, the photoionization factor $\mathbf{e} \cdot \mathbf{k}_e$ and the interference factor $\cos(\mathbf{k}_e \cdot \mathbf{R}/2)$ work in concert and the

two-center interference affects strongly the first stage of the KO mechanism and the DPI process as a whole. For the perpendicular orientation $\mathbf{R} \perp \mathbf{e}$, the interference factor is equal to unity in the direction of $\mathbf{e}$. The interference affects the primary photoelectron only in directions close to perpendicular to $\mathbf{e}$, where single photoionization is close to zero. That is why interference effects do not appear in DPI in the case of the perpendicular molecular orientation.

In the rest of the Brief Report, we expand and elaborate on these ideas in more detail. First, we generate a set of FDCS of DPI of H_2 at various internuclear distances R and molecular axis orientations. To assure numerical accuracy of our DPI calculations, we employ two complementary computational methods. In the first method, we solve the molecular time-dependent Schrödinger equation (TDSE) in spherical coordinates and project the solution on the scattering states of the singly charged H_2^+ ion [18]. In the second approach, we employ the exterior complex scaling method in the prolate spheroidal coordinates (PSECS) [19]. As an additional test, we reproduce the experimental FDCS of Ref. [11] and make comparison with corresponding earlier theoretical results [12,13].

At the next stage, we derive the DPI amplitudes for the Σ and Π orientations. We follow the procedure, outlined in our previous work [18], and define the amplitudes as

$$|g_{\Sigma/\Pi}(\theta_{12})| = \left[\frac{d^3\sigma(\theta_N = 0^\circ/90^\circ)}{dE d\theta_1 d\theta_2} \right]^{1/2} \frac{1}{\cos\theta_1 + \cos\theta_2}, \quad (2)$$

Here $d^3\sigma(\theta_N = 0^\circ/90^\circ)/(dE d\theta_1 d\theta_2)$ is the equal energy sharing FDCS resolved with the molecular orientation angle θ_N and the photoelectron escape angles θ_1, θ_2 that are counted from the direction of the polarization vector of light. For the angles $\theta_N = 0^\circ/90^\circ$, the whole contribution to the FDCS comes from the Σ or Π amplitudes, respectively. The kinematic factor $\cos\theta_1 + \cos\theta_2$ assumes the prevalence of the dipole $S \rightarrow P$ transition in the molecular DPI. Other multipoles contribute higher powers of the sum cosine term but the linear term is leading near the kinematic node corresponding to the back-to-back emission of the two photoelectrons.

In Fig. 1 we plot the symmetric amplitude g_Σ of DPI of H_2 at the photon energies of 75 eV (left) and 90 eV (right) which correspond to the photoelectron energies $E_1 = E_2 = 12.5$ eV and 20 eV, respectively. The left set of amplitudes corresponds to the experimental kinematics [9–11], while the right set is chosen at a slightly increased excess energy for completeness of our analysis. The respective internuclear distances R (indicated on each panel) range from 0.8 a.u. to 1.8 a.u. (from top to bottom). The TDSE and PSECS calculations are shown with blue dots and red solid lines, respectively. At the internuclear separations $R = 0.8$ and 1.0 a.u., both calculations produce nearly identical amplitudes. At $R = 1.4$ and 1.8 a.u., the TDSE amplitude has to be scaled up by 20% to match its PSECS counterpart. At $R = 1.2$ a.u., there is some small shape variation between the two methods. This internuclear distance is peculiar as the amplitude g_Σ collapses nearly an order of magnitude from either small $R = 0.8$ a.u. or large $R = 1.8$ a.u. There is also a strong variation of shape from small to large R . At $R = 0.8$ a.u. the amplitude g_Σ

FIG. 1. (Color online) Symmetric amplitudes of DPI of H_2 for the parallel Σ orientation. Left: $E_1 = E_2 = 12.5$ eV. Right: $E_1 = E_2 = 20$ eV.

has a heliumlike Gaussian shape, whereas at $R = 1.8$ a.u. it acquires a considerable pedestal. At the same kinematical conditions, the g_Π amplitude retains its Gaussian shape at all the internuclear separations.

