Photoionization of diatomic molecules: effect of coulombic interactions

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Abstract. We analyze the angular distribution of electrons in the laser-assisted photoionization of HeH$^{2+}$ molecular targets. By means of a simple model, we obtain the observables for the reaction and we compare them with previous results obtained with more elaborated ones. The two-center interference effect and the asymmetric emission in the monochromatic ionization persist in the presence of a near infrared laser bath leading to a characteristic spectrum.

1. Introduction
The development of extreme ultraviolet (XUV) pulses with durations of a few hundreds of attoseconds (ATP) has opened the way to study the photoionization dynamics with a time resolution close to the electronic time scale. In the pump-probe experiments ([1] and references therein) where the reaction is assisted with a near infrared laser (NIR), it is possible to extract information about ATP [2] as well as monitoring and/or steering electron dynamics in molecules [3, 4]. In this perspective, both single ATP (SATP) and attosecond pulse trains (ATPT) turn out to be promising tools to control the electronic properties in molecular systems [4, 5].

The numerical resolution of the time dependent Schrödinger equation (TDSE) for pump-probe reactions with molecular targets represent a computational challenge [6, 7]. In this context, the use of a simplified model leading to reasonable results could be very helpful to understand the underlying physical processes. Among them, we could mention the Strong Field Approximation (SFA) in which the electron is supposed to evolve without interacting with the Coulomb field created by the target [8]. An improvement on this approximation is given by the Separable Coulomb-Volkov (SCV) model to treat atomic or molecular targets [9, 10], in which the coulombic interaction between the photoelectron and the residual target is included.

In this work, we show that the SCV model gives a qualitative agreement with ab initio calculations of photoionization cross sections [7] of HeH$^{2+}$ molecules and we analyze the case where the reaction is assisted by a NIR. Employing approximate initial and final wavefunctions, analytical expressions for the observables of interest, namely, photoionization spectrum and photoelectron angular distributions (PADS), are obtained.

Atomic units are used otherwise explicitly stated.

2. Theory
In the following, we summarize the basic ingredients of the SCV model [10]. The coordinate system describing the fixed-in-space molecule is one where $\mathbf{R}$ is the internuclear vector pointing...
from nucleus 1 to 2 and \( \mathbf{r}_i \) denotes the electron position vector with respect to the \( i \)-th nuclei. The electron coordinate with respect to the molecular geometric center is given by \( \mathbf{r} = (\mathbf{r}_1 + \mathbf{r}_2)/2 \).

The laser assisted photoionization amplitude within the dipole approximation in the velocity gauge reads [8],

\[
M_{scv}(p) = -i \int_{-\infty}^{\infty} dt \langle \Psi_f(\mathbf{r}, t) | \mathbf{p} \cdot \mathbf{A}(t) | \Psi_i(\mathbf{r}, t) \rangle,
\]  

(1)

where \( \mathbf{p} \) is the momentum operator, and \( \Psi_{i,f}(\mathbf{r}, t) \) are the initial and final wavefunctions, respectively. The vector potential \( \mathbf{A}(t) \) representing the XUV pulse is given by,

\[
\mathbf{A}(t) = (e_z \cos \phi + i e_z \sin \phi) A_0 e^{-i \Omega t} \exp \left[ -\frac{(t - t_0)^2}{2 \tau^2} \right],
\]

(2)

where \( \Omega, \phi, A_0, t_0 \) and \( \tau \) are the central frequency, a phase defining the polarization, the amplitude, the delay and the duration of the attosecond pulse, respectively. For a large Keldysh parameter (\( \gamma \approx 9 \) in our case), the multiphoton ionization of the target by the NIR is negligible as compared to the one-photon XUV case. Also, for the considered NIR intensities, the bound state polarization is expected to be small [11]. Therefore, we consider approximate laser-free wavefunctions given by,

\[
\Psi_i(\mathbf{r}, t) = \psi_{i}^0(\mathbf{r}) \exp(i I_p t),
\]

