Calculations for charge transfer and ionization in heavy-particle collisions from water molecules

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Abstract. A recently introduced method for the description of bare ion-molecule collisions is extended to deal with intermediate-energy He⁺-H₂O collisions, in which both the projectile electron and the target electrons are allowed to undergo transitions. All initially populated orbitals are propagated simultaneously using the same effective single-particle Hamiltonian to ensure their orthogonality at all times. The asymptotic solutions are combined to form many-electron transition probabilities on the level of single determinantal wave functions, thereby respecting the Pauli principle. It is shown that this analysis has interesting consequences for capture, loss, and ionization channels.

1. Introduction

Ion-molecule collision systems represent a serious challenge for theoretical calculations: They have many degrees of freedom, a rather complex geometry, and the electron dynamics can be nonperturbative and involve electron-electron interaction effects. Nevertheless, the interest in accurate calculations has been growing recently, in part due to the relevance of ion-molecule collisions, e.g., in atmospheric science and radiobiology. Obviously, water molecules play an important role in these fields. It is therefore not surprising that ion-H₂O collisions have been addressed in a number of theoretical works despite the difficulties mentioned above.

In fact, the full problem of many Coulomb-interacting electrons and nuclei need not be addressed unless one studies collisions at very low impact energies and/or specific details involving fragmentation processes. If this is not the case, it is safe to neglect the rovibrational motion of the target molecule, and to assume that the projectile travels on a classical (straight-line) trajectory. Still, it is a challenging task to deal with the electronic degrees of freedom in a multi-centre external potential, and further approximations are needed. To date, most of the theoretical works for ion-H₂O collisions are either based on perturbative approaches (e.g., [1, 2, 3]), or on classical trajectory Monte Carlo (CTMC) methods (e.g., [4, 5, 6]).

We have recently developed a nonperturbative quantum mechanical approach and have applied it to the p-H₂O collision system [7]. Its key ingredients are an expansion of the initially populated molecular orbitals in terms of a single-centre basis and a spectral representation of the molecular Hamiltonian. In essence, this results in a separation of molecular geometry and collision dynamics and makes it possible to adapt ion-atom methods to the latter.

In this paper, we present an extension of the approach to deal with situations, in which not only target but also projectile electrons are allowed to undergo transitions. The method is
applied to the He$^+$-H$_2$O collision system, for which experimental data are available over a broad range of impact energies. The theoretical method is described in section 2, while cross section results are compared with measurements in section 3. Conclusions are offered in section 4. Atomic units ($\hbar = e^2 = m_e = 1$) are used unless stated otherwise.

2. Theory

2.1. Collision dynamics

We consider collisions which are fast enough to neglect rotations and vibrations of the target molecule and which allow to describe the motion of the projectile ion in terms of a classical straight-line trajectory. Furthermore, we make use of the independent-electron approximation and assume that the electronic Hamiltonian is of single-particle form $\hat{H}_{el}(t) \to \sum_{i=1}^{N_o} \hat{h}_i(t)$. The time-dependent Schrödinger equation then separates into a set of single-particle equations for the initially occupied orbitals

$$
i \partial_t |\psi_{i\alpha\beta\gamma}^j(t)\rangle = \hat{h}_{\alpha\beta\gamma} |\psi_{i\alpha\beta\gamma}^j(t)\rangle, \quad i = 1, \ldots, N_o$$

with

$$
\hat{h}_{\alpha\beta\gamma} = -\frac{1}{2} \nabla^2 + v_{\alpha\beta\gamma}^T + v^P.
$$

The orientation of the molecule with respect to the projectile beam direction is characterized by the three Euler angles $\alpha, \beta, \gamma$ [7]. $v_{\alpha\beta\gamma}^T$ and $v^P$ are effective potentials of the target molecule and the projectile ion, respectively, and are specified further below. We place the origin of the coordinate system in the oxygen nucleus and measure the electronic coordinate $r$ with respect to this centre. The projectile nucleus is located at $R(t) = (b, 0, vt)$, where $b$ is the impact parameter and $v$ the constant speed.

