Erasing the traces of classical mechanics in ionization of H_2 by quantum interferences

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The single ionization of hydrogen molecules by fast electron impact is studied theoretically for transitions from the ground (*gerade*) state to final ground (*gerade*) and first-excited (*ungerade*) states of H_2^+. It is shown that under definite conditions and for particular orientations of the molecule, the main physical features of the ionization reaction, which are the binary and recoil peaks usually associated with classical mechanisms, are completely erased by quantum interference effects that resemble the ones predicted previously for photoionization reactions. However, these new effects cannot be derived from photoionization results, as the electromagnetic field cannot transfer momentum. In addition, it is found that the emission spectra of transitions leading to the final *gerade* and *ungerade* states of the H_2^+ residual target are analogous in certain cases to the patterns of two sources emitting waves in phase or antiphase, respectively. Finally, we show how an average of the emission from randomly oriented molecules produces a binary peak at the classical expected position, in agreement with experiments.

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I. INTRODUCTION

Interference effects lie at the very heart of quantum mechanics, and analogies with the Young's two-slit experiment [1] play a fundamental role in the understanding of the dual nature of quantum objects [2]. However, the experiment of electrons passing through two slits was accomplished only in 1961 [3]. After that, interference effects were exposed for beams of neutrons, atoms, and molecules [4–7]. Also in the 1960s, a fascinating method was suggested to detect quantum interference in the ejected electron spectra of diatomic molecules [8].

However, only recently, these kind of oscillations were measured for the case of fast krypton ions impacting on H_2 [9]. In the calculations that supported the experiments, and in almost all subsequent studies with massive particles, the observables of the reactions (i.e., the cross sections) are described as atomic contributions modulated by an interference factor. After that pioneering work, a lot of research were devoted to the study of the coherent emission with heavy ions [10–13], electrons [14–18], and photons [19–22] as projectiles.

As is well known, electronic emission induced by the impact of massive particles on atomic targets is most probable in the direction given by the momentum transfer. Consequently, this fact may be ascribed to a binary collision between the projectile and the ejected electron. This classical ionization mechanism may be traced in the observables of the reaction, i.e., the multiple differential cross sections (MDCS), by the presence of a prominent peak, which is the so-called binary peak being one of the most important physical features of the MDCS [23]. Another important physical characteristic of the MDCS is the so-called recoil peak observed in measurements at almost the opposite direction at which the binary one appears. This may be related to a two-step mechanism in which the active electron suffers a binary collision with the projectile and then the electron is backscattered elastically by the target nucleus, which in turn recoils to conserve the total momentum. The same scenario occurs for ground-state molecular hydrogen targets, where experimental results for randomly oriented molecules also show the presence of both the binary and recoil peaks [24] nicely reproduced by theoretical models (see, for instance, [25] and [26]). To our knowledge, it has been accepted so far that the binary and recoil peaks must appear in every MDCS in asymmetric collisions at sufficiently high impact energy for atomic as well as for molecular hydrogen as the omnipresent fingerprint of classical mechanics in the quantum predictions [27]. Nevertheless, in what follows, we will report the unexpected fact that under definite conditions, both peaks may be suppressed in the ionization of molecular hydrogen by electron impact. Atomic units will be used in the following, except where otherwise explicitly stated.

II. THEORY

The reaction of interest,

$$e^- + H_2(^1\Sigma_g^+) \rightarrow 2e^- + H_2^+(^2\Sigma_{g,u}^{\pm}), \tag{1}$$

may be treated as a pure electronic transition by applying closure relations over all possible final rotational and vibrational states of the residual target [28,29]. We analyze asymmetric kinematic conditions where a slow and a fast electron are detected in the final channel of the reaction, so exchange effects are disregarded. Moreover, at the energies considered, the collision time is much less than the rotational and vibrational ones. So, only vertical transitions at the equilibrium distance ($\rho_0 = 1.4$) are assumed. We obtain MDCS by employing the molecular molecular Brauner-Briggs-Klar (MBBK) model [26], motivated by the previous atomic BBK one [30] in which the final continuum wave function includes a product of three Coulomb functions associated to the three two-body pairs present in the final channel, which we assume to have three bodies, i.e., the scattered and ejected electrons, and the residual target taken as a whole body. In the MBBK model, the exact final state wave function is approximated as