(3)

where \( I_p \) is the ionization potential of the molecule. We describe the continuum states of the electron by the Coulomb-Volkov ansatz [9] in which the interaction of the ejected electron with both the residual ionic target and the laser bath is taken into account, i.e.,

\[
\Psi_f(\mathbf{r}, t) = \psi_i^0(\mathbf{r}) \exp \left\{ -\frac{i}{2} \int^t [\mathbf{p} + \mathbf{A}_L(t)]^2 dt \right\},
\]

(4)

with \( \mathbf{p} \) the asymptotic value of the photoelectron momentum and \( \mathbf{A}_L(t) \) the potential vector describing the NIR. The wavefunctions \( \psi_i^0(\mathbf{r}) \) describe the bound and continuum molecular states in the absence of both the XUV and the NIR fields. As exact wavefunctions are in general available only in numerical form, we approximate them by analytical ones that simplify the calculation. For the bound states, we employ two-center expansions with Slater type orbitals (STOs) located on each molecular center whereas for the continuum states we used coulombic wavefunctions satisfying the correct asymptotic coulombic conditions,

\[
\psi_i^0(\mathbf{r}) = \sum_i c_i^{(1)} \phi_i(\mathbf{r}_1) + \sum_j c_j^{(2)} \phi_j(\mathbf{r}_2)
\]

(5)

\[
\psi_{f}^0(\mathbf{r}) = (2\pi)^{-3/2} e^{i \mathbf{p} \cdot \mathbf{r}} N_p^2 G(\mathbf{r}_1) G(\mathbf{r}_2)
\]

(6)

where \( \phi_i(\mathbf{r}) \) are STOs, \( N_p = \Gamma(1 + i \nu) \exp(\pi \nu/2) \) and \( G(\mathbf{r}_i) = i F_i(-i \nu; 1; -1(p \mathbf{r}_i + \mathbf{p} \cdot \mathbf{r}_i)) \) is the confluent hypergeometric function. The Sommerfeld parameter is \( \nu_i = Z_i/p \) with \( Z_i \) being the residual effective charge of the \( i \)-esime atom.

The vector potential corresponding to the NIR field may be written as

\[
\mathbf{A}_L(t) = -\frac{\mathbf{E}_1}{\omega_1} \sin(\omega_1 t),
\]

(7)

where \( \mathbf{E}_1 \) and \( \omega_1 \) are the NIR electric field and frequency, respectively.

Replacing Eqs. (2) and (7) into Eq. (1), and recalling that in the velocity gauge spatial and temporal integrals are separable [10], it can be shown that the matrix transition amplitude given by Eq. (1) is proportional to the monochromatic transition matrix elements \( M_{ph}(\mathbf{p}) \) corresponding to the absorption of one XUV photon of frequency \( \Omega \), which are given by

\[
M_{ph}(\mathbf{p}) = \chi_1 M_1 + \chi_2 M_2,
\]

(8)
where we have employed the Coulomb Continuum approximation [9, 10] in which the molecular interference factors denoted by $\chi_{1,2}$ are given by,

$$\chi_{1,2} = N_p e^{\pm i p \cdot R / 2} F_1(i \nu_{2,1}; 1; i(pR \mp p \cdot R)),$$

and the $M_{1,2}$ factors are the atomic photoionization amplitudes from the molecular centers 1, 2, respectively.

Therefore, the photoelectron spectrum is given by,

$$\frac{d^3P_{scv}}{dp \, d\Omega_e} = p^2 |M_{scv}(p)|^2.$$  \hspace{1cm} (10)

where $d\Omega_e = \sin \theta_e \, d\theta_e \, d\phi_e$ denotes the solid angle in the direction of $p$.

