The $p$–H symmetry breaking in dissociative ionization of $\text{H}_2$ due to the molecular ion interaction with the ejected electron

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We propose a mechanism of electron localization and molecular symmetry breaking in dissociative photoionization of the $\text{H}_2$ molecule. The Coulomb field of the ejected electron can induce transition of the remaining $\text{H}_2^+$ ion from the gerade $^2\Sigma_{u}^+(1s\sigma_u)$ to the ungerade $^2\Sigma_{u}^+(2p\sigma_u)$ electronic state when the nuclei in a bound vibrational state are near the outer turning point. The superposition of this process with a direct transition to vibrational continuum should produce a non-gerade ionic state which results in observed asymmetry in the $p$–H ejection relative to the electron ejection direction at a small kinetic energy release.

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Dissociative photoionization (DPI) of the hydrogen molecule has been a subject of considerable interest in recent years. Even though it is a relatively weak single photoionization channel, the breakup of the $\text{H}_2^+$ ion into the ionic $\text{H}^+$ and neutral $\text{H}$ atomic fragments allows for determination of the molecular axis orientation when the reaction products are detected in coincidence. Because the dissociation is fast compared with molecular rotation, the direction of fragmentation coincides with the molecular axis at the instant of photoionization. This allows for the molecular frame photoelectron angular distribution to be determined.

One of striking observations following from these coincident studies was breakup of the photoelectron emission symmetry with respect to the ionic $p$ and neutral $\text{H}$ atomic fragments. This asymmetry was found in single-photon induced DPI process [1–4] as well as in multi-photon regime [5, 7, 10]. The finding of this asymmetry was indeed surprising. The two single photoionization channels lead from the ground $\text{H}_2$ state to the ionic gerade $^2\Sigma_{g}^+(1s\sigma_g)$ and ungerade $^2\Sigma_{u}^+(2p\sigma_u)$ states that are well separated in energy and do not normally mix. Hence, the ionic state possesses a well-defined exchange symmetry which leads to the fully symmetric photoelectron emission. The $p$–H asymmetry in dissociation means that the asymptotics of the wave function of the state with a fixed ejected electron energy and a fixed nuclear kinetic energy release (KER) is non-gerade by the coordinates of the bound electron. From the mathematical point of view, this means that the bound electron is in a superposition of gerade and ungerade $\text{H}_2^+$ wave functions.

It was Martín and Fernández [2] who showed that the two ionic states can actually mix because of autoionization via the $Q_1$ and $Q_2$ doubly excited states. This creates a mixed parity ionic state that allows for the localization of the bound electron and angular asymmetry of the photoelectron. Since the autoionizing states lives few femtoseconds, the nuclei have enough time to move outside the Franck-Condon (FC) region before the electron is ejected. Theoretical description of such a process therefore requires going beyond the fixed nuclei Born-Oppenheimer approximation.

An additional mechanism that can be responsible for the photoemission symmetry breaking is the effect of an intense IR field from few-cycle laser pulses [5, 7, 10]. The strong laser field may act in conjunction with quantum mechanical interference involving autoionizing states and the laser-altered wave function of the departing electron. Alternatively, the charge localization may be due to laser-driven transition between different electronic states of the molecular ion.

An alternative mechanism that could be responsible for the DPI asymmetry was discussed briefly by Martín et al. [2] in the form of a preferred attractive interaction between the proton and the escaping electron. However, the photoelectron is too fast to be efficiently perturbed by the slow proton, except possibly in the region of the maximum allowed KER. In the present work, we consider a similar mechanism of direct photoelectron interaction with the remaining ion. The Coulomb field of the ejected electron can induce transition of the remaining $\text{H}_2^+$ ion from the gerade $^2\Sigma_{g}^+(1s\sigma_g)$ to the ungerade $^2\Sigma_{u}^+(2p\sigma_u)$ electronic state when the nuclei in a bound vibrational state are near the outer turning point. The superposition of this process with a direct transition to vibrational continuum should produce asymmetry in the $p$–H ejection relative to the electron ejection direction at a small kinetic energy release.

