Single electron ionization of NH$_3$ and CH$_4$ by swift proton impact

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Abstract. Single ionization from ammonia and methane molecules by impact of protons is analysed. Double differential cross sections are calculated, within the post- and prior-versions of the continuum distorted wave-eikonal initial state (CDW-EIS) model, considering two different representations of the initial bound state of the active electron. A comparison between both set of results shows a very little sensitivity of the double differential cross sections to the initial state representation in the case of ammonia molecules. On the other hand, discrepancies are found when CH$_4$ molecular target is considered, showing that in this case the description of the corresponding molecular orbitals influences the cross section calculations.

1. Introduction

Electron ionization from atoms and molecules due to bare ion impact have an important role in a variety of processes related to different areas of physics and chemistry. For example, methane and ammonia molecules are components of some planetary atmospheres and of the interstellar medium, and their interaction with UV photons and with charged particles may provoke the appearance of highly reactive radicals, as well as ionic and neutral species (for more details see, for example, [1] and references therein). It is necessary then to posses accurate theoretical and experimental cross sections not only for ionization, but also for capture and fragmentation processes in order to modelling, as well as possible, the physical situation of interest.

In this work, we extend our previous theoretical investigations for H$_2$O targets [2] to other molecules, namely ammonia and methane, whose present a strong monocentric character. Our aim is to analyse the influence of the molecular orbital characterization in the description of the single ionization reaction. To this end, double differential cross sections (DDCS) are computed within the post- and prior-versions of the CDW-EIS approximation. Regarding the molecular target, two different representations of its initial bound states are considered: the MO-LCAO-SCF (molecular orbitals constructed from a linear combination of atomic orbitals in a self-consistent field) approach and the description proposed by Roberto Moccia [3–5]. In both cases, the continuum state of the emitted electron is represented by a double product of a plane wave and continuum factors corresponding to the coulombic interaction with the projectile and the target. The effective nuclear charges used in the formulation of these continuum factors are chosen according to the representation employed to describe the molecular orbitals. Details
concerning the theory used in the present study have been already outlined in [2], thus, only a brief description of the method will be presented here. Atomic units are used throughout unless otherwise stated.

2. Theory
Let us consider the single ionization of a molecule due to the interaction with a bare ion of nuclear charge \(Z_p\) and velocity \(\vec{v}\) parallel to the z-axis of a laboratory reference frame. Since the energy of the incident particle is high enough, the molecular rotational and vibrational times are much larger than the collision ones and, in consequence, a frozen-core picture where the molecular nuclei remain fixed in their initial positions during the ionization process can be considered. Concerning the multielectronic character of the target, the corresponding analysis is reduced to the study of a single-electron system, where the active electron (the one to be ionized) evolves in an effective coulomb field of a residual target consisting of the molecular cores and the remaining passive electrons [6].

As it was mentioned before, our purpose is to analyse the influence of the \(\text{NH}_3\) and \(\text{CH}_4\) molecular orbital representation in the calculation of DDCS. Double differential cross sections, as a function of the energy \(\varepsilon_k\) and the angle \(\Omega_k = (\varphi_k, \theta_k)\) subtended by the emitted electron, can be obtained using both the post (+) and the prior (-) forms of the scattering matrix element, \(R_{i;f}^{\pm}\), through the following expression:

\[
\sigma^{(2)}_{\text{MO}}(\varepsilon_k, \theta_k) = \frac{d\sigma}{d\varepsilon_k d\Omega_k} = \frac{k}{8\pi^2} \int \int d\Omega d\vec{\eta} |R_{i;f}^{\pm}(\vec{\eta}, \Omega)|^2,
\]

where \(k = \varepsilon_k^2/2\) is the momentum of the emitted electron, \(\vec{\eta}\) is the transverse momentum transfer, and \(\Omega\) identifies the spatial orientation of the molecule (see [2] for theoretical details). In order to model the molecular orbitals (MO) of the target, two different approaches were considered. In the MO-LCAO-SCF one, each MO is constructed from a linear combination of atomic orbitals in a self-consistent field, being these atomic states centred on each molecular nuclei [7, 8]. In order to simplify the computation of DDCS, we employed the procedure proposed by Senger et al. [9–11], where is assumed that the DDCS for a given molecular orbital can be reduced to a weighted sum of atomic DDCS corresponding to the atomic constituents of the molecule, the weights of this linear combination being obtained via a population analysis. The atomic double differential cross sections needed in the present calculations were obtained employing Roothaan-Hartree-Fock wavefunctions [12] to describe the electron initial bound state. Finally, all these partial DDCS are added in order to get the DDCS for the complete molecule.