The minimum of the amplitude g_Σ at $R = 1.2$ a.u. can be related to the analogous minimum of the singly differential cross section (SDCS), which is defined as an angular integral of the FDCS $\sigma_\Sigma^{(1)} = \frac{1}{4\pi} \iint \sigma_\Sigma^{(3)} d\Omega_1 d\Omega_2$. On the top panel of Fig. 2, we show the SDCS calculated using the PSECS method, tabulated on R with a step of 0.2 a.u., and spline interpolated to smooth curves. As one can see from this figure, SDCS does indeed have a minimum near $R = 1.3$ a.u. for $E_1 = E_2 = 12.5$ eV and near $R = 1.2$ a.u. for $E_1 = E_2 = 20$ eV. A very similar R dependence can be seen on the bottom panel where we show the SDCS of SPI of H_2 calculated at the ejection angle $\theta_e = 0$. Qualitatively, this dependence agrees with predictions of the simplified expression (1), which is also indicated in the figure, even though the precise position of the destructive interference minimum is shifted down by 0.3 a.u. for $E_{\text{exc}} = 25$ eV and by 0.2 a.u. for $E_{\text{exc}} = 40$ eV.

The full dependence of SDCS of SPI on the ejection angle θ_e at various R and the parallel field orientation is shown in Fig. 3

FIG. 2. (Color online) Top: the SDCS of DPI of H_2 as a function of R for the parallel Σ orientation for $E_1 = E_2 = 12.5$ eV (solid line) and $E_1 = E_2 = 20$ eV (dashed line). Bottom: the SDCS of SPI for the parallel field orientation and the ejection angle $\theta_e = 0$ as a function of R . The black thick line shows the PSECS calculation, whereas the thin red line visualizes the interference term in Eq. (1).

for the excess energy of 25 eV (top) and 40 eV (bottom). This dependence agrees qualitatively with the expected interference pattern. Indeed, for R less than a certain value, the angular distribution has two peaks, exactly as follows from Eq. (1) for small R , whereas for larger R , the angular distribution has six peaks, as also follows from Eq. (1).

In the present study, we are interested in the $(e, 2e)$ reaction on H_2^+ as a second stage of the KO mechanism of DPI of H_2 . The primary photoelectron, far from the molecule, is described by the outgoing spherical wave $f^{SPI}(\mathbf{k}_e) \exp(i\mathbf{k}_e \mathbf{r})/r$, modulated with the single photoionization amplitude $f^{SPI}(\mathbf{k}_e)$. Each primary photoelectron scatters inelastically on the molecular ion and knocks out the secondary electron with the probability amplitude $f_{\mathbf{k}_e}^{(e, 2e)}(\mathbf{k}_1, \mathbf{k}_2)$. The resulting expression for the on-shell contribution of the KO process to the DPI amplitude is

$$f^{KO}(\mathbf{k}_1, \mathbf{k}_2) \propto \oint f_{\mathbf{k}_e}^{(e, 2e)}(\mathbf{k}_1, \mathbf{k}_2) f^{SPI}(\mathbf{k}_e) d\Omega_{\mathbf{k}_e}. \quad (3)$$

The moduli of the symmetric $(e, 2e)$ amplitudes $|f_{\mathbf{k}_e}^{(e, 2e)}(\mathbf{k}_1 = \mathbf{k}_2)/(\cos \theta_1 + \cos \theta_2)|$, expanded over the angular momentum of the projectile electron $\ell = 1, 3$, and 5 , are shown in Fig. 4. These amplitudes are shown as functions of the mutual electron angle $\theta_{12} = \theta_2$ with the fixed angle $\theta_1 = 0$. All angles are counted from the direction of incidence taken as the $\hat{z}$ axis. The shape of the $(e, 2e)$ symmetric amplitude for $\ell = 1$ is close to a Gaussian. The $(e, 2e)$ symmetric amplitudes for $\ell = 3$ and $\ell = 5$ have nodes and look like Gaussian multiplied by second-order polynomial and four-order polynomial, respectively. The positions of the nodes

FIG. 3. (Color online) SDCS of SPI as a function of the ejection angle θ_e for various R : $E_{exc} = 25$ eV (top); $E_{exc} = 40$ eV (bottom).

in $(e, 2e)$ $\ell = 3$ and $\ell = 5$ symmetric amplitudes do not depend on R and the excess energy.

