Ultrafast molecular orbital imaging based on attosecond photoelectron diffraction

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Abstract: We present ab initio numerical study of ultrafast ionization dynamics of H$_2^+$ as well as CO$_2$ and N$_2$ exposed to linearly polarized attosecond extreme ultraviolet pulses. When the molecules are aligned perpendicular to laser polarization direction, photonionization of these molecules show clear and distinguishing diffraction patterns in molecular attosecond photoelectron momentum distributions. The internuclear distances of the molecules are related to the position of the associated diffraction patterns, which can be determined with high accuracy. Moreover, the relative heights of the diffraction fringes contain fruitful information of the molecular orbital structures. We show that the diffraction spectra can be well produced using the two-center interference model. By adopting a simple inversion algorithm which takes into account the symmetry of the initial molecular orbital, we can retrieve the molecular orbital from which the electron is ionized. Our results offer possibility for imaging of molecular structure and orbitals by performing molecular attosecond photoelectron diffraction.

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References and links
1. Introduction

Advances in the understanding of the interaction of intense laser pulses with matter have opened versatile perspectives in ultrafast optics, for observing new phenomena and developing new technologies [1–4]. Among this, the generation of attosecond extreme ultraviolet (XUV) pulses in atomic and molecular gases based on high harmonic generation (HHG) has attracted considerable attentions for its potential use of probing the structure and ultrafast electron dynamics in matters with unprecedented temporal and spatial resolutions [5–8].

The application of the XUV pulses can be summarized into two categories. In the first category, during the HHG process, the recolliding electron wavepacket encodes information on the generating molecule in the emitted harmonics. Thus the harmonic signal is used to retrieve temporal and structural insight into the generating targets itself, known as “self-probing” schemes [9–11]. Specifically, it can be used to create a tomographic reconstruction of molecular orbitals, called molecular orbital tomography [12–15]. On the other hand, the availability of isolated attosecond XUV pulses extends the femtosecond spectroscopy and femto-chemistry to the attosecond domain, which is the natural time scale of the electron motion [16–18]. Also, it was recently shown that the attosecond XUV pulses could also provide Ångström resolved images of electron wavepackets in molecules [11]. The combination of attosecond and Ångström resolution makes it possible to imaging the most fundamental process of physics and chemistry in real time [3, 19].

In the ultrafast imaging experiments, one usually exploits available information of molecular structure in the molecular photonionization spectra. The original idea was proposed by Cohen and Fano [20] more than forty years ago that the photonionization of a diatomic molecule can be viewed as a microscopic version of Young’s double-slit experiment. The emitted electrons, which are initially shared between the two indistinguishable nuclei, would be coherent when their de Broglie wavelengths are comparable to the molecular equilibrium internuclear distance. Such that the electron wavepacket interference effect would appear in the oscillatory behavior of photonionization cross sections in perturbative single-photon ionization. When extending to nonperturbative regime, a new imaging technique called laser induced electron diffraction (LIED) was proposed by Zuo et al [21]. When molecules are exposed to few cycle femtosecond laser pulse, laser induced electrons may rescatter with different nuclei. The interference between the amplitudes arising from different scattering centers would appear in the photonionization momentum distributions (PMD), carrying structure information of the molecule. However, in a femtosecond laser pulse, a train of several electron wavepackets recollides within
one pulse and one recollision is convoluted by several recollisions and diffraction events. The overlap of multiple diffraction events, each yielding different energy spectra due to changing laser intensity, leads to extra complications in the diffraction patterns. Besides, the presence of the laser field would distort the electron energy spectra and add an extra dependence on recollision time of the spectra. All these problems make it extremely complicated to retrieve the structure information of the target molecule [22–27].

The fast development of ultrashort free-electron lasers (FELs) and attosecond XUV pulse by HHG make it available of high-energy XUV light sources [28–30]. A fascinating ultrafast imaging technique called molecular attosecond photoelectron diffraction (MAPD) [31–33] emerges, making use of the interaction between and XUV pulses and molecules. The sketch of MAPD is shown in Fig. 1. A molecule is aligned perpendicular to polarization direction of XUV pulse. The XUV photons eject the single electron from molecule. Photonization takes place when the electron is close to one of the two nuclei, which therefore act as two “slits”. The interference pattern appears in PMD of the emitted electrons. When the PMD is measured, the internuclear distance can be determined. Further, if the molecular orbital is expressed as linear combination of atomic orbitals (LCAO), the symmetry of the combined atomic orbitals is encoded in the detailed structure of the interference image, which allow us to retrieve the molecular orbital using PMD.