In the description proposed by Roberto Moccia [3–5], each molecular orbital is expressed as a linear combination of Slater-type functions (STF) all referred to a common origin, being this point chosen to coincide with the position of the heaviest nucleus. DDCS for the complete molecule is calculated by adding all the partial contributions of the different molecular orbitals of the target, and multiplying them by the corresponding occupation number.

3. Results and discussion
In order to analyse the influence of the molecular orbital characterization in the description of the single ionization reaction of \(\text{NH}_3\) and \(\text{CH}_4\) targets, we calculate for each molecule the corresponding double differential cross sections considering either the Moccia representation or the MO-LCAO-SCF one.

In figure 1, a comparison between DDCS for ionization of \(\text{NH}_3\) by 250 keV-proton impact, as a function of the electron emission angle and for different emission energies, is shown. DDCS presented in the left panel of figure 1 corresponds to calculations made within the post version of CDW-EIS formalism (post-DDCS), whereas the curves shown in the right panel were obtained within the prior version (prior-DDCS). In general, it seems that differences between results for
both initial state descriptions are not significant over all the angular range for post- results as well as for the prior- ones. In the case of post calculations, Moccia's double differential cross sections show in general a small enhancement with respect to the MO-LCAO-SCF ones in the region of backward scattering, and this effect seems to be more pronounced as the emission energy increases. On the other hand, from the plots corresponding to prior-DDCS, it can be seen that both sets of theoretical data are so close that they are almost indistinguishable. The same behaviour was observed for single ionization of water molecules by bare ion impact [2].

From figure 1, it can be seen that theoretical results, for both post- and prior-versions, underestimate the experiments in the region of backward emission at high enough emission energies. Under these conditions, we may consider that the electron is first impacted by the projectile, suffering consequently a recoil scattering by the target nucleus. Thus, if the effective charge used to represent the target continuum state in the exit channel is replaced by the target nuclear one a better agreement between theoretical results and experiments was found for impact of protons on helium targets [13]. A similar behaviour could be expected for the targets here analysed.

Preliminary post-DDCS for CH₄ targets and for 2 MeV-proton impact, as a function of the electron emission angle and for different emission energies, are presented in figure 2. In the case of the Moccia description, and in order to simplify the computation of DDCS, we have decided to truncate the original basis set, leaving out from the calculation the contribution of Slater-type orbitals corresponding to values of n equal or greater than 7 (see [3] for the complete list of STF contribution to each MO of CH₄), since these states have in general coefficients that are at least one order of magnitude lower than the states with n ≤ 4 (with the exception of the 2a₁ MO), so it could be considered that their contribution to a given molecular orbital is negligible.

From figure 2 it can be seen that, unlike the ammonia case, there are some discrepancies between results obtained with both molecular orbital characterizations. These differences seem to be larger as the emission energy decreases. Moreover, Moccia’s results seem to give a worst agreement with experiments than the MO-LCAO-SCF ones for all the considered emission energies. These differences could be attributed to the fact that in the computation of these quantities we employed, as a first approximation, a truncated Moccia basis set to describe the molecular orbitals of methane and maybe the contribution of the neglected wavefunctions is more important than we think in a first moment. In a forthcoming work, those CH₄- Moccia states
4. Conclusions
Single electron ionization of ammonia and methane molecules by swift proton impact was investigated. In the case of ammonia targets, DDCS are found to be not very sensitive to the molecular initial state description. On the other hand, angular spectra for methane molecules, obtained within the post version, showed differences between results obtained with Moccia and with MO-LCAO-SCF representations. These discrepancies may be attributed to the use of a truncated Moccia basis set, where Slater-type function with principal quantum number equal or greater than seven were neglected. Future calculations for methane will be made including these states with \( n \geq 7 \).

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