Strong Orientation Effects in Ionization of H$_2^+$ by Short, Intense, High-Frequency Light Sources

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We present three dimensional time-dependent calculations of ionization of arbitrarily spatially oriented H$_2^+$ by attosecond, intense, high-frequency laser fields. The ionization probability shows a strong dependence on both the internuclear distance and the relative orientation between the laser field and the internuclear axis.

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The ionization dynamics of one- and two-electron processes in diatomic molecules in short, strong laser fields are at present under intense experimental investigation [1 2 3]. A part of these investigations also focus on the sensitivity of such processes to molecular orientation with respect to the light polarization [4]. This is again related to the ultimate goal of controlling chemical reactions by aligning the reactive molecules with respect to each other prior to the intermolecular interaction [5].

From a theoretical viewpoint such studies are extremely complex in the strong-field regime and have been of continuous interest for nearly two decades (for reviews, see, e.g., [6]). In general, only results based on approximate theories such as the molecular strong-field approximation [7, 8] and tunneling [9] models have been applied to calculate effects related to molecular orientation with respect to the light polarization vector. Such approximate theories are, however, often gauge dependent [10] and limited in their applicability to describe complex processes. The “slowness” of past and present computers have, combined with computational challenges related to Coulombic multi-center problems, restricted exact theoretical calculations including both electronic and nuclear degrees of freedom to cases where the internuclear axis is parallel with the linear polarization direction [11 12 13] or models of reduced dimensionality [14 15 16]. These studies have given insight into the fascinating interplay between electronic and nuclear degrees of freedom: phenomena which at present are beyond reach of full dimensional computations.

In this Letter, we present the first full time-dependent three dimensional calculations for the electronic degrees of freedom in H$_2^+$ exposed to a short, strong, attosecond laser pulse. The purpose is to follow the behavior of the system with internuclear distance and in particular to display the dependence of the dynamics on the angle between the internuclear axis and the linear polarization of the field. Calculations are performed for 6 cycle pulses with $\omega = 2$ a.u. (23 nm) central frequency. This corresponds to pulse durations around 450 as, which have already been demonstrated [16]. The ionization probability for H(2p) atoms exposed to similar light sources [17] showed a factor 10 stronger modulation with changing orientation than what was measured with femtosecond pulses [4]. Similar effects in diatomic molecules may thus indicate that attosecond pulses may be sensitive probes of the internal nuclear quantum state as well as its orientation. The calculations indeed display that the ionization probability depends strongly on these parameters. Atomics units ($\hbar = m_e = e = 1$) are applied throughout.

As the nuclear vibrational period is approximately $10^3$ times larger than the pulse duration, the nuclear degrees of freedom can be considered frozen during the attosecond pulse. Post pulse interplay between nuclear and electronic degrees of freedom, which are important for weaker fields, are also found to be unimportant here as direct electronic ionization dominates.

The vector potential for the light source is given by

$$A(t) = \frac{E_0}{\omega} \sin^2 \left( \frac{\pi}{\omega} t \right) \sin(\omega t + \phi) \mathbf{u}_p, \quad (1)$$

where $\mathbf{u}_p$ is a unit vector defining the orientation of the linearly polarized field, and $\phi$ is chosen such that the field corresponding to (1) represents a physical field [10]. The validity of the dipole approximation was investigated in detail very recently for the present intensity and frequency regime, and was found to be well-justified for ionization [18]. The vector potential determines the electric field, $\mathbf{E}(t) = -\partial_t A(t)$, and the translation, $\alpha(t) = \int_0^t A(t') dt'$, which enter the length $H_I$ and the Kramers-Henneberger $H_{KH}$ form [19] of the interaction Hamiltonian, respectively.

$$H_I = \frac{p^2}{2} - \frac{1}{|r + \mathbf{R}/2|} - \frac{1}{|r - \mathbf{R}/2|} + \mathbf{E}(t) \cdot \mathbf{r}, \quad (2)$$

$$H_{KH} = \frac{p^2}{2} - \frac{1}{|r + \mathbf{R}/2 + \alpha(t)|} - \frac{1}{|r - \mathbf{R}/2 + \alpha(t)|} \quad (3)$$

with $\mathbf{R}$ the internuclear distance. Both versions of the Hamiltonian have been applied here to secure invariant results.

