Partial localization and symmetries in coherent electron emission from molecules

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Abstract. The presence of interference patterns due to coherent electron emission from the proximities of the nuclei of diatomic molecules is investigated for impact of fast ions on symmetric and asymmetric targets. This last case allows us also to analyze the influence of the initial partial localization of the emitted electron around one of the molecular centers. Coherent ionization of multiorbital targets is also studied. Electron emission is found to depend on the gerade or ungerade character of inner shell orbitals.

1. Introduction
This work deals with electron ionization of diatomic molecules interacting with fast charged ion beams. Coherent electron emission from the proximities of the nuclei of the target was theoretically predicted forty-five years ago in a seminal work [1] in order to explain the measured photoabsorption spectra of N₂ and O₂ targets [2]. In fact, the photoabsorption reaction was qualitatively related through a simple picture to the process of photoionization of H₂⁺ targets. However, it was only after a further thirty-five years that experimental evidence of this phenomenon was discovered. Electron emission from H₂ targets impacted by 60 MeV/u-Kr³⁴⁺ ions, showed the signature of interference patterns appearing in the form of oscillations in double differential cross sections (DDCS), which are obtained as function of the final energy of the ionized electron at fixed angles subtended by this particle [3]. Following this work numerous experimental and theoretical investigations were reported for the cases of photon, electron and ion impact (for a short review the reader is referred to [4]) and continue to be a matter of active research.

In this paper we focus on the case of ion impact. In particular we revisit some of our recent results where we showed that for asymmetric (heteronuclear) systems fingerprints of coherent emission can remain [5–7]. This is the case for the HeH⁺ fundamental state.

As in the majority of previous works on homonuclear systems only the H₂ target was considered, we extend here the research on the possible presence of interference patterns in the electron ionization spectra of the multiorbital fundamental state of N₂ molecules. This will allow us to explain recent experimental results where primary interference was not observed on DDCS [8, 9] and to give deeper information on the studied reaction.
Atomic units will be used except where otherwise indicated.

2. Theoretical approach

Let us consider the single ionization reaction of a diatomic molecule due to the impact of a bare nucleus of charge $Z_F$ moving with a velocity $v'$ parallel to the z axis of a reference frame fixed at the centre of mass of the target. In this work we consider intermediate and high impact energies, so that it can be assumed that the molecular nuclei remain fixed in their initial positions during the collision. Also, the multielectron problem can be reduced to the analysis of a one-active electron system where the active electron is the one to be ionized and the passive electrons remain in their initial states during the reaction [10].

The straight line version of the impact parameter approximation is employed. Within the molecular version of the continuum distorted wave-eikonal initial state (CDW-EIS) approximation, the initial and final distorted-wave-functions $\chi_i^+$ and $\chi_f^-$, respectively, are described as:

$$\chi_i^{+,\text{EIS}}(\vec{r},t) = \varphi_i(\vec{r}) \exp\left(-i\varepsilon_i t\right) \mathcal{L}_i^{+,\text{EIS}}(\vec{s})$$

$$\chi_f^{-,\text{CDW}}(\vec{r},t) = \varphi_f(\vec{r}) \exp\left(-\frac{k^2}{2} t\right) \mathcal{L}_f^{-,\text{CDW}}(\vec{s})$$

with $\varphi_i$ and $\varphi_f$ the bound and continuum states of the active electron in the entrance and exit channel, respectively, $\varepsilon_i$ the initial orbital energy, and $k$ the modulus of the momentum $\vec{k}$ corresponding to the ionized electron. Vectors $\vec{r}$ and $\vec{s}$ represent the electron coordinates with respect to the centre of mass of the target and to the projectile nucleus, respectively. The eikonal and continuum distortion factors $\mathcal{L}_i^{+,\text{EIS}}$ and $\mathcal{L}_i^{-,\text{EIS}}$ are defined as follows:

$$\mathcal{L}_i^{+,\text{EIS}}(\vec{s}) = \exp\left[-i\nu \ln(p\vec{s} + \vec{v}' \cdot \vec{s})\right]$$ \hspace{1cm} (3)

$$\mathcal{L}_f^{-,\text{CDW}}(\vec{s}) = N^*(\zeta) F_1[-i; 1; -i(p\vec{s} + \vec{p} \cdot \vec{s}),]$$ \hspace{1cm} (4)

respectively. In expressions (3) and (4), $\nu = Z_F/v$, $N(a) = \exp(\pi a/2)\Gamma(1 + ia)$ where $\Gamma(z)$ is the Gamma function, $F_1(b;c;z)$ is the Kummer confluent hypergeometric function, $\vec{p} = \vec{k} - \vec{v}'$ is the momentum of the electron in the final channel in the projectile frame, and $\zeta = Z_F/p$.