3. Results

We compare our SCV results with more elaborated ones [7], where the TDSE of the HeH$^{2+}$ ion exposed to an attosecond x-ray pulse is solved in two-center prolate spheroidal coordinates within the fixed nuclei approximation. At first, we test our monochromatic transition amplitudes by computing the PADs for the fixed-in-space HeH$^{2+}$ molecular target. Setting the polarization vector $\Pi(\phi) = e_z \cos \phi + i e_z \sin \phi$ with $\phi = 0 \left( \pi / 2 \right)$ we get the linear parallel (perpendicular) polarization case with respect to the internuclear vector $R$. We also include the case of right circular polarization, which is obtained by setting $\phi = -\pi / 4$.

![Figure 1. Monochromatic PADs for the excited bound $2p\sigma$ state of HeH$^{2+}$ at $R = 3.898$ a.u., with XUV polarization parallel and perpendicular to $R$ as well as circular polarization. The nuclei are indicated by an orange sphere for the $\alpha$ particle and a smaller dark gray sphere for the proton. In the linear case, the polarization vector is indicated by a different color axis (violet). For circular polarization, the violet axis indicates the incidence direction. Angular distributions (green-blue plots) are computed for photon energies of $\Omega = 200$ eV and 300 eV.](image)

In Fig. 1, our computed PADs for photon frequencies of $\Omega = 200$ eV and 300 eV are shown. Both linear polarizations results are in qualitative agreement with ab initio ones [7]. As expected, in the parallel case asymmetric PADs are obtained due to the different charge of each nucleus in the target. It is worthy to mention that the SFA will fail to describe these asymmetries [7, 9].

For perpendicular polarization, the PADs are also asymmetric. The asymmetry is more clear in the completely parallel geometry ($p \parallel \Pi(\phi) \parallel R$), however in this case asymmetries are concentrated for emission around the polarization direction.

In the case of circular polarization, our PADs exhibit a mixture of both linear parallel and perpendicular cases with an additional torsion [6] of the PADs, arising from the cross product between ionization transition amplitudes of the two independent components of the XUV. This is in agreement with the homonuclear results reported previously [6, 13]. For 200 eV, the perpendicular polarization PADs are too small compared to the parallel ones. Therefore this, leads to circular polarization PADs dominated by the later ones. On the contrary, for $\Omega = 300$
eV, the parallel and perpendicular PADs are of comparable size giving place to a more important torsion, particularly in the perpendicular direction.

In Fig. 2(a), we present the laser assisted photoelectron spectrum centered at frequency $\Omega= 200$ eV for linear parallel polarization as a function of the photoelectron energy and the polar ejection angle $\theta_e$ of the photoelectrons. We observe typical sidebands located around the central frequency. These sidebands are produced by quantum interferences occurring during the interaction of the photoelectron with the laser NIR bath [1]. Sidebands are separated roughly by twice the NIR frequency. As the duration of the XUV pulses increases reaching the period of the NIR, the separation between sidebands is given by the NIR frequency [12]. As can be seen, the preferred ejection direction, i.e., 0 and $\pi$ radians coincides with the molecular orientation. The observed up-down asymmetry is a consequence of the monochromatic effects explained before.

In Fig. 2(b), the photoelectron spectrum show a marked decrease for the emission in the direction of the proton, while emission in the $\alpha$ particle direction remains important. Moreover, the emergence of new structures is clearly visible. In this way, the asymmetry effects observed in the case of monochromatic pulses leave their trace in the photoelectron spectrum when the NIR is added.

4. Conclusions
We have studied PADs for the monochromatic photoionization of fixed-in-space HeH$^{2+}$ molecular targets. A good qualitative agreement with ab-initio results is found. For circularly polarized radiation, the PADs exhibit a mixture of the linear parallel and the linear perpendicular cases with an additional torsion. Moreover, the laser-assisted reaction spectra present sidebands with asymmetries that may be explained through the monochromatic contribution that include the asymptotic coulombic conditions. We note that a SFA model will fail to describe these asymmetries. The present study may be extended without great effort to more complex diatomic molecules. Work in this direction is in progress.

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