$$|\Psi_f^-\rangle \cong |\mathbf{k}_s\rangle \otimes |\Phi_{g,u}\rangle \otimes |\xi_c(\mathbf{k}_e,\mathbf{k}_s)\rangle, \tag{2}$$

where $|\mathbf{k}_s\rangle$ represents a plane wave describing the fast scattered electron with momentum $\mathbf{k}_s$, and $|\Phi_g\rangle$ and $|\Phi_u\rangle$ stand for the wave function corresponding to the *gerade* $^2\Sigma_g^+$ or *ungerade* $^2\Sigma_u^-$ states of the residual H_2^+ molecular ion, respectively.

The continuum wave function $|\xi_c\rangle$ is taken in the coordinate representation as

$$\xi_c(\mathbf{k}_e,\mathbf{k}_s;\mathbf{R},\{\mathbf{r}\}) = \frac{e^{i\mathbf{k}_e\cdot\mathbf{r}_1}}{(2\pi)^{3/2}} C(\mathbf{k}_e,\mathbf{r}_{1j},\gamma_e) \times C(\mathbf{k}_s,\mathbf{R}_j,\gamma_s) C(\mathbf{k}_{1p},\mathbf{r}_{1p},\gamma_{ep}), \quad (3)$$

where $j = a$ or b indicates the center from which the target electron is assumed to be ionized, and $\mathbf{k}_e$ is the ejected electron momentum. $\mathbf{R}_j$ and $\mathbf{r}_{1j}$ are the position vectors of the incident electron and the electron 1 with respect to the center labeled j, respectively. $\mathbf{r}_{1p}$ denotes the position of the incident electron with respect to the electron 1. The position of the latter is given by $\mathbf{r}_1$ in the molecule mass center. Moreover, the following Sommerfeld factors are defined:

$$\gamma_e = -Z_T/k_e, \quad \gamma_s = -Z_T/k_s, \quad \gamma_{ep} = \frac{1}{2k_{1p}}, \quad (4)$$

where $\mathbf{k}_{1p} = \frac{1}{2}(\mathbf{k}_s - \mathbf{k}_e)$ is the momentum conjugate to $\mathbf{r}_{1p}$. The Coulomb factors denoted by $C(\mathbf{k},\mathbf{r},\gamma)$ are given by

$$C(\mathbf{k},\mathbf{r},\gamma) = \Gamma(1-i\gamma)e^{-\pi\gamma/2}\,{}_1F_1[i\gamma;1;-i(kr+\mathbf{k}\cdot\mathbf{r})]. \quad (5)$$

In the preceding equations, it is assumed that electron 1 is ionized from the center labeled j, while the *passive* electron (the one not ionized) is supposed to screen completely the charge of the other nucleus from which ionization is not produced ($Z_T = 1$). The form of the wave function ξ_c is inspired by the one used previously to describe ionization of atoms [30]. The MBBK model provides an excellent approximation to describe experiments [26], as can be seen in Fig. 1.