To describe each molecular orbital of the active electron, we employed a basis of Slater-type orbitals (STO) $\phi_{h,j}^{\text{STO}}$ centred on each nucleus of the molecule:

$$\varphi_i(\vec{r}) = \sum_{h,j} \omega_{h,j} \phi_{h,j}^{\text{STO}}(\vec{x}_h)$$ \hspace{1cm} (5)

where the index $h$ ($h = 1, 2$) identifies the nucleus of the molecule in which the STO are centred, the subscript $j$ represents the quantum numbers $nlm$, and $\vec{x}_h$ denotes the electron coordinate with respect to the molecular centre [5–7]. To optimize the values of the STO characteristic exponents and the coefficients $\omega_{h,j}$ the quantum chemistry program Gaussian 98 was employed [11]. In particular, these quantities were calculated by using a minimal STO-6G basis set within the Hartree-Fock (HF) approximation, where each STO is represented as a linear combination of six Gaussian-type orbitals (GTO) (see references [12] and [13] for more details). The equilibrium internuclear distance and the orbital energies $\varepsilon_i$ for each molecular orbital of the target were calculated by employing a larger HF/6 – 311 G* basis set.

In order to describe the dynamics of the emitted electron in the exit channel a two-effective centre approximation (TEC) [10, 14] is employed, so that the final continuum wavefunction is chosen as:
\[ \varphi_f(\vec{r}) = (2\pi)^{-3/2} \exp \left[ i\vec{k} \cdot (\vec{x}_h + \vec{b}_h) \right] \times N^*(\xi) F_1(-i\xi; 1; -i k x_h - i\vec{k} \cdot \vec{x}_h), \]  

(6)

when the component \( \phi_{h,j}^{\text{initial}}(\vec{x}_h) \) of the initial orbital wavefunction is considered. In equation (6), \( \xi = (-2 n^2 \varepsilon_1)^{1/2} k^{-1} \) with \( n \) the corresponding principal quantum number, and \( \vec{b}_h \) is the position of the \( h \)-nucleus with respect to the centre of mass of the molecular nuclei.

For the sake of simplicity in the computing of differential cross sections, we employ the post-form of the scattering matrix element \( R_{i,f}^{+} \). Consequently, three-fold differential cross sections for each molecular orbital in the CDW-EIS approximation are defined as:

\[ \sigma^{(3)}(\varepsilon_k, \Omega_k, \Omega_b) = N_{el} k \int d\vec{q} \left| R_{i,f}^{+}(\vec{q}) \right|^2, \]  

(7)

with \( N_{el} \) the occupation number of the orbital and \( \vec{q} \) the transverse momentum transfer. Double differential cross sections for each molecular orbital are calculated by averaging equation (7) over all possible molecular orientations:

\[ \sigma^{(2)}(\varepsilon_k, \Omega_k) = \frac{N_{el} k}{4\pi} \int d\vec{q} d\Omega_b \left| R_{i,f}^{+}(\vec{q}) \right|^2. \]  

(8)

If the molecular target has more than one molecular orbital (MO) in its fundamental state (for example, \( N_2 \) molecules), then TDCS and DDCS are obtained by adding the partial contributions corresponding to each MO, being these partial differential cross sections given by expressions (7) and (8), respectively.