Fig. 1. The sketch of molecular attosecond photoelectron diffraction. The ultrashort XUV laser pulse is polarized perpendicular to the molecular axis and the blue dashed line indicates its propagation direction. The XUV photons eject the electron from the molecule when the electron is close to one of the nuclei. Therefore the two nuclei act as “slits” in the microscopic double-slit experiment. By measuring the momentum distribution of the ejected electrons, the molecular internuclear distance can be determined and the symmetry of molecular orbital can be retrieved.

In this paper, we present a systematic study of ultrafast imaging of molecular orbitals with different symmetries using MAPD technique. Three typical molecules (and molecular ions), i.e., H$_2^+$, CO$_2$ and N$_2$ are chosen. The PMD of each molecule is obtained by solving the two-dimensional time-dependent Schrödinger equation (TDSE) within Born-Oppenheimer (BO) approximation. The effective single-active-electron (SAE) potential is adopted to correctly reproduce the highest occupied molecular orbitals (HOMO) of each molecule. Clear diffraction patterns appear in PMD. The internuclear distance can be determined with respect to the position of interference fringes. By stretching the molecules, the diffraction patterns change accordingly which in turn determine the change of internuclear distance with high precision. Furthermore, the detailed structure of the interference image, i.e., the relative heights of the interference fringes reflects the structure information of molecular orbitals. Using a simple two-center interference model, we successfully reproduced the difference pattern and it shows good agreement.
with the TDSE calculations. These results enable us to retrieve the molecular orbital for PAD with an inversion algorithm invoking the symmetry of the initial molecular orbital.

2. Theoretical model

To simulate the photoionization process in attosecond XUV pulse, we use the split-operator spectral method [34] to numerically solve the corresponding two-dimensional TDSE (atomic units are used unless stated otherwise)

\[ i \frac{\partial}{\partial t} \psi(\vec{r}, t) = H(\vec{r}, t) \psi(\vec{r}, t), \]  

where \( \vec{r} \equiv (x, y) \) denotes the electron position in \((x, y)\) plane. Below we assume that the molecular orbital is aligned in the \(x\) direction. The Hamiltonian reads

\[ H(\vec{r}, t) = -\frac{1}{2} \nabla^2 + V(\vec{r}) + \vec{E}(t). \]  

\( \vec{E}(t) \) is the electronic field which is polarized along the \(y\) direction, perpendicular to the molecular axis. We use a ten-cycle linearly polarized XUV pulse with wavelength of 5 nm. The electron field with a sine-squared envelope is expressed as

\[ \vec{E}(t) = E_0 \sin^2(\frac{\pi t}{T}) \cos(\omega t) \hat{e}_y, \]  

in which \( E_0, \omega \) and \( T \) is the amplitude, angular frequency and the duration of the XUV pulse, respectively. The laser intensity is chosen to be \(1.0 \times 10^{15} \text{W/cm}^2\). The high intensity and short wavelength of the XUV pulse enable us to generate photoelectrons with energy as high as 200eV in the nonperturbative single-photon ionization process. The corresponding de Broglie wavelength of the high-energy electron is about 1.8 a.u., which is less than the molecular equilibrium internuclear distance. Thus the diffraction of high-energy electrons can achieve accurate measurement of the molecular internuclear distance. The effective SAE soft-core potential [35–37] is in the form of

\[ V(\vec{r}) = -\sum_{j=1}^{N} Z_{j}^n + (Z_j^0 - Z_{j}^n) \exp(-|\vec{r}_j|^2/\sigma_j^2) \frac{1}{\sqrt{|\vec{r}_j|^2 + \xi_j^2}}. \]  

The subscript \( j = 1, \ldots, N \) labels the nuclei at fixed positions \( \vec{r}_j \) and \( \vec{r}_j = \vec{r} - \vec{r}_j \). \( Z_{j}^n + (Z_j^0 - Z_{j}^n) \exp(-|\vec{r}_j|^2/\sigma_j^2) \) denotes the position-dependent screened effective charge for the \( j \)-th nucleus, where \( Z_{j}^n \) is the effective nuclear charge of the nucleus \( j \) as seen by an electron at infinite distance and \( Z_j^0 \) is the bare charge of nucleus \( j \). Parameter \( \sigma_j \) characterizes the decrease of the effective charge with the distance to the nucleus. \( \xi_j \) is the soft-core parameter. For \( \text{H}_2 \), the effective charge is chosen to be constant and the ordinary soft-core potential [38] is reproduced. For \( \text{CO}_2 \) and \( \text{N}_2 \), the values of \( Z_{j}^n \) were derived from a Mulliken analysis carried out in \textit{ab initio} study. The values of the parameters of three molecules are summarized in Tab. 1.