The main peaks in $\ell = 1$ and $\ell = 3$ symmetric amplitudes have similar magnitudes for any considered R . The central part of $\ell = 3$ symmetric amplitude angular distribution can be considered as Gaussian with a smaller width than the Gaussian in $\ell = 1$. In the total KO amplitude, these amplitudes are summed with coefficients equal to the expansion coefficients of the SPI amplitude over the spherical harmonics, because ℓ can be considered as angular momentum of intermediate (primary ionized) electron.

A typical dependence of distribution of primary ionized electrons over angular momentum on R can be examined using an approximate expression (1) which accounts for the two-center interference. The interference factor $\cos^2(k_e R/2)$ and expansion coefficients of the simplified amplitude (1) over spherical harmonics are shown in Fig. 5. We emphasize that in our actual computations we used the exact SPI amplitude calculated using the PSECS method, and Eq. (1) is only used here to demonstrate the role of two-center interference. The $\ell = 5$ component is small for the present case where R is not much larger than the position of the first interference minimum. The $\ell = 1$ and $\ell = 3$ components of SPI amplitude have opposite signs, and the minimum of interference factor $\cos^2(k_e R/2)^2$ corresponds to cancellation of $\ell = 1$ and $\ell = 3$ components in the $\theta_e = 0$ direction. This direction coincides with the external field polarization direction, which is the direction of most probable ejection of the primary photoelectron for the single center system. As a result, the position of minimum of SPI TICS is close to the position of the minimum of SPI SDCS in the $\theta_e = 0$ direction. From this argument, it is clear why the SDCS of DPI, as a function of R , has the minimum close to the minimum of SPI TICS, and why near this minimum the symmetric Σ amplitude of DPI has the most pronounced multipeak pattern. It is a result of summation of two Gaussians

FIG. 4. (Color online) Moduli of symmetric amplitude of $(e, 2e)$, for the case when incoming electrons have fixed initial angular momentum ℓ , as a function of the ejection angle θ_2 for $\theta_1 = 0^\circ$ and various R . Top: $\ell = 1$; middle: $\ell = 3$; bottom: $\ell = 5$.

with close magnitudes that are formed on the $(e, 2e)$ stage of DPI. The relative sign of this summation is opposite due to a two-center interference on the SPI stage.

In conclusion, we demonstrated the effect of two-center interference on single-photon double ionization of the aligned

FIG. 5. (Color online) Interference factor $\cos^2(k_e R/2)$ (solid black line) and coefficients of the partial wave expansion of the approximated SPI amplitude [Eq. (1)] are shown as functions of R for $\ell = 1$ (dashed red line), $\ell = 3$ (dotted green line), and $\ell = 5$ (dot-dashed blue line).

and deformed (stretched or shrunk) H_2 molecule. We adopted the knockout mechanism of DPI in which the primary photoelectron ejects the secondary electron by ionizing collision with, or $(e, 2e)$ reaction on, the singly charged ion H_2^+ . The primary photoelectron is ejected predominantly along the polarization axis of light and its geometrical interference factor is most sensitive to the internuclear distance in the parallel (Σ) orientation of the internuclear and polarization axes. This explains a deep interference minimum in the dipole channel of single photoionization of H_2 in the parallel field orientation [20,21]. However, it is in the DPI process that this interference can be detected most efficiently. Indeed, DPI is followed by the molecular breakup which allows one to make orientation and deformation specific measurements by detecting the receding protons. We hope that our investigation will stimulate further interest in DPI of H_2 .

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