

Orientation effects in ion-molecule collisions

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Abstract. The charge transfer process is studied in proton collisions with BeH. Given the anisotropy of the target molecule, two approaches are considered, and compared, in order to calculate orientation-averaged cross sections. The necessary molecular data (electronic energies and non-adiabatic couplings) are obtained from full configuration-interaction wavefunctions.

1. Introduction

Charge transfer (CT) in ion-molecule collisions at energies above 0.1 keV/u has usually been studied using extensively tested ion-atom collision methods [1] and codes, in which the target is assumed to have spherical symmetry. However, molecules can show a pronounced anisotropy in the electron density (and electronic wavefunctions) that could influence the cross sections. In previous works [2, 3, 4], the orientation-averaged cross-sections were obtained by averaging results produced from different orientations of the molecular target with respect to the projectile initial velocity. More complex trajectory-averaging procedures were applied in [5] and were extended to collisions with three-center molecules in [6, 7]. However, the use of this last procedure is cumbersome when employing a basis set of molecular electronic wavefunctions, and simplified methods have been employed that permit to carry out the calculation. To check the approximations in order to extend the calculations to collisions with large molecules, which are specially important in the biological damage of ion beams, we address the comparisons of the two averages procedures using, in both, the same high-quality *ab initio* wavefunctions.

In this work we consider proton collisions with BeH as a benchmark of ion collisions with heteronuclear targets. In a recent work [4], orientation-averaged electron-capture cross sections in proton collision with BeH were obtained from a set of isotropic calculations, and an effort is made to gauge the uncertainties in the cross-sections related to the use of the vibrational-sudden (see, e.g. [8]) and Franck-Condon (see e.g. [9]) approximations. The vibrational-sudden approximation is reasonable when the interaction time of the projectile with the molecule is shorter than its vibrational period, which is normally about a few tens of femtoseconds. This requires projectile speeds of 0.1 a.u. for a collisional interaction region of about 10 bohr, which is equivalent to projectile energies of about 250 eV/u. The validity of the sudden approximation for rotation and vibration has been discussed for the benchmark system $\text{H}^+ + \text{H}_2$ in [10], where it was shown that it is not appropriate at low collision energies (< 200 eV/u), because the transitions leading to the EC process take place between quasi-degenerate vibronic levels, as suggested in [11], and a method beyond the sudden approximation must be applied, as in the calculations of [12]. The Franck-Condon approximation is usually valid for energies above 1 keV/u.



While the orientation-average procedure used in both quantal and semiclassical calculations of [4] is parallel to that employed in the infinite order sudden (IOS) approximation [13], we use here a more exact procedure, similar to that employed in [14], in which the molecular data (electronic energies and non-adiabatic couplings) are required along the projectile trajectory. The results of both methods are compared in order to gauge the applicability of the IOS-type averaging method to collisions with non-symmetric heteronuclear targets.

Atomic units are used unless otherwise stated.

2. Theory

As mentioned before, the eikonal semiclassical approximation (e.g. [1]) is valid at impact energies $E > 200$ eV/u and it has been used in previous publications (see [3] and references therein). It assumes that the projectile follows straight-line trajectories with impact parameter \mathbf{b} and velocity \mathbf{v} :

$$\mathbf{R} = \mathbf{b} + \mathbf{v}t \quad (1)$$

In the eikonal treatment, the electrons are described by a wavefunction $\Psi^{\text{EIK}}(\mathbf{r}, \rho, t)$, solution of the equation:

$$H_{\text{int}}\Psi^{\text{EIK}} - i \left. \frac{\partial \Psi^{\text{EIK}}}{\partial t} \right|_{\mathbf{r}, \rho} = 0. \quad (2)$$