The initial normalized wavefunction is obtained by imaginary-time propagation and orthogonalization under symmetry conditions corresponding to HOMO of each molecule. After that, the initial wavefunction is served as the initial condition for the real-time propagation. The time-dependent wavefunction \( \psi(\vec{r}, t) \) is propagated using the second-order split-operator spectral method [34] in real time on a Cartesian grid. Due to the linearity of the Schrödinger equation, the electron wave function \( \psi(t_i) \) (\( t \) is omitted for simplicity) at a given time \( t_i \) can be split into two parts:

\[ \psi(t_i) = \psi(t_i)[1 - F_s(R_c)] + \psi(t_i) F_s(R_c) = \psi_I(t_i) + \psi_{II}(t_i). \]  

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Table 1. Values of all parameters used for soft-core potentials of \( \text{H}_2^+ \), CO\(_2\) and N\(_2\) [37].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \zeta_j ) (a.u.)</th>
<th>( \sigma^2_j ) (a.u.)</th>
<th>( Z^0_j )</th>
<th>( Z^\infty_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2^+ )</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>1.0</td>
<td>0.750</td>
<td>0.577</td>
<td>0.700</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>1.73</td>
<td>0.654</td>
<td>0.173</td>
<td>0.500</td>
</tr>
</tbody>
</table>

Here, \( F_s(R_c) = 1/(1 + e^{-(r-R_c)/\Delta}) \) is a split function that separates the whole space into the inner \((0 \rightarrow R_c)\) and outer \((R_c \rightarrow R_{\text{max}})\) regions smoothly [39, 40]. \( \psi_I \) represents the wave function in the inner region and it is propagated under the full Hamiltonian using the split-operator algorithm. \( \psi_{II} \) stands for the wave function in the outer region and it is propagated under the Volkov Hamiltonian analytically. We first calculate

\[
\psi(\vec{p}, t_f) = \int \psi_{II}(t_i) e^{-i[\vec{p} + \vec{A}(t_i)] \cdot \vec{r}} 2\pi d^2 \vec{r},
\]

where \( \vec{A}(t_i) = \int_{t_i}^{t_f} \vec{E}(\tau) d\tau \) is the vector potential of the laser pulse. Then we propagate \( \psi_{II} \) from \( t_i \) to the end of the laser pulse as

\[
\psi(\infty, t_i) = \int \psi_I(\vec{p}, t_i) e^{i\vec{p} \cdot \vec{r}} 2\pi d^2 \vec{p},
\]

with \( \psi_I(\vec{p}, t_i) = \exp \left(-i \int_{t_i}^{t_f} \frac{1}{2} [\vec{p} + \vec{A}(\tau)]^2 d\tau \right) \psi(\vec{p}, t_i) \). Finally, the electron momentum distribution is obtained as

\[
\frac{d^2 \mathcal{P}(\vec{p})}{dE d\Omega} = \left| \sum_i \psi_I(\vec{p}, t_i) \right|^2,
\]

where \( E \) is the electron energy associated with \( \vec{p} \) as \( E = |\vec{p}|^2/2 \) and \( \Omega \) is the angle of the emitted electron. After the end of the pulse, the wave function is propagated for additional few femtoseconds to collect the “slow” photoelectrons. In our simulations, the grid size is the same for x and y directions: \( \Delta x = \Delta y = 0.1 \) a.u. and the grid ranges from -300 a.u. to 300 a.u. in each direction. The boundary of the inner region \( R_c \) is 100 a.u.. The real time step is chosen as \( \Delta t = 0.001 \) a.u. which satisfies the convergence condition \( \Delta t/\Delta x^2 < 0.5 \). After the pulse, the wave function propagates freely for 3 fs.

3. Results and discussions

Figure 2 shows the molecular orbitals of \( \text{H}_2^+ \) and the corresponding electron diffraction patterns for three different internuclear distances under the nonperturbative single-photon ionization process. With high intensity XUV pulse, there are also multiphoton absorptions. However, electrons due to multiphoton ionization process appear at higher momentum region and have no influence for electrons with low momentum. Below we will concentrate on the single-photon ionized electrons. Clear diffraction fringes are observed in the electron momentum distributions and these fringes are markedly well resolved in the ponderomotive motion “circle” corresponding to the momentum region of the ejected electrons by single-photon ionization. Moreover, by stretching the molecules from \( R = 2 \) a.u. to \( R = 6 \) a.u., the number of diffraction fringes increase with the internuclear distance, which is similar to Young’s double-slit experiment [20].
Fig. 2. Upper panels: the molecular orbitals of H\textsuperscript{+}\textsubscript{2} for three different internuclear distances of (a) \( R = 2 \) a.u., (b) \( R = 4 \) a.u. and (c) \( R = 6 \) a.u. Lower panels: the corresponding electron diffraction patterns (wider logarithmic scale) for different internuclear distances. The wavelength of the driving laser pulse is 5 nm and the intensity is 1.0 \times 10^{15} \text{W/cm}^2.