The $p$–H asymmetry in DPI means that the wave function of a state with a fixed ejected electron energy and a fixed nuclear KER is non-gerade by coordinates of the bound electron. From the mathematical point of view, this means that the bound electron is in superposition of gerade and un-gerade $\text{H}_2^+$ wave functions. The amplitudes of generation of the gerade and ungerade ionic states are proportional to the corresponding FC factors.
states

\[ S_{gK} = \langle gK | H_2 \rangle, \quad S_{uK} = \langle uK | H_2 \rangle. \]  \(1\)

Here \(|H_2\rangle \equiv \chi_{H_2}(R)\) is the ground vibrational state of \(H_2\), \(|gK\rangle \equiv \chi_{K g}(R)\) and \(|uK\rangle \equiv \chi_{K u}(R)\) are vibrational continuum functions of \(H_2^+\) in gerade and ungerade electronic states, respectively, \(K = \sqrt{2mE_R}\) is the relative momentum of ion and atom after dissociation, \(E_R\) is the kinetic energy release, \(m\) is the reduced mass of a nucleus, \(L\) is the angular momentum transferred to the rest ion in a ionization.

The DPI amplitude via the \(2p\sigma_u\) state for \(E_R = 1\) eV is lesser then that via the \(1s\sigma_g\) state by 10 orders of magnitude (see Fig. 1). Therefore, for small KER, a direct transition to an ungerade state cannot induce an observable asymmetry. It is also clear from a classical physics consideration. The turning point in the \(1s\sigma_g\) adiabatic potential for \(E_R = 1\) eV is \(R = 1.023\) a.u. The turning point in the \(2p\sigma_u\) adiabatic potential at the same KER is \(R = 4.45\) a.u., well outside the FC region and where the \(H_2\) ground vibrational state wave function is extremely small.

The overlap integrals are equal for the gerade and ungerade electronic states. The overlap between vibrational states is maximal. As it is clear from the above arguments, DPI with a small KER proceeds solely via the \(H_2^+\) ground state. In result, the original asymmetry in the bound electron wave function is lost entirely. To make a transition to a vibrational continuum of \(2p\sigma_u\) with a small KER, the ion should reach an internuclear distance close to the turning point in the \(2p\sigma_u\) adiabatic potential for a small above-threshold energy. After that, the \(H_2^+\) ion should interact with some external field, which can excite it to the \(2p\sigma_u\) state. There are a number of experiments in which an IR laser field with a small energy is used for this purpose [3, 4, 11].

One should note, however, that in the DPI process of \(H_2\) there is always present an external field that interacts with the \(H_2^+\) ion. It is the field of the ejected photoelectron. During the time while the inter-nuclear separation reaches sufficient distance to make a transition to a small-KER ungerade state, the ejected electron have already flown far away, its interaction with the ion is small. However, several effects can conspire to help the asymmetry from interaction with far ejected electron to be observable:

1. When the ion is in the bound vibrational state with the outer turning point close to inner turning point in the \(2p\sigma_u\) adiabatic potential (see Fig. 2), the nuclei spend a long time near the point \(R\) were the overlap between vibrational states is maximal.

2. The number of ions in bound vibrational states after ionization is much larger then ones in vibrational continuum states, and even a small conversion to ungerade dissociative state can give result comparable to a direct transfer to a gerade vibrational continuum state.