In the sudden-vibrational (SV) approximation [8], the scattering wavefunction is expanded on a set of molecular wavefunctions $\phi_j(\mathbf{r}; R, \rho, \theta)$, eigenfunctions of the electronic hamiltonian:

$$H_{\text{el}}(\mathbf{r}; R, \rho, \theta) = T_r + V(\mathbf{r}; R, \rho, \theta), \quad (3)$$

while the rotation and vibration of the molecular nuclei are kept frozen:

$$\begin{aligned} \Psi_{0jm}^{\text{SV}} &= \rho^{-1} Y_{jm}(\hat{\rho}) \chi_0(\rho) D(\mathbf{r}, t) \sum_k a_k(t; b, E, \rho) \\ &\times \phi_k(\mathbf{r}; R, \rho, \theta) \exp \left[-i \int_0^t \epsilon_k dt' \right]. \end{aligned} \quad (4)$$

Here $D(\mathbf{r}, t)$ is a common translation factor (CTF) [15] with the explicit form proposed in Ref. [16].

Substitution of (4) into (2), leads, for each ρ , to:

$$i \frac{da_j}{dt} = \sum_l \left[\mathbf{v} \cdot \mathbf{M}_{jl} + v^2 B_{jl} \right] a_l \exp \left[-i \int_0^t (\epsilon_l - \epsilon_j) dt' \right], \quad (5)$$

after neglecting the coupling terms proportional to $\nabla_\rho \phi_k$. Here \mathbf{M}_{jl} are the non-adiabatic couplings (NACs), which include the correction terms due to the introduction of the CTF.

The system (5) is solved for each ρ , subject to the initial condition:

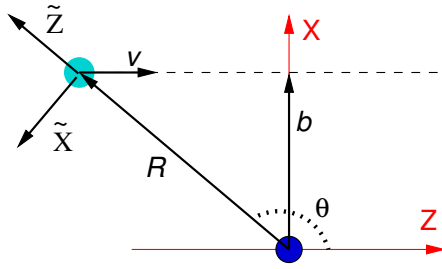
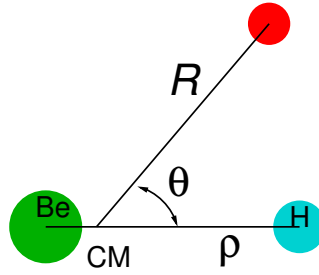
$$\lim_{t \rightarrow -\infty} a_k(t; b, E, \rho) = \delta_{ki}. \quad (6)$$

The transition probability to the final electronic state f , in the final vibrational state ν , and with rotational quantum numbers j' and m' is:

$$P_{i0jm}^{f\nu j'm'}(b, E) = \lim_{t \rightarrow \infty} \left| \langle \Psi_{f\nu j'm'} | \Psi_{0jm}^{\text{SV}} \rangle \right|^2 \quad (7)$$

It is convenient to define the simple probabilities

$$P_f(b, E, \rho) = \lim_{t \rightarrow \infty} |a_f(t; b, E, \rho)|^2 \quad (8)$$

**Figure 1.** Collision scheme.**Figure 2.** Internal coordinates of the BeH₂ system.

and the corresponding cross sections are:

$$\sigma_f(E, \rho) = 2\pi \int_0^\infty db P_f(b, E, \rho) \quad (9)$$

The closure relation for the vibrational functions allows us to get the sudden-vibrational cross section

$$\sigma_f^{\text{SV}}(E, \hat{\rho}) = \int_0^\infty d\rho \sigma_f(E; \rho) \chi_0^2(\rho), \quad (10)$$

which, using the Franck-Condon approximation, reduces to:

$$\sigma_f^{\text{FC}}(E, \hat{\rho}) = \sigma_f(E, \rho_e), \quad (11)$$

where ρ_e is the equilibrium geometry of the molecule. Orientation-averaged cross sections are obtained by integrating over $\hat{\rho}$:

$$\sigma_f^{\text{SV,FC}}(E) = \frac{1}{4\pi} \int d\hat{\rho} \sigma_f^{\text{SV,FC}}(E; \hat{\rho}) \quad (12)$$

This orientation averaged can be performed in two ways:

- Trajectory-averaging: approximating the integral in eq. (12) by a sum of N_t cross sections obtained with different values of $\hat{\rho}$:

$$\sigma^{\text{T}}(E) = \frac{1}{N_t} \sum_t^{N_t} \sigma_t(E) \quad (13)$$

- θ -averaging: using the IOSA-type averaging in eq. (12) with cross sections obtained using energies and non-adiabatic couplings from a fixed values of θ :

$$\sigma^{\text{iso}}(E) = \frac{1}{2} \int_0^\pi d\theta \sin \theta \sigma^{\text{iso}}(E, \theta) \quad (14)$$

where $\sigma^{\text{iso}}(E, \theta)$ have been obtained after solving eq. (5) using coupling matrix elements (\mathbf{M}_{jl} , B_{jl}) and electronic energies (ϵ_j) corresponding to a single θ .

3. Results

In this work, the molecular wavefunctions and energies used in the eq. (4) to build the scattering wavefunction were obtained in full configuration interaction calculations with the Be(1s) orbital always doubly occupied (see more details in [4]). In figure 3, we show the potential energy

curves corresponding to a projectile approaching the center of mass of the target at $\theta = 90^\circ$ (see figure 2), while figure 4 shows the asymptotic energies as a function of ρ when the projectile is at $R = \infty$. The equilibrium geometry of $\text{BeH}(X^1\Sigma)$ is $\rho_e = 2.568$ bohr, marked with a gray vertical line in figure 4. The collisional entrance channel is the fourth state (the lowest blue solid line), just above the channel corresponding to electron capture leaving the BeH^+ in its second $^1\Sigma$ state, which is not dissociative. Channel number 2 in figure 3 is the only dissociative one, as shown in figure 4, and leads to the fragmentation of BeH^+ into $\text{Be}^+(2s) + \text{H}(1s)$.

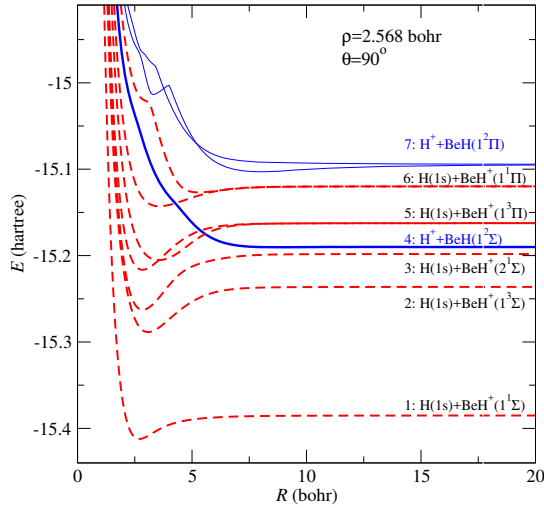


Figure 3. Energies of the system $(\text{H-BeH})^+$ as a function of R for $\rho = 2.568$ bohr and $\theta = 90^\circ$. The asymptotic limits are indicated.

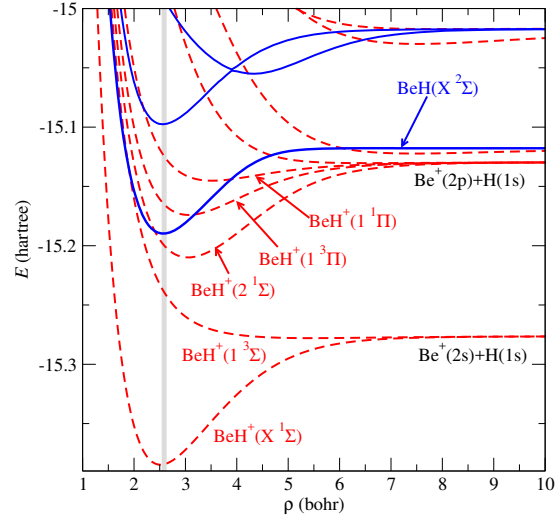


Figure 4. Energies of H+BeH^+ and H^++BeH systems as a function of ρ and $R = \infty$. The vertical grey line is at $\rho_e = 2.568$ bohr.