The initial conditions to be considered in (1) are the ground-state molecular orbitals (MOs) of the target, which depend on $\alpha, \beta, \gamma$, and the moving ground-state atomic orbital (AO) of the projectile. In contrast to previous works for ion-atom collision systems with projectile and target electrons [8, 9, 10, 11] we are using the same Hamiltonian for all these orbitals. This has the advantage that the propagated states $|\psi_{i\alpha\beta\gamma}^j(t)\rangle$ are orthogonal at all times $t$ and the final-state analysis is straightforward. The disadvantage of this procedure is that one has to compromise on the physics that a Hamiltonian of the form (2) can describe: it is readily shown that one cannot construct potentials $v_{\alpha\beta\gamma}^T$ and $v^P$ that have the correct asymptotic properties for both initial target and projectile electrons at the same time. Since we consider a rather asymmetric situation with one initial projectile and ten initial target electrons, we choose a Hamiltonian that is better adapted to describe the dynamics of the latter. Specifically,

$$
\hat{h}_{\alpha\beta\gamma}^T = -\frac{1}{2} \nabla^2 + v_{\alpha\beta\gamma}^T
$$

is taken as the Hartree-Fock (HF) Hamiltonian of H$_2$O, i.e.,

$$
\hat{h}_{\alpha\beta\gamma}^T |\Lambda_{\alpha\beta\gamma}\rangle = \epsilon_{\Lambda} |\Lambda_{\alpha\beta\gamma}\rangle
$$

with HF MOs $|\Lambda_{\alpha\beta\gamma}\rangle$ and energy eigenvalues $\epsilon_{\Lambda}$, and

$$
v^P(r_P) = -\frac{2}{r_P} + \int \frac{|\varphi_{1s}^{He}(r')|^2}{|r' - r_P|} d^3r',
$$

where $\varphi_{1s}^{He}$ is the (normalized) ground-state HF AO of (neutral) helium and $r_P = r - R(t)$. Note that $v^P \to -1/r_P$ for $r_P \to \infty$, which is the correct asymptotic potential the target electrons experience before the collision. This asymptotic situation would be described even better if
one would use the hydrogenic He\(^+\)(1s) orbital instead of the neutral He orbital in equation (5). Such a choice, however, would be inconsistent with the He(1s\(^2\)) formation process in (restricted) HF theory. Since capture is a strong process in the He\(^+\)-H\(_2\)O collision system (see section 3), we model the projectile electron as a neutral-He HF state. From a more practical standpoint we note that we have tested both options in previous studies of He\(^+\)-atom collisions and have obtained very similar results for the transitions of the target electrons.

The more problematic shortcoming of our choice of single-particle Hamiltonian is associated with the dynamics of the projectile electron itself: from its viewpoint the second term in \(v^P\) (5) represents an unphysical self-screening potential—regardless of the orbital density used in the integral—and the Hamiltonian (3) does not correspond to the short-ranged asymptotic potential that a neutral H\(_2\)O molecule exerts on it. If one were to emphasize the projectile electron loss process, while ignoring electron capture, one clearly would prefer a different Hamiltonian. For ion-atom collisions we have looked into more sophisticated models to describe such complex situations, e.g., models that include time-dependent screening terms [8]. Since these models are not easily carried over to the multi-centre problem of an ion-molecule collision system and are in practice afflicted by nonorthogonality problems, we here content ourselves with considering the seemingly simple Hamiltonian (2) — with the caveat that projectile electron loss may be exaggerated.