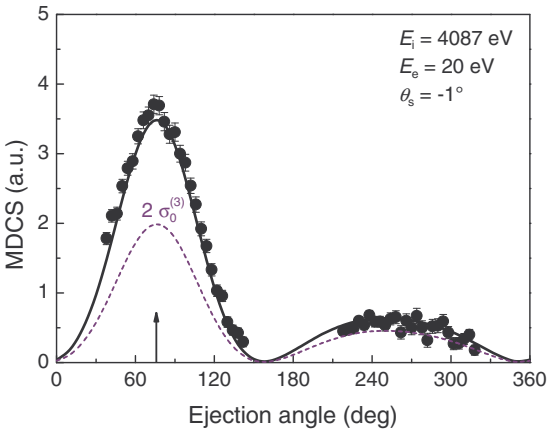

FIG. 1. (Color online) MDCS as a function of the ejection angle θ_e for the initial H_2 ground state and final H_2^+ ground state, averaged over all molecular orientations in space, for a coplanar geometry at fixed incident and ejection energies E_i and E_e, respectively, and scattering angle θ_s (positive orientation for the polar angles is taken clockwise). MBBK results: solid line. Twice effective atomic cross sections $\sigma_0^{(3)}$: dashed line [see Eq. (6)]. Experiments taken from Ref. [24]. The arrow indicates the classical binary peak angle.

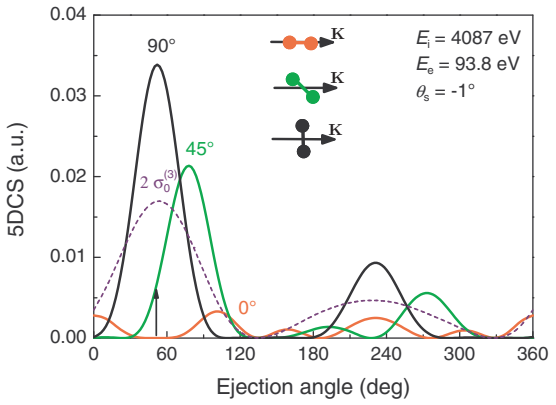

FIG. 2. (Color online) 5DCS as a function of the ejection angle θ_e for the initial H_2 ground state and final H_2^+ *gerade* state for an internuclear axis in the collision plane for molecular orientations of 0° (red line), 45° (green line), and 90° (blue line) with respect to **K** at fixed incident and ejection energies E_i and E_e, respectively, and scattering angle θ_s (positive orientation for the polar angles is taken clockwise). MBBK results: solid line. Twice effective atomic cross sections $\sigma_0^{(3)}$: dashed line [see Eq. (6)]. The arrow indicates the classical binary peak angle.

It can be shown that the MBBK five differential cross sections (5DCS), for a coplanar geometry in which the momenta $\mathbf{k}_i$, $\mathbf{k}_s$, and $\mathbf{k}_e$ lie all in the collision plane (defined by $\mathbf{k}_i$ and $\mathbf{k}_s$), reduce to the following approximate expression [14]:

$$\sigma_{g,u}^{(5)} \simeq 2[1+(-1)^n \cos(\boldsymbol{\chi}\cdot\boldsymbol{\rho}_0)]\sigma_n^{(3)} \quad (6)$$

for *gerade* ($n = 0$) or *ungerade* ($n = 1$) final H_2^+ states described by the linear combination of atomic orbitals with effective charge Z^* [31]. We define $\boldsymbol{\chi} = \mathbf{k}_e - \mathbf{K}$, where $\mathbf{K} = \mathbf{k}_i - \mathbf{k}_s$ is the momentum transfer, and $\sigma_n^{(3)}$ represents a one-center triply differential cross section corresponding to *effective* atoms (with nuclear charge Z^*) placed at the position of either molecular nuclei [14]. Therefore, interferences due to the coherent emission from both molecular centers, when the de Broglie wavelength of the ejected electron is of the same order as the internuclear distance, appear explicitly in the 5DCS as a factor modulating the atomic cross sections given by $\sigma_n^{(3)}$. For *gerade* final states, this factor is analogous to the one from the Young's two-slit experiment.

III. RESULTS AND DISCUSSIONS

The typical interference patterns [14] can be seen in Fig. 2, where MBBK 5DCS are computed by using Eq. (6) for the particular case in which the internuclear axis is in the collision plane. In contrast, these patterns are absent in the atomic cross sections $\sigma_0^{(3)}$, which in turn show clearly the binary and recoil peaks.