The full-CI wavefunctions obtained by solving (3) are used to calculate NACs and CTFs correction terms of (5):

$$\mathcal{M}_{jl} = \left\langle \phi_j \left| \frac{\partial}{\partial Z} \right|_{X,\rho,\theta,r} \phi_l \right\rangle \approx \frac{1}{\delta} \langle \phi_j(Z) | \phi_l(Z + \delta) \rangle \quad (15)$$

NACs are evaluated numerically [17] with $\delta = 10^{-4}$ bohr, sign-corrected as explained in [18] and removed singularities following [19].

The five trajectory families shown in figure 5 were run in order to obtain the trajectory-averaged cross sections of eq. (13), while eleven values of θ between 15° and 165° in steps of 15° were considered to compute the cross section of eq. (14). The results of the different approaches are compared in figure 6, where we can note several features. First, the CT cross sections are rather flat in both averages, this shape has been discussed in [4] for the θ -average case and holds for the new trajectory-average. In short, we can say that it is a consequence of the electronic structure of the system that, as shown in figure 3, has a CT channel (number 3) with an electronic energy slightly lower than the one of the entrance channel (channel 4) and dominates the CT process at low energies (below about 700 eV/u), and CT channel number 2, with lower energy, takes the lead at energies above 700 eV/u. Second, the θ -averaged cross section is about 30 Å, while the trajectory-average is around 20 Å. This difference did not show up in the study of H^++H_2 collisions of [20], where both approaches gave very close results. The large difference in the present case could be related with the larger anisotropy of BeH compared to H_2 .

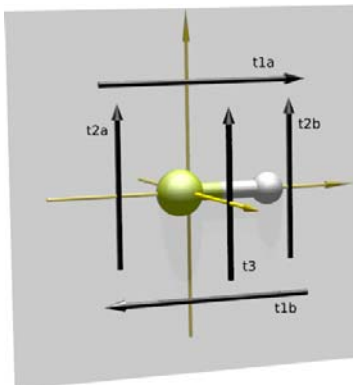


Figure 5. Trajectories families employed in the trajectory-averaged procedure for eq. (13).

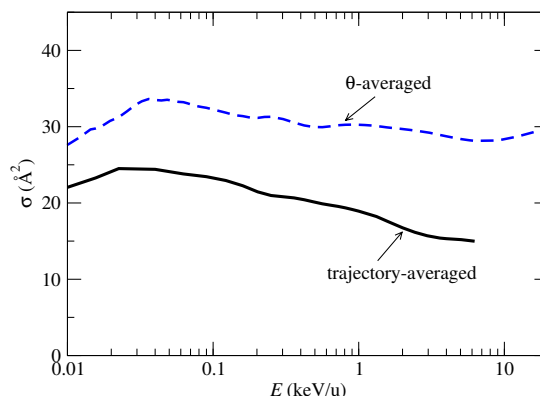


Figure 6. Orientation-average charge transfer cross sections obtained with the θ -averaged procedure of eq. (14) and the trajectory-averaged of eq. (13).

4. Conclusions

We have studied the orientation-dependence of the charge transfer cross sections in collisions of protons with BeH in its ground electronic and vibrational states. Transition probabilities have been obtained using the semiclassical formalism. We have tested two approaches to calculate the orientation-averaged cross sections. In the first one, molecular data (energies and non-adiabatic couplings) are obtained along the projectile trajectory and used to integrate eq. (2). This is a computationally expensive method since it needs to solve the electronic time-independent Schrödinger equation of the triatomic system, and cumbersome task of ensuring the sign-coherence of the non-adiabatic couplings, in a large number of geometries. In the second approach, molecular data are obtained in trajectories with fixed values of θ , and then used to integrate eq. (2). This last method requires fewer evaluations of wavefunctions and molecular properties of the collisional system. Our results point to sizable differences between the two averaging procedures, contrary to what was found in $H^+ + H_2$ collisions in [20].

Acknowledgments

This work has been partially supported by a project UAM-Santander de Cooperación Interuniversitaria con Asia and Ministerio de Economía y Competitividad (Spain) (ENE2014-52432-R). We also acknowledge the computational hosting service of the CCC-UAM.

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