The variation of diffraction patterns as the increase of the internuclear distance is one of the key point of MAPD, which allows us to extract the geometrical information, i.e., the internuclear distance of the molecules.

Another feature can be observed in PMDs of H\textsuperscript{+}\textsubscript{2} is that the diffraction stripes are always perpendicular to the molecular axis and there is a interference maximum for \( p_\chi = 0 \), independent of the internuclear distance. This can be attributed to the symmetry of molecular orbital of H\textsuperscript{+}\textsubscript{2}. We show that the diffraction pattern can be well reproduced by one step model of photoemission (PE). For laser wavelength as short as 5 nm used in our study, the ejected electrons energy is as high as 200 eV such that the effect of the parent ion can be neglected. The single-photon ionization can be treated as a single transition process from a molecular orbital to the final state, where the final state is approximated by plane waves. The transition amplitude reads

\[ \mathcal{C}_{PE}(\vec{p}) = i \int_{-\infty}^{\infty} e^{-iS(\vec{p},t)} E(t) d_\chi(\vec{p} + \vec{A}(t)) dt. \]  
(9)

Here, \( S(\vec{p}, t) \) is the semiclassical action

\[ S(\vec{p}, t) = \int_{\tau}^{\infty} \left[ \frac{1}{2}(\vec{p} + \vec{A}(\tau'))^2 + I_p \right] d\tau' \]  
(10)

and \( d_\chi(\vec{p}) \) is the dipole moment which takes the form

\[ d_\chi(\vec{p}) = \langle \phi_{\vec{p}}(\vec{r}) | \psi(\vec{r}) \rangle = \frac{1}{(2\pi)^{3/2}} \int e^{-i\vec{p} \cdot \vec{r}} \psi(\vec{r}) d\vec{r}, \]  
(11)

where the initial molecular orbital is obtained with the \textit{ab initio} Gaussian 03 code. The finally PMD can be obtained by

\[ \frac{d^2 \mathcal{P}(\vec{p})}{dE d\Omega} = |\mathcal{C}_{PE}(\vec{p})|^2. \]  
(12)
Fig. 3. Photonelectron momentum distributions of $\text{H}_2^+$ for three different internuclear distances of $R = 2$ a.u. (left column), $R = 4$ a.u. (middle column) and $R = 6$ a.u. (right column). The upper panels (same as Fig. 1 (d)-(f) but a narrower logarithmic scale) are the results of TDSE calculations and the lower panels are calculated by PE.

Figure 3(d)-3(f) display the PMDs of different internuclear distance calculated by PE and the results of TDSE are also presented in Fig. 3(a)-3(c) for comparison. One can see that the these two results agree perfectly with each other. The PMDs calculated by PE well reproduce all the features of diffraction images, including the positions and shapes of the interference fringes. This indicates that the distortion of the molecular orbital due to the XUV pulse is ignorable. Slightly difference appears at larger $p_x$, which can be attributed to the fact that PE predicts a little higher ionization probability of the molecules thus the high-order interference peaks in the TDSE calculation are not well resolved as the PE results. Nevertheless, the good agreement between the PE and TDSE calculations indicates the validity of classical double-slit predictions when de Broglie wavelength of the ejected electrons is less than the internuclear distance in a MAPD experiment [31, 33].

By integrating the PMDs over $p_y$, the corresponding electron momentum spectra along $p_x$ direction are obtained, as displayed in Fig. 4. Again, the agreement between TDSE and PE calculations is achieved. The number of interference peaks is related to the internuclear distance. For $R = 2$ a.u., there are three peaks within the interval [-5 a.u., 5 a.u.]. For $R = 4$ a.u., six peaks appear (although the highest-order peaks are weak), twice as the interference peaks for $R = 2$ a.u.. For $R = 6$ a.u. one can observe nine peaks, triple as those for $R = 2$ a.u.. This observation can be summarized in accordance with the classical double-slit experiment as