It has been shown in a previous work [5] that in the TEC approximation, the scattering matrix element \( R_{i,f}^{+} \) can be written as a linear combination of effective one-centre scattering amplitudes associated with the set of Slater-type orbitals centred on each \( h \)-nucleus:

\[ R_{i,f}^{+}(\vec{q}) = \sum_h \exp[-i(\vec{k} + \vec{K}) \cdot \vec{b}_h] R_{h}^{+}\text{eff}(\vec{q}), \]  

(9)

where \( \vec{K} = -\vec{q} + K_z \hat{v} = -\vec{Q} \), being \( -\vec{Q} \) the total momentum transfer, and:

\[ R_{h}^{+}\text{eff}(\vec{q}) = \sum_j \omega_{h,j} R_{h,j}^{+}\text{eff}(\vec{q}). \]  

(10)

3. Results and discussions

The aim of this work is to investigate the existence of interferences due to coherent electron emission from the vicinities of the nuclei of diatomic molecules. To this end we analyze the single ionization reaction of the heteronuclear molecular ion \( \text{HeH}^+ \), as well as the homonuclear nitrogen molecule.

3.1. The \( \text{HeH}^+ \) molecular ion

According to the values of the coefficients of the linear combination (5), it can be shown that for the \( \text{HeH}^+ \) molecular ion the electron is preferentially distributed around the alpha particle and that the corresponding density is not so different from that of the fundamental state of the atomic helium orbital [5].

To investigate the possible existence of interference patterns on the angular distribution of electrons, we have analyzed the case of proton impact at 1 MeV on \( \text{HeH}^+ \) targets. To obtain these angular spectra we consider a fully coplanar geometry in which the molecule, the projectile
Figure 1. Three-fold differential cross sections ratios for impact of protons at 1 MeV on HeH$^+$ molecular ion, for the molecule aligned (a) parallel and (b) perpendicular to the direction of the projectile. The helium nucleus is considered to be placed on the semi-axis coinciding with the emission angles $\theta = 0^{\circ}$ and $\theta = 90^{\circ}$ for parallel and perpendicular orientations, respectively.

and the emitted electron are all in the same plane, and we analyze two particular orientations of the target, parallel and perpendicular to the direction of incident particle.

Results shown in figure 1 correspond to the ratio between the three-fold differential cross section for the HeH$^+$ molecular ion and the partial three-fold differential cross section corresponding only to the monocentric electronic distribution around the alpha particle. It allows us to discriminate the presence of interference patterns in the complete molecule. Calculations are done for different ejection energies ranging from 10 eV to 900 eV. For molecular orientation parallel to the impact velocity we observe that as the energy of the ionized electron increases different lobes appear. The number of them increases as the ejection energy increases, presenting the typical signature of interference patterns. We should remember that to obtain these triple differential cross sections integration on the transverse momentum transfer is necessary. For molecular orientation parallel to the impact velocity the exponential terms of equation (9) which contain the oscillatory information related to coherent emission are not affected by this integration. However, for perpendicular molecular orientation the integration on the transverse momentum transfer clearly affects the exponential terms, shadowing thus the presence of interferences.

In figure 2, a comparison between DDCS-ratios for HeH$^+$ and the ones corresponding to the homonuclear molecule H$_2$ is shown. For the heteronuclear ions, the quotient $R_{\text{HeH}^+}(\varepsilon_k, \Omega_k)$ is calculated by dividing the molecular two-fold differential cross section by the partial double
Figure 2. DDCS ratios corresponding to impact of protons on HeH$^+$ molecular ions (——) and H$_2$ molecules (—····) for different impact energies and different values of the electron emission angle $\theta_k$. ECC and BE denote the electron capture to the continuum and the binary encounter regions, respectively.

differential cross section corresponding to the electronic contribution around the alpha particle centre. Incident protons with 1 MeV, 13.7 MeV and 100 MeV impact energies are considered. The ratio $R_{\text{HeH}^+}(\varepsilon_k,\Omega_k)$ is obtained by dividing the DDCS corresponding to the H$_2$ molecule by two times the double differential cross sections for H atoms (see reference [6]). At large enough electron energies, for both the asymmetric and symmetric systems, interference patterns due to coherent emission from the molecular centres appear. However, for HeH$^+$ the amplitude of oscillations is smaller than for the H$_2$ case. This reduction of the effect has been attributed to partial localization of the electron around the alpha particle in the initial state of the asymmetric target [6].