3. The \(1s\sigma_g\) and \(2p\sigma_u\) states form pair of so-called charge-resonance (CR) states. The energy gap between the CR states is decreasing with the internuclear distance \(R\), while the dipole transition matrix

![FIG. 1: Absolute values of the overlap integrals between the \(H_2\) vibration ground state wave function and the \(H_2^+\) vibration continuum for the \(1s\sigma_g\) (solid line) and \(2p\sigma_u\) (dashed line) electronic states.](image1)

![FIG. 2: (Color online) The energy diagram of the proposed DPI process. Exhibited in the figure are the adiabatic potentials for the ionic gerade \(1s\sigma_g\) (solid line) and ungerade \(2p\sigma_u\) (dashed line) states, the initial \(H_2\) vibration state wave function (red solid line), the vibrational continuum energy level and vibrational bound energy level, and the two pathways of dissociation — the direct transition to the continuum energy level \(E_k\) (dashed blue line) and via an intermediate vibrational bound state \(E_v\) following transition of the ion to the \(2p\sigma_u\) state (dotted green line).](image2)
element $\langle 2p\sigma_u | 1s\sigma_g \rangle \to R/2$. Thereby, CR states are strongly coupled to external field for large $R$.

Let us estimate the asymmetry due to this process. We assume that a duration of the ionizing pulse is much smaller than the characteristic time of the nuclear motion. After ejection of the photoelectron, the evolution of the vibrational state can be described by a time-dependent Schrödinger equation

$$i \frac{\partial \chi_g(R,t)}{\partial t} = \left[ -\frac{1}{2m} \frac{\partial^2}{\partial R^2} + \frac{L(L+1)}{2mR^2} + U_{1s\sigma_g}(R) \right] \chi_g(R,t),$$

where $U_{1s\sigma_g}(R)$ is the adiabatic potential. The initial condition imposed on Eq. (2) is that its solution coincides with the $H_2$ vibrational ground state

$$\chi_g(R,0) = \chi_{H_2}(R).$$

The matrix element of transition between the gerade and ungerade ionic states in the field of the ejected electron is given by the following expression

$$\mu(R, r_e) \simeq \frac{d(R)}{r_e^2}.$$  

Here $r_e$ is the distance to the ejected electron and

$$d(R) = \langle 2p\sigma_u | n_e \cdot r | 1s\sigma_g \rangle$$

is the dipole matrix element, $r$ is a coordinate of the bound electron, $n_e = r_e/r_e, |1s\sigma_g \rangle \equiv \varphi_{1s\sigma_g}(r; R)$, $|2p\sigma_u \rangle \equiv \varphi_{2p\sigma_u}(r; R)$. Eq. (4) is derived by the Taylor’s expansion of $V(r, r_e) = 1/|r - r_e|$. In a case $R \gg 1$, the dipole matrix element $d(R) \approx n_e \cdot R/2$.

As we expect that the ejected electron is far from the ion at the time of transition, we can describe this electron quasi-classically and assign to it a trajectory $r_e(t)$. Under this assumption, the amplitude of transition to the ungerade state with the asymptotic relative nuclear momentum $K$ can be written as

$$A_{uK} = -i \int_0^\infty \frac{1}{r_e^2(t)} \langle uK | d(R) | \chi_g(R,t) \rangle e^{iE_K t} dt .$$

Here $|uK \rangle \equiv \chi_{2p\sigma_u}^{2p\sigma_u}(R)$ is a solution of the stationary Schrödinger equation

$$\left[ -\frac{1}{2m} \frac{\partial^2}{\partial R^2} + \frac{L(L+1)}{2mR^2} + U_{2p\sigma_u}(R) \right] \chi_{2p\sigma_u}^{2p\sigma_u}(R) = E_K \chi_{2p\sigma_u}^{2p\sigma_u}(R),$$

with $E_K = E_R + U_{2p\sigma_u}(\infty)$. The asymptotic form of the continuum function is $\chi_{KL}^{2p\sigma_u}(R \to \infty) = \sin(KR + \delta_u)$, where $\delta_u$ is a scattering phase. For all the results shown below, the wave functions were obtained by numerical solution of Eqs. (2) and (7).

The results are weakly depended on the angular momentum $L$, while $L$ is not very large. Typically $L$ is small when the $H_2$ molecule is initially in a low rotational state and the angular momentum exchange due to recoil of the ejected electron is also small. The latter condition is always satisfied when the ejected electron has low energy. For this reasons, the angular momentum $L = 1$ (that corresponds to ground rotational state of the ortho-hydrogen) was assumed in all examples shown below.