In order to avoid an explicit consideration of multi-centre terms we work with the spectral representation of (3)

\[
\hat{h}^T_{\alpha\beta\gamma} = \sum_{\Lambda} |\Lambda\alpha\beta\gamma\rangle \epsilon_{\Lambda} \langle\Lambda\alpha\beta\gamma|
\]

and expand the MOs in an orthonormal single-centre basis located on the oxygen atom

\[
|\Lambda\alpha\beta\gamma\rangle = \sum_{s} d^A_s |s\rangle.
\]

We then use the two-centre basis generator method (TC-BGM) [12, 13] to solve the single-particle equations (1). This involves a matrix representation of the Hamiltonian (2) which can be written as

\[
\langle\chi_k|\hat{h}^T_{\alpha\beta\gamma} + v^P|\chi_j\rangle = \sum_{\Lambda} \sum_{su} \epsilon_{\Lambda}\langle\chi_k|s\rangle d^A_s d^A_u \langle u|\chi_j\rangle + \langle\chi_k|v^P|\chi_j\rangle.
\]

Since the TC-BGM basis \(\{|\chi_k\}\) has two-centre character, we are facing at most two-centre integrals in (8). Moreover, we do not propagate the three-centre MOs \(|\Lambda\alpha\beta\gamma\rangle\), but the single-centre states \(|s\rangle\) in the TC-BGM and reconstruct the molecular solutions by using the linearity of the single-particle equations (1). For the results presented in section 3 we have used the same basis sets and parameters as in our pilot study for p-H\(_2\)O collisions [7].

2.2. Final-state analysis

The first step in the construction of observables is the calculation of the single-particle state-to-state transition amplitudes

\[
A^i_f = \langle f|\psi^i_\alpha\beta\gamma(t_f)\rangle
\]

at a sufficiently large final time \(t_f\) for \(i = 1, \ldots, N = 2N_o - 1\) = 11 electrons\(^1\) and the final states \(|f\rangle\) of interest. Note that these amplitudes depend on the Euler angles \(\alpha, \beta, \gamma\), i.e., they

\(^1\) Each MO that contributes to the molecular ground state is occupied by two electrons, while the (1s) initial state of the projectile is populated by a single electron, i.e., \(N_o = 6\) orbitals are to be considered in equation (1).
are different for each molecular orientation to be considered. The average (net) numbers of electrons bound to the projectile (P) and the target (T) after the collision are found as

\[ P_{\text{net}}^{P,T} = \sum_{i=1}^{N} \sum_{f} |A^i_f|^2, \]  

(10)

where the sums over \( f \) include all bound projectile and target states, respectively. The net recoil-ion and net free-electron production yields, which are accessible to experiments, are given by

\[ P_{\text{net}}^{\text{rec}} = N - 1 - P_{\text{net}}^{T}, \]  

(11)

\[ P_{\text{net}}^{\text{free}} = N - P_{\text{net}}^{T} - P_{\text{net}}^{P}. \]  

(12)

Since the orientation of the molecule with respect to the projectile beam direction is normally not fixed in experiments, we have to calculate these net numbers for a set of Euler angles \( \alpha, \beta, \gamma \) and average them appropriately. In our previous work for p-H\(_2\)O collisions we have found that considering just two orientations\(^2\) is enough to obtain reasonably-converged total cross sections \[7\]. We are using the same prescription in the present study.

More detailed observables are calculated according to the inclusive-probabilities formalism \[14\], which is built on the construction of antisymmetric \( N \)-electron wave functions, thereby respecting the Pauli principle. Specifically, we consider inclusive probabilities which correspond to measurements, in which the final charge state of the projectile is fixed to zero (capture), one (pure target ionization) and two (projectile electron loss). They are extracted from the one-particle density matrix

\[ \langle f_i | \hat{\gamma}^1(t_f) | f_k \rangle = \sum_{i=1}^{N} A^i_{f_i} A^{i*}_{f_k}, \]  

(13)

\[ \hat{\gamma}^1(t) = \sum_{i=1}^{N} |\psi^i_{\alpha,\beta,\gamma}(t)\rangle \langle \psi^i_{\alpha,\beta,\gamma}(t)|, \]  

(14)

in the manner explained in references \[9, 11\]. The only difference is that in contrast to \[9, 11\] no renormalization of \( \hat{\gamma} \) is required in the present study, since we are working with orthonormal orbitals \( |\psi^i_{\alpha,\beta,\gamma}(t)\rangle \).