$$ R = 2\pi / \Delta p_x, $$

in which $\Delta p_x$ denotes the momentum separation between the adjacent interference peaks. The internuclear distance derived from Eq. (13) is summarized in Tab. 2 and $\Delta p_x$ is obtained by the momentum separation between the zero-order and first-order interference maximum. The measured internuclear distance from both TDSE and PE shows good agreement with the exact internuclear distance. The maximum error for $R = 2$ a.u. is 4.5%. For $R = 4$ a.u. and 6 a.u.,
Fig. 4. Electron momentum spectra of $H_2^+$ along the $p_x$ direction by integration over $p_y$ for $R = 2$ a.u. (left column), $R = 4$ a.u. (middle column) and $R = 6$ a.u. (right column). The upper panels are the results of TDSE calculations and the lower panels are calculated by PE.

we also calculated the internuclear distance averaged over high-order interference peaks. The error of measured internuclear distance is less than 3%. All these results imply that the MAPD serves as an efficient tool to measure the internuclear distance of $H_2^+$.

Table 2. Measured internuclear distance of $H_2^+$ from TDSE as well as PE in comparison with the exact internuclear distance. The internuclear distance is calculated using the zero-order and first-order ionization peaks

<table>
<thead>
<tr>
<th>Internuclear distance of $H_2^+$ R(a.u.)</th>
<th>Measured R(a.u.) from TDSE</th>
<th>Measured R(a.u.) from PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>2.091</td>
<td>2.068</td>
</tr>
<tr>
<td>4.0</td>
<td>4.069</td>
<td>4.042</td>
</tr>
<tr>
<td>6.0</td>
<td>6.064</td>
<td>6.013</td>
</tr>
</tbody>
</table>

Next, we will turn to a slightly more complicated molecule, CO$_2$. Figure 5(b) and 5(e) display the electron momentum distributions of CO$_2$ from equilibrium to stretched internuclear distance. Similar as $H_2^+$, The PMDs of CO$_2$ also show clear diffraction patterns on the ponderomotive motion circle. By stretching the molecule from $R = 2.24$ a.u. to $R = 3$ a.u., the number of diffraction fringes increases with the internuclear distance. However, there is a clear difference of the PMDs between CO$_2$ and $H_2^+$. For $H_2^+$ it is an interference maximum at $p_x = 0$, while for CO$_2$ it is an interference minimum. This fact can be attributed to the symmetry properties of HOMO of CO$_2$. Figure 5(a) and 5(d) show the HOMO of CO$_2$ for $R = 2.24$ a.u. and $R = 3$ a.u., respectively. The HOMO of CO$_2$, which is of $\Pi_g$ symmetry, is antisymmetric with respect to two nodal planes: one containing the molecular axis and another containing the carbon ion and perpendicular to the molecular axis. During the interaction between the molecule and the XUV pulse, the structure properties of molecular orbital are converged in the propagation of the electron wavepacket and the initial symmetry persists to some extend under the force of laser
fields [37]. Thereby, the symmetry properties are imprinted onto the PMDs, leading to distinct diffraction patterns for molecule with different symmetries. This fact is also confirmed by PE calculations, as presented in Fig. 5(c) and 5(f). The electron momentum distributions calculated by PE show clear diffraction patterns and interference minimum appears at $p_x = 0$. Although the high-order diffraction fringes are not well resolved for TDSE calculations compared with PE, the information contained in low-order fringes is enough for reading the internuclear distance and retrieving the symmetry properties of the molecular orbital. This issue only becomes critical for molecules with short internuclear separations. For these molecules, the number of interference fringes is limited, so it is hard to measure the internuclear distance from the diffraction pattern. This shortcoming can be overcome by using XUV pulse with shorter wavelength, such that more energetic electron can be ejected and the radius of the ponderomotive motion circle becomes larger to include more interference fringes. Thereby the short internuclear distance can be readily read out from the diffraction pattern.