For fixed nuclei, we solve the time-dependent Schrödinger equation numerically based on a split-step operator approximation on a spherical grid. The method was described in detail elsewhere [20 21]. The wave function is expanded on the grid points $|r_i, \Omega_{jk}\rangle = |r_i, \theta_j, \phi_k\rangle$. The wave function is expanded on the grid points $|r_i, \Omega_{jk}\rangle = |r_i, \theta_j, \phi_k\rangle$. The wave function is expanded on the grid points $|r_i, \Omega_{jk}\rangle = |r_i, \theta_j, \phi_k\rangle$.

$$\Psi(r_i, \Omega_{jk}, t; \mathbf{R}) = \sum_{l,m} f_{l,m}(r_i, t; \mathbf{R}) Y_{l,m}(\Omega_{jk}) \quad (4)$$

with origin at the center of the internuclear axis, and with parametrical dependence on $\mathbf{R}$. The field-free initial state
Fig. 2 exposes the ionization probability as a function of internuclear separation $R$ and the electric field strength $E_0$ with $\omega = 2$ a.u. and $T = 6\pi$ a.u.

$|\Psi_0\rangle$ is obtained by the substitution $t \to -i t$ in the propagator. At internuclear separation $R = 2$ a.u. this gives an electronic ground state energy, $\varepsilon_0^{\text{grid}} = -1.099$ a.u., which can be compared to the exact value of $\varepsilon_0 = -1.103$ a.u. Reflections at the edges $r = r_{\text{max}} = 60$ a.u. are avoided by imposing an absorbing boundary. We include up to $l_{\text{max}} = 15$, $N_r = 1024$ radial points, and in the propagation we use $\Delta t = 5 \times 10^{-3}$ a.u. Here we stress that for a given $l_{\text{max}}$, specified at input, the quadrature rule of the spherical harmonics uniquely fixes the angular points.

At the end of the pulse, $t = T$, a fraction of the wave function has been removed by the absorber. Since excitation is found to be a minor channel, the ionization probability can be calculated as $P_{\text{ion}} = 1 - |\langle \Psi_0 | \Psi(T) \rangle|^2$.

The ionization probability as a function of internuclear separation and electric field strength is displayed in Fig. 1 for field polarization parallel with the internuclear axis. Two striking maxima are observed, one for small internuclear separation, $R \approx 1$ a.u., and another for $R \approx 3$ a.u. When the field strength is further increased, the ionization probability decreases, i.e., the molecule is partly stabilized in the intense field. This rather counterintuitive mechanism has been studied in detail for atoms [23]. What happens, is that for increasing intensity, the final channels corresponding to single and multiphoton ionization close while shake-off dynamics with characteristic low-energy electron emission becomes the dominating ionization mechanism [13]. Between these two regions a "valley" in the ionization curve with increasing intensity may occur as indicated around $R \approx 1$ a.u. and $R \approx 3$ a.u. for field strengths beyond $E_0 \approx 7$ a.u. At the ground state equilibrium distance, $R \approx 2$ a.u., and for $R \approx 5$ a.u., the ionization probability is significantly smaller, indicating strong dynamic self-interference effects of the electronic charge clouds associated with each scattering center.

From Fig. 1 we see that the variation in the ionization signal is most pronounced for $E_0 \approx 3$ a.u. At this field strength, Fig. 2 exposes the ionization probability as a function of internuclear separation and as a function of the angle $\theta$ between the internuclear axis and the polarization direction of the field.

An oscillatory behavior of the ionization probability in the parallel geometry ($\theta = 0^\circ$) is seen. As $\theta$ increases the oscillations gradually decrease, and in the perpendicular geometry ($\theta = 90^\circ$), the ionization probability drops monotonically with $R$. In the figure, we also observe opposite functional dependence with $\theta$: At $R \approx 2$ a.u. the ionization probability increases with $\theta$ while at $R \approx 3$ a.u. it decreases.

We now turn to the detailed dynamics and a qualitative understanding of the processes underlying the phenomena observed in Fig. 2. Figure 3 shows snapshots of the wave function in the $xz$-plane at various times for parallel and perpendicular polarization (the molecule has its internuclear axis directed along $z$). In general the photoelectron is ionized in the directions of the field. For $\theta = 0^\circ$ the initial charge cloud is partly dragged back and forth along the field, and this gives rise to a strong interference between various momentum components of the wave function and hence the oscillatory dependence with $R$ in Fig. 1. This effect is absent at $\theta = 90^\circ$ where the two atomic-like charge clouds pertaining to each nucleus oscillates in phase back and forth with the electric field. In the lower right panel, secondary intensity maxima appear at $30^\circ$ and $150^\circ$ with respect to the internuclear axis. These structures look similar to double slit scattering but have a more subtle dynamical origin.

