Full 3D ab initio studies of interference effects in high-energy ion-molecule collisions

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Abstract. We present an investigation of the interference effects which have been observed experimentally and predicted for ionizing collisions between highly charged projectiles and molecular hydrogen targets. The present data have been obtained from a non perturbative treatment of the collision system, using the semiclassical impact parameter method and solving the time-dependent Schrödinger equation fully numerically, the scattering wavefunction being discretized in the electron position space and, for detailed analysis, on spaces of reduced dimensionality. We discuss the oscillatory structures observed in differential cross sections as function of outgoing electron energy and angle in Kr34+ – H2 collisions. Emphasis is placed on the discussion on Young-type interference pattern as well as extra high frequency oscillations which have been observed experimentally but not confirmed by theoretical calculations.

1. Introduction

An important activity has developed in recent years to observe, predict and interpret in terms of interference effects, the oscillatory structures showing up in differential cross sections for processes inducing single ionization of simple diatomic homonuclear molecules, such as H2 and N2. Since the early work of Cohen and Fano [1] on photoionization numerous results have been published for inner and valence shell ionization induced by photon, electron and heavy particle impact; see for example [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Common to the different kind of particles inducing the ionization process is the observation of a primary oscillation in the differential cross sections and ratio of cross-sections. The ratio is taken to compensate for the very fast decaying cross-section at increasing ejected electron energy. For ion impact these structures have small magnitudes and due to experimental uncertainties at high electron energies they cannot in general be recorded over more than one period. However, they were clearly interpreted as the signature of interference effects stemming from the coherent emission of an electron from two indistinguishable sites of the molecular target: the two nuclei play the role of emitters as the slits in Young’s famous double-slit experiment in optics. The features (interfringe separation and contrast) are then mainly dependent on the internuclear distance R between the two slits and on the domain of velocities (and related de Broglie wavelength) of the outgoing electrons. The equivalence between the scattering processes under consideration...
and the Young’s experiment cannot be further extended since (i) the two slits have not a fixed-in-space geometry with respect to the detector, and (ii) they can emit in $4\pi$ sr, though anisotropically in general. For the former difference it was demonstrated that the averaging over the molecular target orientation does not eradicate the interferinges [9] although it significantly decreases their contrast. The latter difference gives rise to original behavior of the interference pattern, as for example in ion-molecule collisions where asymmetries have been observed in energy distributions between forward and backward emission with respect to the projectile propagation direction. The parallel with double-slit experiments seems to be very reasonable for inner shell ionization for which the emitted electron is initially localized in well defined, distinct volumes centred around both nuclei with equal probability; cf. Fig. 1(a) for $N_2$ core level [2]. This is not the case for valence shell ionization for which the outgoing electrons are initially shared between the two nuclei to insure the binding of the structure, as shown in Fig. 1(b) for $H_2$ [9]. It is then surprising to observe similar interference patterns for a molecular double slit in which the two slits are barely separated.

Experimental studies of ion impact [14, 15] displayed additional, high frequency, oscillations embedded in the Young (first-order) pattern. The amplitude of these higher order interferences was shown to be very weak (about one order of magnitude lower than those of the primary oscillations) and the frequency independent of the emission angle. Multiple scattering phenomena between the two emitting centers were invoked to explain the observations, but no theoretical model nor calculations to date has confirmed the presence of these structures. In this context it should also be noted that well defined frequencies to characterize the oscillations could not be extracted by Fourier analysis of the experimental data [12].

The fact that there is no unquestionable evidence of structures due to interferences between primary electronic waves emitted by one center with the ones being first back-scattered by the other center is rather puzzling. Indeed multiple scattering processes are the origin of a powerful X-ray technique to probe the atomic surrounding of an ionized target atom in condensed matter samples i.e. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. Near the absorption edges the EXAFS-spectra present clear oscillatory structures. These can be explained by the coherent superposition of scattering amplitudes and phase shifts related to the different paths which may follow the photoelectron; cf. for example [16].