The integrated electron momentum spectra for different internuclear distances over $p_y$ are shown in Fig. 6, calculated by TDSE (left column) and PE (right column), respectively. These two results also agree well with each other. For both internuclear distances, there is a interference minimum at $p_y = 0$, so a direct analogy to the double-slit experiment is not feasible for CO$_2$, due to the symmetry properties of HOMO. Using the linear combination of atomic orbitals (LCAO) scheme, the HOMO of CO$_2$, which possess $\Pi_g$ symmetry, can be expressed as the antisymmetric combination of two $2p_y$ atomic orbitals of oxygen that are oriented perpendicular to the molecular axis. The two oxygens’ $2p_y$ orbital is antisymmetric, which can be also viewed as two “slits”. The difference is that one slit is masked by a phase function, changing the phase of the electron wavepacket ejected from this slit by $\pi$. As a consequence, the interference maximum and minimum exchange their positions. We calculate the internuclear separations of the two oxygen ions using the zero-order and first-order interference minimum and then the
C-O bond length is obtained by dividing the measured internuclear separations by two. The results are summarized in Tab. 3. The measured C-O bond length from TDSE and PE shows good agreement with the exact one. The maximum error is less than 3% for both cases. More precisely, we calculated the averaged C-O bond length over three interference minimums for $R = 2.24$ a.u. and four minimums for $R = 3$ a.u.. The results are $R = 2.197$ a.u. and $R = 3.045$ a.u., respectively, with error less than 2%. Therefore, it is apparent to see that MAPD is also useful for probing molecules with antisymmetry properties.

Table 3. Measured C-O bond length of CO$_2$ from TDSE as well as PE in comparison with the exact bond-length from equilibrium to stretched geometries. The C-O bond length is calculated using the zero-order and first-order interference minimum.

<table>
<thead>
<tr>
<th>C-O bond length of CO$_2$ R(a.u.)</th>
<th>Measured R(a.u.) from TDSE</th>
<th>Measured R(a.u.) from PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.24 (equilibrium)</td>
<td>2.189</td>
<td>2.254</td>
</tr>
<tr>
<td>3.00 (stretched)</td>
<td>2.989</td>
<td>3.062</td>
</tr>
</tbody>
</table>

Another molecule for the demonstration of MAPD is N$_2$. In the case of N$_2$, the HOMO, of $\Sigma_g$ symmetry, is symmetry about the molecular axis and with two nodal planes, each of them containing one nitrogen ion, perpendicular to the molecular axis. The upper panels of Fig. 7 shows HOMO of N$_2$ for three different internuclear separations 2.05 a.u., 4 a.u. and 6 a.u. The HOMO is a bonding orbital which can be expressed as a combination as two $p_z$ nitrogen orbitals aligned along the molecular axis. These structure properties make the corresponding PMDs a little more complicated, as shown in Fig. 7 (middle panels for TDSE and lower panels for PE). The general trend of the PMDs is the same as H$_2^+$ and CO$_2$: as the internuclear distance stretched from equilibrium 2.05 a.u. to 6 a.u., the number of diffraction stripes increases accordingly. However, the detailed structure is different. At $p_z = 0$, there is a small maximum, which becomes invisible for large internuclear separations. Then the intensity becomes more pronounced for higher-order fringes. This characteristic is attributed to the structure properties...
The HOMO of N₂ shows alternating positive and negative lobes along the molecular axis and electron wavepackets ejected from different parts of the orbital interfere with each other. So it is not a trivial task to directly relate to the double-slit experiment without additional assumptions. Nevertheless, we can at least measure the value of the internuclear distance from the period of the oscillations in its fringe pattern.

The integrated electron momentum spectra of N₂ for different internuclear distances over \( p_y \) are shown in Fig. 8, calculated by TDSE (upper panels) and PE (lower panels), respectively. The relative heights of the diffraction fringes can be more clearly viewed from Fig. 8. The height of the interference peaks increases for high-order fringes, which originate from the interplay between the interference of the positive and negative lobes of HOMO. For our purpose of measuring the internuclear distance, We calculated it from one period of the oscillation located at moderate \( p_x \), as indicated by the dashed lines in Fig. 8. The value of internuclear distances are obtained from Eq. (13), summarized in Tab. 4. For stretched \( R = 4 \text{ a.u.} \) and 6 a.u., the measured internuclear distances show good agreement with the exact ones, including the TDSE and PE results. While for equilibrium \( R = 2.05 \text{ a.u.} \), The maximum error is 12%, which is due to the complicated diffraction pattern of N₂ and the limited numbers of interference fringes. Our results suggest that in order to precisely measure the equilibrium internuclear distance of N₂ one should use XUV pulses with shorter wavelength.

Above discussions are based the assumption that the molecule is perfectly aligned perpendicular to the electric field. Next we will go one step further to investigate the influence of molecular alignment effects. In reality, the alignment is achieved by exciting the molecule into a rotational wave packet by a moderately intense pump pulse. In this case, perfect alignment can not be achieved and the effect of angular dispersion should be taken into account in the experiment of MAPD. We take CO₂ for example to investigate the alignment effect on the PMD. The effect of molecular partial alignment is simulated by incoherent superposition of PMD of
Fig. 8. Electron momentum spectra of N$_2$ along the $p_x$ direction by integration over $p_y$ for $R = 2.05$ a.u. (left column), $R = 4$ a.u. (middle column) and $R = 6$ a.u. (right column). The upper panels are the results of TDSE calculations and the lower panels are calculated by PE. The black dashed lines in each panel indicate one oscillation period used for measuring the internuclear distance.