The oscillatory behavior in $P_{\text{ion}}(R)$ was discussed in a one dimensional model earlier in terms of the concept of enhanced ionization [23]. Related phenomena were also discussed in fast ion-molecule collisions [24]. The following simple ansatz gives a qualitative explanation of the oscillations and their absence at $\theta = 90^\circ$: Assume that the outgoing waves from each of the scattering centers are a superposition of two outgoing spherical waves,

$$\psi_{\text{out}} = f_1(\Omega_1) \frac{e^{ik|\mathbf{r} + \mathbf{R}/2|}}{|\mathbf{r} + \mathbf{R}/2|} + f_2(\Omega_2) \frac{e^{ik|\mathbf{r} - \mathbf{R}/2|}}{|\mathbf{r} - \mathbf{R}/2|}, \quad (5)$$

If we take the two scattering amplitudes to be equal, $f_1(\Omega_1) = f_2(\Omega_2)$, the differential ionization probability can be brought...
for that for parallel polarization, the main contributions will be ing wave follows the orientation of the field. Hence we expect $R$ dominates, we find the wave number as

to the form

$$dP_{\text{ion}}/d\Omega \propto 2|f_1(\Omega)|^2 (1 + \cos(k\hat{r} \cdot \mathbf{R}))$$  \hspace{1cm} (6)

for $r \gg R$. As seen from Fig. 3 the main part of the outgoing wave follows the orientation of the field. Hence we expect that for parallel polarization, the main contributions will be for $\hat{r}$ parallel to $\mathbf{R}$, which again gives raise to oscillations in $R$ with wave number $k$. Given that the one-photon ionization dominates, we find the wave number as $k \approx \sqrt{2(\omega - \bar{I}_p(R))}$, where $\bar{I}_p$ is the effective ionization potential. This is seen to be consistent with the results in Figs. 1 and 2 and we have also confirmed these findings for other values of $\omega$. The absence of oscillations in the case for perpendicular polarization is understood accordingly: The wave is sent out mainly in the direction given by $\theta = 90^\circ$, and since the outgoing waves will have no phase difference due to the separation of the scattering centers in this direction, no interference pattern will occur ($\hat{r} \cdot \mathbf{R} = 0$).

The monotonous decrease in $P_{\text{ion}}$ with $R$ at $\theta = 90^\circ$ is reasonable since the decrease in the ionization potential leads to an effective higher final state electronic momentum with increasing $R$.

The angular distribution of the ionization probability can be calculated from the time integral of the radial current density through the solid angle element $d\Omega$ at a chosen distance $a$ from the origin

$$\frac{dP_{\text{ion}}}{d\Omega} = \int_0^\infty dt \text{J}(a,t) \cdot \hat{r} = \int_0^\infty dt \text{Im} \left( \Psi^* \frac{\partial \Psi}{\partial r} \right)$$  \hspace{1cm} (7)

where the distance $a$ is chosen large enough to exclude contribution to the current from the quiver motion of an electron close to the nucleus and small enough to avoid effects induced by the absorber. The application of this procedure to the outgoing waves of the lower panel of Fig. 3 results in the intensity spectrum of Fig. 4. As already observed from Fig. 4, the photoelectrons are most likely ejected in the direction of laser polarization. In the perpendicular arrangement the two peaks around $30^\circ$ and $150^\circ$ can also be quantified: The integrated probability connected to these secondary maxima amounts to about 25% of the total ionization probability. As these peaks originate from interference of the outgoing waves, it is interesting to note that in a very recent calculation of High Harmonic Generation (HHG) in a reduced model with respect to the electronic degrees of freedom such interference does not occur. In that work it is pointed out that orientational effects are very important for HHG.

In conclusion, fully non-perturbational calculations of the ionization dynamics of $\text{H}_2^+$ molecules in intense attosecond light sources have been carried out. Very strong orientation effects have been found, demonstrating that in order to obtain a full understanding of the molecular ionization dynamics, all three electronic degrees of freedom must be included. The qualitative features are determined by interference effects re-
lated to double-center scattering and the distinct features in the electron spectra show that intense attosecond pulses can resolve the instantaneous vibrational and orientational quantum state of diatomic molecules.

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