3. Results and discussion

Figure 1 shows cross sections for the net recoil-ion yield \( \sigma_+ \) and the net free-electron production \( \sigma_- \) obtained from equations (11) and (12). The dashed curves correspond to calculations, in which only the initial target electrons are taken into account (‘T electrons only’), while the full curves are obtained from full calculations, in which the projectile electron also contributes to \( P_{\text{net}}^{T} \) and \( P_{\text{net}}^{P} \) (‘electrons at both T and P’). Obviously, this has a significant effect on both cross sections. It reduces \( \sigma_+ \) due to transfer from the projectile to the target and brings it in close agreement with the experimental data. Note that in contrast to Rudd et al. \[15\], Garcia et al. \[16\] did not measure \( \sigma_+ \) directly, but looked at charge-state coincidences between the projectile and (singly) charged target molecules or molecular fragments. As suggested in their paper we include the sum over all measured cross sections for capture (cap), pure target ionization (ion), and projectile electron loss (loss) in figure 1(a).

\(^2\) namely those characterized by the Euler angles \( \alpha = \beta = \gamma = 0 \) and \( \alpha = \pi/2, \beta = \gamma = 0 \) with respect to the geometry specified in figure 1(a) of \[7\].
Figure 1. Total cross sections in He\textsuperscript{+}-H\textsubscript{2}O collisions as functions of impact energy. (a) Net recoil-ion yield. Full curve: full calculation according to equation (11), dashed curve: only initial target electrons are considered. Experiments: Rudd (1985) [15], Garcia (2008) [16] extracted from the tabulated data as described in the text. (b) Net free-electron production. Full curve: full calculation according to equation (12), dashed curve: only initial target electrons are considered, dash-dotted curve: pure loss subtracted from full calculation. Experiments: Rudd (1985) [15], Garcia (2008) [16] extracted from the tabulated data as described in the text.

In the case of $\sigma_-$ displayed in figure 1(b) the projectile electron has the opposite effect: It enhances the cross section, simply because it can also be ionized. The agreement with the experimental data of [15] is somewhat less satisfactory than in the case of $\sigma_+$. At projectile energies $E_P$ ranging from 20 to 80 keV/amu the full calculation overestimates the measurements, whereas the ‘T electrons only’ calculation agrees nicely with the data, when the projectile electron loss channel, denoted as $\sigma_{12}$ in [15], is subtracted from $\sigma_-$. This indicates that, as expected, our model tends to overestimate projectile electron loss. Figure 4, which is discussed further below, shows this explicitly.

The included data points of reference [16] correspond to sums of measured pure ionization and projectile electron loss cross sections and do not exactly correspond to $\sigma_-$. For instance, these sums do not include the pure loss channel, in which the projectile electron is ionized, while the target molecule remains intact. We have calculated pure loss using the inclusive-probabilities formalism and have subtracted it from $\sigma_-$. The obtained results (‘P pure loss removed’) still lie above the measurements of Garcia et al., and in stark contrast they give no indication of a structure around $E_P = 160$ keV/amu. The structure in the measurements was explained by a competition between loss, capture, and ionization channels peculiar to dressed-projectile impact collisions [16]. It was found in practically all measured channels, whereas we obtain smooth cross section curves in all cases considered in this work.

Figure 2 shows the situation for single capture, i.e., neutral He production. It demonstrates that the Pauli exclusion principle plays an important role for this channel. The dashed curve is obtained by summing up all contributions due to the initial target electrons, i.e., it would correspond to net capture if the projectile were bare. However, it is not, but carries an electron in the $K$ shell. Hence, another electron can only be captured to this shell if it has antiparallel spin\textsuperscript{3}. This Pauli blocking effect is ignored by the simple analysis that results in the dashed

\textsuperscript{3} unless the projectile electron is excited or removed in the same event.
Figure 2. Total cross section for single capture (i.e., neutral He production) in He\(^+\)-H\(_2\)O collisions as a function of impact energy. Full curve: calculation according to the inclusive-probabilities formalism, dashed curve: net capture from initial target electrons. Experiment: Rudd (1985) [15], Garcia (2008) [16].