As expected, the presence of both the binary and recoil peaks is verified for molecules oriented at 90° with respect to **K**. At variance, *the binary peak is practically suppressed for molecules oriented in the* **K** *direction*, which is precisely the classical one for electron ejection as explained above. This effect is produced by destructive interferences originated by the coherent emission from both molecular centers. To support

this hypothesis, one can check that the interference factor in Eq. (6) predicts the total destructive interference when the condition $\boldsymbol{\chi} \cdot \boldsymbol{\rho}_0 = m\pi$ is verified for some (positive or negative) odd m value and, of course, for momenta magnitudes satisfying conservation laws. With the conditions of Fig. 2, it can be shown easily that $k_e \sim m\pi/\rho_0 + K$. This result can be related to the one obtained for photoionization of H_2 [20,21]. Indeed, for photon impact, it was shown that no photoelectrons are emitted if the condition $k_e \sim m\pi/\rho_0$ holds for molecules aligned in the polarization direction of the incident linearly polarized radiation. So, the classically expected direction for photoelectron emission is also forbidden for this particular orientation of the target and final *gerade* symmetry. It is worth noting that even if the photoionization conditions may be inferred by making $K = 0$ in the present results, the underlying physics is completely different, as the electromagnetic field cannot transfer momentum in the mentioned case of photoionization. Thus, it is clear that the corresponding observables are also different. As a matter of fact, neither binary nor recoil peaks are produced in photoionization. In Fig. 2, we can also see that the maximum value of the 5DCS for molecules oriented at 45° is shifted from the binary peak position due to partial destructive interferences produced precisely at that location. Even more, the recoil peak is practically suppressed for this orientation.

Differences in behavior between the 5DCS for the ground (*gerade*) and excited (*ungerade*) final states are apparent after inspection of Fig. 3. First, the ordering in magnitude of the cross sections is reversed, being 5DCS for *ungerade* final states and for parallel alignment in general greater than the ones for the perpendicular orientation, in a similar way to the ones measured in Ref. [32] for transitions to final vibrational dissociative states. Perhaps this similarity is only fortuitous, but it is worth noting that the $^2\Sigma_u^-$ final state of H_2^+ is also a dissociative one. Second, we can observe the following feature: *the binary and recoil peaks are suppressed for molecules with their axis normal to the momentum transfer*. The condition for this suppression is given by $\boldsymbol{\chi} \cdot \boldsymbol{\rho}_0 = \pm l\pi$ for $l = 0$ or an even number and momenta values fulfilling conservation laws. This condition is always satisfied ($l = 0$) for electrons emitted in the **K** direction and molecules oriented perpendicularly to **K**, as in this case $\boldsymbol{\chi}$ is normal to $\boldsymbol{\rho}_0$. This leads to the conclusion that electrons cannot be ejected perpendicularly to the internuclear axis when H_2 molecules are oriented normal to the **K** direction. Therefore, a nodal plane for electron ejection just in the classical direction of emission is observed for final *ungerade* states. Interestingly, the electronic distribution of the *ungerade* state exhibits a nodal plane perpendicular to the internuclear axis passing through its midpoint. This feature recalls the characteristic pattern of two coherent sources emitting mechanical or electromagnetic waves in antiphase, where there also exists a nodal plane perpendicular to the line joining both sources. In contrast, for two sources emitting in phase, no nodal plane exists. By taking into account these similarities, one is tempted to claim that the ionization spectra from ground state H_2 molecules to final *gerade* or *ungerade* states of the H_2^+ residual target are analogous to the interference patterns of two sources emitting coherently in phase or antiphase, respectively. However, for massive projectiles, there is a phase shift $\Delta = -\mathbf{K} \cdot \boldsymbol{\rho}_0$ with respect to the case of the impact of photons for which $K = 0$. So, only in the case of perpendicularly oriented molecules (for which $\Delta = 0$), the analogy with two sources is direct (of course, this is valid only for the interference factor and not for the cross sections, where binary and recoil peaks appear).