In the present paper we present a theoretical study of ionization occurring in the course of collision between $Kr^{34+}$ ions and hydrogen molecules for 63 MeV/u impact energy. Our results stem from a non-perturbative semiclassical treatment of the collision, with the space spanned by the active electron being discretized in 3D and in 1D for further detailed analysis. We focus on the various questions raised by previous experimental and theoretical investigations.

In the following atomic units (a.u.) are used except where otherwise stated.
2. Theory

To describe the collision system and include most of the mechanisms which give rise to ionization, we have used a semiclassical non-perturbative treatment within the single active electron approximation. The inclusion of the two electrons has been shown not to give any significant differences with respect to the interference patterns under consideration [13]. Since the focus is on high impact energy $E$ and outgoing electron momenta $k_e$ larger than 1 a.u., the nuclei of the molecular target are considered fixed during the collision time. The vibrational degree of freedom can only be taken into account by averaging the results over the initial internuclear distribution of the $H_2$ vibrational ground state (not shown in the present paper).

Within this model the time-dependent Schrödinger equation (TDSE) is expressed using a spatial discretization of the electronic wavefunction on 3D and 1D Cartesian grids [17]. The TDSE is then solved by propagating [18] the initial electronic $H_2$ ground state by the Crank-Nicolson (in 1D) or the split-operator (in 3D) schemes [19]. The latter, being a computationally weighty problem, involves a high degree of parallelization. The initial state and the lowest excited states of the molecular target are created using the inverse iteration method (in 1D) or the implicitly restarted Arnoldi method [20] (in 3D). The ionization probability densities and differential cross sections are obtained by projecting out the most important excited $H_2$ states populated during the collisions from the scattering wavefunction and by analyzing the resulting $\psi_{\text{ion}}$ in momentum space by applying a fast Fourier transform.

All data presented in the following are obtained and tested using the 3D and 1D models and original codes [21] which implement the various strategies described briefly above.

3. Results

In this section we present the preliminary results for the collision $Kr^{34+} - H_2$ at the impact energy $E = 63$ MeV/u. This system is representative of high energies, highly charged projectile conditions used in former experimental and theoretical investigations, e.g. [9, 10, 12, 22, 23]. The differential ionization cross sections obtained from the 3D description of the collision are the results of several averaging procedures, namely over impact parameters and molecular target.

![Figure 2](image)

**Figure 2.** (a) Differential ionization cross sections ratio between molecular and atomic hydrogen as function of the outgoing electron momentum $k_e$: solid (dashed) line for $0^\circ$ forward ($180^\circ$ backward) emission; (b) Ionisation probability density as function of the algebraic value of the outgoing electron momentum $k_e$: $<0$ ($>0$) for backward (forward) emission. The $H_2$ target is aligned parallel to the projectile velocity and the two curves correspond to impact parameters 0.5 a.u. (solid line) and 10 a.u. (dashed line).
orientations. Therefore any interference patterns can hardly be seen on the four orders of magnitude decrease of the cross sections for outgoing electron energies ranging from a few eV to 300 eV. As in the experimental investigations we are therefore showing in Fig. 2(a) the ratio of these cross sections over those obtained for atomic hydrogen targets. Since no effective nuclear charge (which leads to different binding energies for atomic and molecular hydrogen) have been used to obtain these data the ratio does not oscillate around unity. However the curves present a large valley with a minimum (destructive interferences) at about 2.3 a.u. electron momentum (70 eV kinetic energy) for forward emission (emission angle $\theta_e = 0^\circ$ i.e. in the direction of propagation of the projectile) and 2.0 a.u. (50 eV) for electrons emitted opposite to the projectile ($\theta_e = 180^\circ$). This is in good agreement with previous data obtained experimentally [14, 23] and theoretically [22]. Especially the asymmetry between forward and backward emissions is well predicted in our calculations. For further evidence of this feature, which was not well described theoretically (cf. Fig. 2 in [12]), we present in Fig. 2(b) the ionization probability density in the electron momentum space for the same two detection angles, two significative values of the impact parameter [24] and molecular target aligned parallel to the projectile velocity. The existence of two minima due to destructive interference effects is clearly demonstrated. The figure shows also a shift of the position of the minima for increasing values of impact parameter (lower curve) which partly accounts for the weak contrast obtained in the differential cross sections. No higher frequency oscillations are apparent in the 3D results presented in Fig. 2.