3.2. The nitrogen molecule
The fundamental state of this molecule presents a $^1\Sigma_g^+$ configuration. In figure 3, angular threefold differential cross sections for impact of 1 MeV-protons on N$_2$ molecules are shown. They correspond, as previously considered, to a fully coplanar geometry and in this case to a fixed 900 eV-ejection energy. Contributions from the different molecular orbitals are discriminated for targets oriented parallel or perpendicular to the collision velocity. For the first case, evidence of interference patterns appears for some of the molecular orbitals, mainly for the inner ones, for
which the active electron has high density close to the target nuclei. Some structures are found also for the external orbitals, mainly for the $2p_{\pi_u}$. As for the one-orbital case before considered contributions from different transverse momentum transfer shadow any possible presence of interference patterns in the case of molecular orientation perpendicular to the impact velocity. We have also verified that when contributions from all molecular orbitals are added the possibility to observe interference patterns is strongly reduced.

![Figure 3](image)

**Figure 3.** Three-fold differential cross sections for each orbital of the nitrogen molecule, for impact of protons at 1 MeV and for an electron emission energy $\varepsilon_k = 900$ eV, for the molecule aligned (a) parallel and (b) perpendicular to the direction of the projectile.

In figure 4, cross section ratios $C(\varepsilon_k, \Omega_k)$ corresponding to experimental and theoretical N$_2$-DDCS divided in both cases by twice theoretical atomic N-DDCS are represented. Molecular DDCS are again obtained after averaging over all possible molecular orientations. A good qualitative agreement between theory and experiments is found. For the electron energy range considered at fixed emission angles of $30^\circ$ and $45^\circ$ no evidence of interference patterns is observed. This is in agreement with previous experimental predictions [8, 9]. Measured structures due to Auger emission have been eliminated for a better comparison with the theory considering that this mechanism is not included in the present model. We have extended our calculations for larger electron energies (not shown here) and irregular oscillations were obtained for DDCS ratios corresponding separately to each one of the molecular orbitals. However, they were shifted ones with respect to the others in such a way that when all contributions were added no regular structures associated with coherent emission were found.

DDCS ratios for the two inner orbitals $1s\sigma_g$ and $1s\sigma_u^*$ were also obtained but comparing now
only with direct contributions corresponding separately to each orbital in equation (8). It means considering:

\[ |R_{i,j}^+ (\vec{\eta})|^2 = \sum_h |R_{i,j}^{+e I}(\vec{\eta})|^2. \]  

(11)

Results are presented in figure 5. Now, clear evidence of interference patterns is observed. Moreover, according to the gerade or ungerade symmetry of the initial orbital the oscillations in the ratios are in phase opposition. The existence of this behaviour was also analyzed for the case of photoionization of N\textsubscript{2} [15]. A similar effect was also recently predicted for electron emission from the fundamental state of H\textsubscript{2} targets by electron impact when the non-ionized electron is promoted to a gerade or ungerade state [16].

Figure 4. Comparison between theoretical and experimental DDCS ratios for single ionization of N\textsubscript{2} molecules by 1 MeV-proton impact as a function of the energy of the emitted electron, for two different values of the electron emission angle \( \theta_k \). Experiments are taken from references [8, 9].

Figure 5. Theoretical DDCS ratios corresponding to the \( \sigma_g 1s \) and \( \sigma_u 1s \) molecular orbitals of the nitrogen molecule for 1 MeV-proton impact, as a function of the energy of the emitted electron and for an electron emission angle \( \theta_k = 30^\circ \).
4. Conclusions

Interference patterns associated with coherent emission from diatomic molecules interacting with fast protons has been theoretically investigated. A two-effective centre molecular CDW-EIS model has been employed. Two different targets were analyzed: i) the asymmetric HeH$^+$ one, which allows us to study the influence of the initial electronic partial localization of the ionized electron around one of the nuclei of the molecule and, ii) the N$_2$ one, which brings us the possibility to investigate the presence of interference patterns in the case of multiorbital molecules. Moreover, electron interference patterns corresponding to emission in phase opposition is found according to the gerade or ungerade symmetry of the N$_2$ inner orbitals.

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