Table 4. Measured internuclear distance of N$_2$ from TDSE as well as PE in comparison with the exact internuclear distance. The internuclear distance is calculated using the zero-order and first-order ionization peaks

<table>
<thead>
<tr>
<th>Internuclear distance of N$_2$ R(a.u.)</th>
<th>Measured R(a.u.) from TDSE</th>
<th>Measured R(a.u.) from PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.05</td>
<td>2.291</td>
<td>2.314</td>
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<tr>
<td>4.00</td>
<td>4.093</td>
<td>4.022</td>
</tr>
<tr>
<td>6.00</td>
<td>6.097</td>
<td>6.086</td>
</tr>
</tbody>
</table>

different angles given by

$$\mathcal{S} (\vec{p}) = \int |\sum_i \psi_i (\vec{p}, t_i, \theta)|^2 \rho (\theta; \tau) d\theta,$$

(14)

where $\psi_i (\vec{p}, t_i, \theta)$ is calculated by Eq. (6) for different angles and $\rho (\theta; \tau)$ is the weighted angular distribution written as

$$\rho (\theta; \tau) = \frac{1}{Z} \sum_{J_i} Q (J_i) \sum_{M_i = -J_i}^{J_i} \int |\psi_{J_i M_i} (\theta, \phi; \tau)|^2 d\phi.$$

(15)

Here $Q (J_i) = \exp (-BJ_i (J_i + 1) / (k_B T))$ is the Boltzmann distribution function of the initial field-free state $|J_i, M_i\rangle$ at temperature $T$, $Z = \sum_{J_i = 0}^{J_{\text{max}}} (2J_i + 1) Q (J)$ is the partition function, $k_B$ and $B$ are the Boltzmann constant and the rotational constant of the molecule, respectively. $\psi_{J_i M_i} (\theta, \phi; \tau)$ is the time-dependent rotational wave packet excited from the initial state $|J_i, M_i\rangle$ by the pump pulse, and is obtained by solving the TDSE within the rigid-rotor approximation [41, 42]

$$i \frac{\partial \psi (\theta, \phi; \tau)}{\partial \tau} = (BJ^2 - \frac{E_p (\tau)^2}{2} (\alpha_\parallel \cos^2 \theta + \alpha_\perp \sin^2 \theta)) \psi (\theta, \phi; \tau),$$

(16)
where $\alpha_\parallel$ and $\alpha_\perp$ are the anisotropic polarizabilities in parallel and perpendicular directions with respect to the molecular axis, respectively. The degree of alignment is characterized by the alignment parameter $<\cos^2 \theta>$ yielding

$$<\cos^2 \theta> (\tau) = \frac{1}{Z} \sum_{J_i} Q(J_i) \sum_{M_i=-J_i}^{J_i} |\Psi^{J_iM_i}(\theta, \phi; \tau)| \cos^2 \theta |\Psi^{J_iM_i}(\theta, \phi; \tau)|.$$  \hspace{1cm} (17)

![Diagram](image_url)

Fig. 9. (a) The alignment factor $<<\cos^2 \theta>>$ for linearly polarized laser pulse with intensity of $4.0 \times 10^{13}$ W/cm$^2$. The point A indicates the delay of 21.1 ps that the simulation is performed at. (b) The polar plots of the angular distributions at point A. (c) Angular averaged photoelectron momentum distribution for CO$_2$ at equilibrium $R = 2.24$ a.u. and (d) the corresponding electron momentum spectra along the $p_x$ direction.

In our simulations, a 100-fs (FWHM) 800-nm linearly polarized pump pulse with intensity of $4.0 \times 10^{13}$ W/cm$^2$ is used to nonadiabatically align the CO$_2$ molecule. The initial rotational temperature is taken to be 40 K. The time evolution of the alignment factor $<\cos^2 \theta> (\tau)$ is presented in Fig. 9(a). We choose delay of 21.1 ps indicate by point A. The corresponding weighted angular distribution $\rho (\theta; \tau)$ is shown in Fig. 9(b). One can see that strong alignment of CO$_2$ is achieved by the pump pulse. After that, a delayed XUV pulse polarized perpendicular to the pump pulse is used to ionize the molecule. The angular averaged photoelectron momentum distribution is calculated by Eq. (14), as displayed in Fig. 9(c). In comparison with the perfect alignment case shown in Fig. 5(b), the angular averaged PMD successfully reproduces all the fringes of the diffraction pattern, except that the contrast of fringes becomes weak. But we are still able to extract the internuclear distance and symmetry properties of the molecule from the slightly less contrasted diffraction pattern. As shown in Fig. 9(d), the integrated electron momentum spectrum is well resolved and the positions of the interference fringes do not shift compared to Fig. 6(a). The less contrast of the fringes can be overcome by high-repetition and high-accuracy data recording for experimental realization. Thus we conclude that angular dispersion do not affect the extraction of internuclear distance and symmetry properties from the diffraction pattern.