![Figure 3. 1D model: snapshots of the probability density in the electron position space at five collision times for $H_2$ (upper row) and $H$ target (lower row): the position of the projectile is represented as a full circle.](image)

It should be noted that the computations of the cross sections for one impact parameter and one molecular orientation requires about 1500 CPU-hours on a Cray XT4 mainframe and a minimum of 512 cores for data storage during the propagation. A single scattering wavefunction takes in itself $\sim$16GB of memory. In order to save CPU time and memory space we have calculated the ground and first excited states of the target on a smaller grid than the one used in the propagation stage. This introduces some (identifiable) noise in the data which in turn is convoluted using a low-pass (gaussian) filter with half-width corresponding to typical experimental resolution. The plane-wave analysis of the data to compute cross sections is also performed after a limited (though carefully selected) collision time so that the low energy
electron contribution of the ionization wavefunctions is safely analyzed. The limitation in grid size prevents us from (i) showing consecutive Young-type minima over more than one period and (ii) searching for minuscule (< 1 %) oscillatory structures in the cross sections. We now turn to a 1D model which allows for very fast and highly converged evaluations of the cross sections over a wide range of electron velocities. This model, where all particles are confined to move on a single axis, is rather drastic, but intrinsically includes all important features to describe the interference effects under consideration: in that case the criterion for first-order Young-type destructive interferences can be readily expressed as $k_e R = (2n + 1)\pi$ while a criterion for an intramolecular scattering mechanism preventing ionization of electrons of momenta $k_e$ (giving extra minima in the differential cross sections) can be roughly evaluated through confinement conditions (as invoked for photoionization in [4, 25]), i.e. $k_e R = n'\pi$ which give rise to a doubling of the number of minima.

In Fig. 3 we show the evolution of the spatial probability density during the collision. It is clearly seen that (i) the ionization is mainly initiated after the projectile passes and (ii) the scattering probability presents clear structures due to interferences in the case of a molecular target while it does not for atomic hydrogen. Figure 4 shows the (pseudo) differential cross sections obtained by analyzing the 1D scattering wavefunctions [13]. A series of minima corresponding to (1st-order) Young-type destructive interferences can be seen. Their positions verify approximatively the criterion given above, as the ones shown in Fig. 2 for the 3D calculations. Moreover the forward/backward asymmetry is clearly observed and increasing with increasing outgoing electron velocities. The shift in position is very well verified by the model proposed in [13], cf. Eq. (16), based on a modification of the Young-type interference criterion taking into account an extra phase shift between the outgoing waves from both nuclei related to the time delay ($\approx R/v$) to initiate ionization on the two centers. Again no extra structures with double periodicity are seen within this model.

Figure 4. 1D model : probability density related to the ionization wavefunction, see [13] for details, as function of the electron momentum $k_e$ ($< 0$ or $> 0$ for backward or forward emission). The position of the minima is indicated to illustrate the forward/backward asymmetry.

4. Conclusion
We have presented a study of interferences occurring in ionizing ion-molecule collisions. A full ab initio treatment as well as a restricted 1D model of the scattering system both show a clear signature of Young-type interference effects in the differential ionization cross sections vs. outgoing electron velocities. However no evident extra structures due to intramolecular scattering have been observed for $H_2$, in contradiction with several experimental investigations. The presence of high frequency oscillations therefore remains a challenge in that context. Several extensions of the present work should be achieved in the future: (i) the evaluation and interpretations of differential cross section vs. projectile scattering angles, as proposed in
for intermediate energy $H^+ - H_2$ collisions, and (ii) the description of ionization of more complex targets. Indeed recent experimental investigations did observe secondary oscillatory structures but no Young-type patterns for MeV collisions between protons and $N_2$ and $O_2$ molecules [27, 28].

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