With the simplest approximation $r_e(t) = v_e t$, where $v_e = \sqrt{2E_e}$, $E_e$ being the ejected electron energy, the equation for the amplitude (6) can be rewritten as

$$A_{uK} = -i \int_0^\infty \frac{1}{E_e} a(t) dt ,$$

where

$$a(t) = \frac{1}{2t^2} \langle uK | d(R) | \chi_g(R,t) \rangle e^{iE_K t}$$

is the amplitude of transition per unit time.

![Fig. 3](image-url) (Color online) The absolute value $|a(t)|$ of the amplitude of transition per unit time for $E_R = 0.4$ eV from Eq. (6) (solid line) and Eq. (11) (dashed line).

The modulus of this amplitude is shown in Fig. 3 for selected value of $E_R = 0.4$ eV. Fig. 3 supports the qualitative reasoning given above. The noticeable transition begins only when the vibrational wave packet have spread up to the turning point $R(E_R) = 5.49$ a.u. corresponding to $U_{2p\sigma_u}(R) = E_K$. The peak of transition is near $t \approx 700$ a.u. The ejected electron with an energy, say, $E_e = 2$ eV, at this time would reach the distance $r_e \approx 250$ a.u.

It may seem that since the intermediate bound vibrational states contribute predominately to the process under consideration, we can take into account these states only in our consideration. In this approximation, the solution of Eq. (2) can be written as

$$\chi_g(R,t) = \sum_{\nu} \langle \nu | H_2 | 1s\sigma_g \rangle e^{-iE_{\nu} t} .$$

The amplitude of transition per unit time takes the form

$$\tilde{a}(t) = \frac{1}{2t^2} \sum_{\nu} \langle uK | d(R) | \nu \rangle \langle \nu | H_2 | e^{iE_{\nu} t} .$$

FIG. 3. (Color online) The absolute value $|a(t)|$ of the amplitude of transition per unit time for $E_R = 0.4$ eV from Eq. (6) (solid line) and Eq. (11) (dashed line).
where $\omega_{K\nu} = E_K - E_{\nu L}$. However, such approach is unapplicable. In Fig. 3 we compare the moduli of the amplitudes $a(t)$ from Eq. (9) and $\tilde{a}(t)$ from Eq. (11). From this comparison, we see that omitting of continuum from the summation over the intermediate vibronic states causes a serious error. While the position and shape of the main peak does not differ significantly, the amplitude $\tilde{a}(t)$ has an unphysical peak at small $t$ and diverges at $t \to 0$. This peak appears because the omitting of the continuum delocalizes the initial wave packet. That is why in a calculation of $A_{nuK}$ we used the direct solution of Eq. (2) instead of approximated analytical solution given by Eq. (10).

The asymmetry in the $p$–$H$ ejection can be expressed as

$$\beta = \frac{|S_{gK} e^{i\delta_g} - A_{uK} e^{i\delta_u}|^2 - |S_{gK} e^{i\delta_g} + A_{uK} e^{i\delta_u}|^2}{|S_{gK} e^{i\delta_g} + A_{uK} e^{i\delta_u}|^2 + |S_{gK} e^{i\delta_g} - A_{uK} e^{i\delta_u}|^2},$$

$$\approx -2 \frac{\Re[A_{uK} e^{i(\delta_u - \delta_g)}]}{S_{gK}}.$$

(12)

where $\delta_g$ and $\delta_u$ are scattering phases for gerade and ungerade states, respectively. Note that, according to Eq. (12), the asymmetry parameter $\beta > 0$ corresponds to the case when the bare proton prefers to be ejected in the same direction with the photoelectron, while the H atom is ejected in the opposite direction.