Below we aim at retrieving the molecular orbital from the diffraction pattern using a simple two-center interference model [33]. The two-center interference model can be derived from PE, i.e., Eq. (9). In our case, the typical electron momentum on the ponderomotive motion circle is 4.2 a.u. and the amplitude of the vector potential $\hat{A}(t)$ for the 5-nm XUV pulse with intensity of $1.0 \times 10^{15}$ W/cm$^2$ is $E_0/\omega = 0.04$ a.u.. Such that $|\vec{p}| \gg |\hat{A}(t)|$. Under this condition, the laser
The dipole moment $\mathbf{HOMO}$ is an antisymmetric combination of two $2p_x$ atomic orbitals of oxygen aligned along the molecular axis, which can be expressed as $\psi_{\text{O}_2} = \psi_{2p_x}(x - R/2, y) - \psi_{2p_x}(x + R/2, y)$, where $\psi_{2p_x}(x, y)$ is $\alpha \exp(-\beta r)$. Thus the electron momentum spectra for CO$_2$ is

$$\mathcal{T}_{\text{CO}_2}(p_x) \propto \frac{\alpha \cos^2(p_x R)}{(p_x^2 + \beta^2)^{3/2}}.$$  

Again, the C-O bond length $R$ is obtained from Tab. 3 as 2.189 a.u. and the parameter $\beta$ is determined by fitting the experiment with Fig. 5(a). For N$_2$, the HOMO is combined of two $2p_z$ atomic orbitals of nitrogen aligned along the molecular axis, which can be expressed as $\psi_{\text{N}_2} = \psi_{2p_z}(x - R/2, y) - \psi_{2p_z}(x + R/2, y)$, where $\psi_{2p_z}(x, y)$ is $\alpha \exp(-\beta r)$. It is hard to provide an analytical expression for the electron momentum spectra for N$_2$, so we numerically calculate it using Eq. (20) with $R$ obtained from Tab. 4. The fitting parameter $\beta$ is determined to best reproduce Fig. 8(a). For all three molecules, the parameter $\alpha$ is calculated by normalization of the molecular orbital. The reconstructed molecular orbitals are displayed in Fig.
10. They all reproduce the main features of each target molecule and show good agreement with the real molecular orbitals. The results demonstrate that the MAPD technique permits the retrieval of not only the geometrical information but also the orbital structure of the molecule from observable photoelectron momentum distributions. We should remind that the knowledge of the symmetry properties needs to be known a priori in order to retrieve the shape of the orbitals.

4. Conclusion

In summary, we have presented a systematic theoretical analysis of the ionization dynamics of $\text{H}_2^+$, $\text{CO}_2$ and $\text{N}_2$ molecules in intense ultrashort linearly polarized XUV pulses within the framework of molecular attosecond photoelectron diffraction. The momentum distributions of the emitted photoelectrons are calculated by solving the two-dimensional time-dependent Schrödinger equation as well as the photoemission method. We have shown that, if the molecule is initially aligned perpendicular to the field polarization, the internuclear distance of the molecule can be determined from the diffraction pattern of the photoelectron momentum distribution with a high accuracy of a few percent. The partial alignment effect has been considered and the robustness of internuclear distance measurement with respect to the rotational motions has been demonstrated. Besides, we have also shown that the symmetry properties of molecules are also imprint into PMD and the molecular orbitals can be successfully reconstructed using an inversion algorithm based on two-center interference model. Our results provide an theoretical guide for ultrafast attosecond photoelectron imaging of molecules.

All the discussions in this paper are based on single-active-electron approximations. Recent experiments have shown that molecules interacting with a strong laser field could be ionized from several valence orbitals with different symmetries simultaneously [11]. Thus an overlap of multiple diffraction events could appear in the momentum distributions. Due to different symmetries of the orbitals, the contribution of multichannel contributions can be disentangled with a fitted procedure. This implies that the molecular attosecond photoelectron diffraction also offers possibility to study multielectron effect.

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