Figure 3. Total cross section for pure ionization (i.e., no charge change of the projectile) in He\(^+\)-H\(_2\)O collisions as a function of impact energy. Full curve: calculation according to the inclusive-probabilities formalism. Experiment: Garcia (2008) [16].

curve, but it is consistently taken into account in the inclusive-probabilities formalism. The resulting full curve is indeed about a factor of two below the dashed one and in very good agreement with the measurements.

Figure 3 displays cross sections for the pure target ionization channel obtained by summing up all inclusive cross sections which correspond to one electron on the projectile, while less than ten are bound to the target after the collision. The curve is similar in shape to the net free-electron production (cf. figure 1(b)), but more than a factor of two smaller in the maximum due to the more inclusive nature of \(\sigma_-\). The agreement with the measurements of [16] is good at projectile energies above \(E_P = 200\) keV/amu, but in conflict with the two data points at lower \(E_P\), which suggest a rather strong case of the structure mentioned above.

Another manifestation of the interplay between projectile and target electron transfer processes is seen in the projectile electron loss data displayed in figure 4. The He\(^{2+}\) production cross section \(\sigma_{12}\) of Rudd \textit{et al.} [15] starts at rather low values at low projectile energies and appears to be still rising at \(E_P = 100\) keV/amu. At energies above 100 keV/amu it may be expected to connect reasonably well to the data of Garcia \textit{et al.} [16], which however do not include the pure loss channel, in which the target molecule remains intact. According to our calculations this channel dominates at the highest energies. Nevertheless, our results show a much steeper fall-off in this region than the data of Garcia \textit{et al.} One possible reason for this conflicting behaviour is that our model does not account for the so-called antiscreening process. This is a first-order mechanism, in which the projectile electron interacts with one of the target electrons resulting in the ionization of both [17].

Furthermore, the theoretical cross section curves included in figure 4 show the following: (i) at intermediate to lower energies the neglect of target electrons and the model potential result in a huge overestimation; (ii) the inclusive analysis corrects for these deficiencies at intermediate energies by ruling out processes, in which projectile loss is accompanied by transfer from the
target to the projectile; (iii) at lower energies the present modeling cannot account for the data, since the projectile electron is bound too weakly and experiences a charged target potential; (iv) removal of the pure projectile loss contributions (no charge change in the target) lowers the cross section, but does not alter the shape. Overall, projectile electron loss is the channel, for which we obtain the least satisfactory results.

4. Conclusions
The present work shows that the inclusive-probabilities formalism when applied to an independent-electron TC-BGM calculation based on a single-Hamiltonian approach is capable of describing a large fraction of the available data on charge-state production cross sections in He$^+$/H$_2$O collisions. It represents a substantial extension of previous work on the p-H$_2$O system. Some problems remain due to the inadequate description of the projectile electron loss. It will be interesting to observe whether this model deficiency is less marked for projectiles that carry more electrons into the collision, i.e., for more symmetric situations.

We emphasize that the present energy representation of the water molecule Hamiltonian in terms of occupied MOs is likely to be accurate at intermediate and high energies, but may require improvements in the low-energy regime where dynamic response to charge-changing processes may become important. Future work will be concerned with the modeling of these effects.

Acknowledgments
This work has been supported by SHARCNET and the Natural Sciences and Engineering Council of Canada.

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References

Figure 4. Total cross section for projectile electron loss (i.e., He$^{2+}$ production) in He$^+$-H$_2$O collisions as a function of impact energy. Full curve: calculation according to the inclusive-probabilities formalism, dash-dotted curve: pure loss channel subtracted from full curve, dashed curve: single-particle loss due to the initial projectile electron. Experiment: Rudd (1985) [15], Garcia (2008) [16].