Since the matrix element $S_{gK}$ is real, only the real part of $A_{uK} e^{i(\delta_u - \delta_g)}$ contributes to the asymmetry parameter. The imaginary part of $A_{uK} e^{i(\delta_u - \delta_g)}$ is the logarithmically divergent at the upper limit of the integral over $t$ in Eq. (5). This divergence appears in a situation when the ejected electron interacts with the ion born directly in a vibration continuum state. Asymptotically, the internuclear distance in the ion in a vibration continuum state tends to $R(t) \to v_p t$ where $v_p = K/m$ is the relative velocity of the nuclei. The gerade and ungerade states are degenerate at large $R$. Following a secular equation, in this case of the ion in an external field, the nondegenerate right and left states are, respectively, $|r\rangle = (|1s_{\sigma g}\rangle + |2p_{\sigma u}\rangle)/\sqrt{2}$ and $|l\rangle = (|1s_{\sigma g}\rangle - |2p_{\sigma u}\rangle)/\sqrt{2}$. The left and right states describe the two halves of the bound electron cloud which is localized near the nuclei. The difference of the potential that the ejected electron affects on this half-clouds is $2\mu = 2d(R)/v_p^2 = (\mathbf{n}_R \cdot \mathbf{v}_p/v_p^2) t^{-1}$. As the result, the phase difference of the half-clouds is $\sim (\mathbf{n}_R \cdot \mathbf{v}_p/v_p^2) \ln t$. The imaginary part of $A_{uK} e^{i(\delta_u - \delta_g)}$ is proportional to the limit of this phase difference at $t \to \infty$. But, since the half-clouds do not overlap for large $R$, this phase difference has no effect on any observables.

As follows from Eq. (8), the asymmetry parameter is inversely proportional to the ejected electron energy $E_e$. So we can introduce the electron-energy-independent asymmetry parameter $\tilde{\beta}(E_R)$ via

$$\beta = \frac{\tilde{\beta}(E_R)}{E_e}.$$

(13)

In Fig. 4 the parameter $\tilde{\beta} = E_e \beta$ is shown as function of KER. To get an unscaled $\beta$ parameter for a given ejected electron energy $E_e$, $\beta$ should be divided on $E_e$ in eV. As is seen in Fig. 4 for any KER the proton prefers to be ejected in a direction that coincides with the electron ejection direction. When the ejected electron energy is very small and comparable with the excitation energy of the ion, the approximation $r_e(t) = v_p t$ is far too crude because the energy of the ejected electron is changed noticeably after the excitation of the bound electron. So, the condition of the validity of Eq. (13) is $E_e \gg E_R$.

In conclusion, we propose a mechanism of the $p$–$H$ asymmetry breaking in DPI of H$_2$ due to the H$_2^+$ ion interaction with the ejected electron. A seemingly forbidden transition to the ionic $2p_{\sigma u}$ state at low photon energies is enhanced by final-state interaction with the ionized electron due to the breakdown of the Frank-Condon principle. This mechanism may be responsible for a noticeable asymmetry at low KER. It can be readily observed experimentally using a COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS) coincident detection technique and a synchrotron light source. To resolve the dependence seen in Fig. 4 an energy resolution of the order of 0.1 eV is required. This gives an estimate of the required photon bandwidth, the photoelectron energy and the KER resolutions. The modern COLTRIMS apparatus are sensitive to asymmetry down to 5% [10]. For reaching of such an asymmetry, the energy of the ejected electron should be the order of 1 eV.

Our estimates are based on the semi-classical approximation of the ejected electron motion. A fully quantum-mechanical treatment is needed to provide a more rigorous estimate for small values of the ejected electron energies. This will require a solution of the fully dimensional time-dependent Schrödinger equation with respect to the electron and nuclear coordinates. This solution was sought and found in Sansone et al. [5] but the electronic part of the vibrational states was calculated in a sphere of radius 160 a.u. This radius is far too small to account for the effect under present consideration. How-
ever, this approach should reveal the effect after increasing this radius by several times.

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