In Fig. 4, we present MBBK 5DCS for several molecular orientations of the internuclear axis. For the sake of clarity, only orientations in the collision plane are depicted. It can be observed that for orientation angles symmetric with respect to **K**, the MBBK 5DCS are also almost symmetric. Although not shown here, a similar behavior is observed when the molecular axis is out of the collision plane (details will be presented elsewhere). As all internuclear axis orientations are equally probable, deviations from the classical position of the binary peak given by **K** are compensated

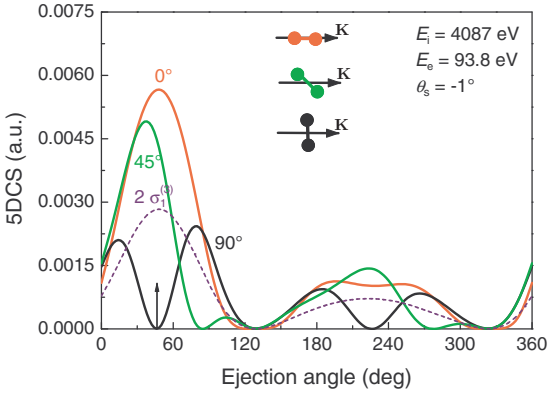

FIG. 3. (Color online) Same as Fig. 2, but final H_2^+ *ungerade* state.

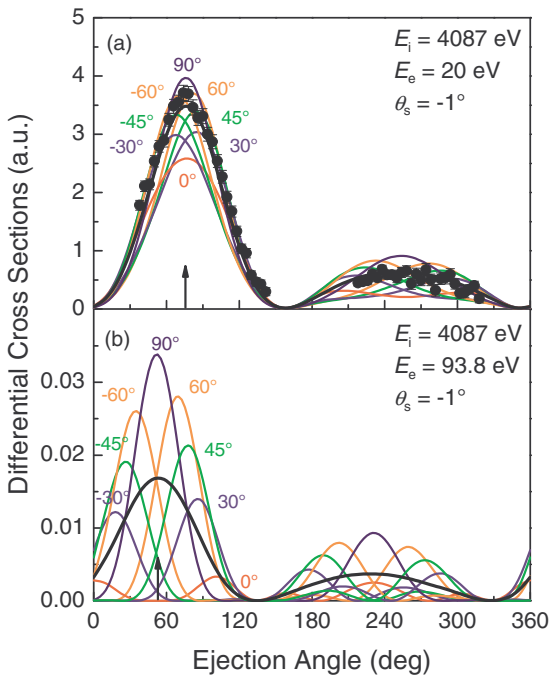

FIG. 4. (Color online) (a) Same as Fig. 1. Moreover, 5DCS for several molecular orientations with respect to **K** and for internuclear axis in the collision plane are included. (b) Same as panel (a), but E_e= 93.8 eV.

and the average obtained by integration over all directions in space gives place to a maximum around this classically predicted position also measured in experiments. This can be seen clearly in Fig. 4(a), where we exhibit the way the contributions for different angles produces the binary peak. The same situation is observed even in Fig. 4(b), where the de Broglie wavelength of the ejected electron is shorter and more pronounced interference effects are expected, leading to the suppression of the binary peak, as we have already discussed.

IV. CONCLUSIONS

In summary, we have shown that under definite conditions, the classical expected directions of electronic emission are forbidden. In this way, no traces of classical mechanics are left in the observables of the reaction by virtue of destructive quantum interferences. Unfortunately, presently there exist no measurements to contrast with our findings. Nevertheless, in this age of COLTRIMS (cold-target recoil-ion momentum spectroscopy) and reaction microscopes [33,34] that enable the accomplishment of complete kinematics experiments, it is possible to envisage, in the near future, experiments with oriented molecules (involving final dissociative states such as the *ungerade* state here studied) to corroborate (or refute) our predictions.

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