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Nonperturbative, quantum-mechanical approach to ion collisions from molecular targets

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A quantum-mechanical approach to ion-molecule collisions is presented. It involves a separation of molecular geometry and collision dynamics and enables the use of the basis generator method developed for ion-atom collisions with relatively minor modifications. As a first application, we consider the p-H_2O collision system in the impact energy range of 20–5000 keV, and we report total cross sections for net electron transfer and ionization. They are in remarkably good agreement with experimental data.

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Significant progress has been made in the theoretical description of ion-atom collisions in recent years. Numerical solutions of the corresponding Schrödinger equation have reached benchmark accuracy for prototype one-electron [1] and two-electron [2] systems even in a range of collision parameters, in which perturbation theory is not applicable. Detailed comparisons with state-of-the-art experiments, which yield information on all kinematical degrees of freedom, are now possible.

The situation is different for molecular targets. Even if one disregards the additional degrees of freedom associated with their nuclear motion, the problem is far more difficult. This is due to the multicenter nature of the target, which also represented a challenge for structure calculations for many years [3]. However, the interest in accurate calculations for collisions involving molecular targets has been growing recently. An important reason for this development is their relevance for a number of fields, such as atmospheric science, and particularly for the understanding of radiation damage of biological tissue (see, e.g., Ref. [4] and references therein).

This has motivated quite a few studies with water molecules as targets. On the experimental side, total cross sections (TCSs) for ionization and electron transfer in p-H_2O collisions were measured, e.g., by Rudd and co-workers over a wide range of impact energies E_P in the 1980s [5]. Detailed information on the fragmentation pathways of the water molecule after the electron removal has been obtained more recently [6–9]. On the theoretical side, perturbative first Born (B1) [10] and continuum distorted-wave eikonal initial-state (CDW-EIS) (e.g., [11,12]) as well as classical trajectory Monte Carlo (CTMC) [13,14] methods have been used, mostly on the basis of rather simple descriptions of the molecular character of the target. A notable exception is a molecular close-coupling calculation for electron transfer and excitation, which is based on electronic states that include configuration interaction [15]. This approach is, however, limited to low energies, i.e., $E_P \leq 10$ keV. The situation is similar for heavier ion impact. A theoretical approach which is suitable over a wide range of collision energies and meets the quantum nature of the electrons without perturbative restrictions is still lacking.

In this Rapid Communication, we introduce such an approach and use it to calculate electron transfer and ionization in the p-H_2O collision system. We start from an impact-parameter picture, in which the projectile passes on a classical straight-line trajectory by a water molecule which is fixed in space. This assumption is well justified unless one considers very slow collisions. Furthermore, the electronic Hamiltonian is assumed to be of single-particle form $\hat{H}_{el}(t) \rightarrow \Sigma_{i=1}^{N} \hat{h}_i(t)$, i.e., the electron-electron interaction is represented by an effective potential.

The equations under discussion in this framework are time-dependent single-particle equations for the initially populated molecular orbitals (MOs), which in atomic units ($\hbar = e^2 = m_e = 1$) read

$$i\partial_t|\psi^{\Gamma}_{\alpha\beta\gamma}(t)\rangle = [\hat{h}^{MO}_{\alpha\beta\gamma} + v_P(t)]|\psi^{\Gamma}_{\alpha\beta\gamma}(t)\rangle, \tag{1}$$

$$|\psi^{\Gamma}_{\alpha\beta\gamma}(t_i)\rangle = |\Gamma_{\alpha\beta\gamma}\rangle, \quad \Gamma = 1, \ldots, N, \tag{2}$$

$$\hat{h}^{MO}_{\alpha\beta\gamma} = -\frac{1}{2}\nabla^2 + v^{MO}_{\alpha\beta\gamma}, \tag{3}$$

$$v_P(t) = -\frac{Q_P}{|\mathbf{r} - \mathbf{R}(t)|}. \tag{4}$$

Here, α, β, γ denote the three Euler angles, which define the orientation of the molecule in the initial state [16,17]; $\hat{h}^{MO}_{\alpha\beta\gamma}$ is the corresponding (single-particle) Hamiltonian that consists of the (nonrelativistic) kinetic energy and the effective potential $v^{MO}_{\alpha\beta\gamma}$; and $|\Gamma_{\alpha\beta\gamma}\rangle$ denote the initially populated MOs of which there are $N=5$. Q_P is the charge of the projectile ($Q_P=1$ in the present case) and $\mathbf{R}(t)=(b,0,v_P t)$ is the straight-line trajectory characterized by the impact parameter b and the velocity v_P. Figure 1(a) displays one possible geometry of the problem, where the molecule lies in the scattering (xz) plane defined by the impact parameter and the projectile velocity. We place the origin of the coordinate system in the oxygen nucleus and measure the electronic coordinate $\mathbf{r}$ with respect to this center. We characterize this geometry by the Euler angles $\alpha=\beta=\gamma=0$. All other geometries can be obtained by rotations of the water molecule using the Euler angles. Figures 1(b) and 1(c) show two such examples.

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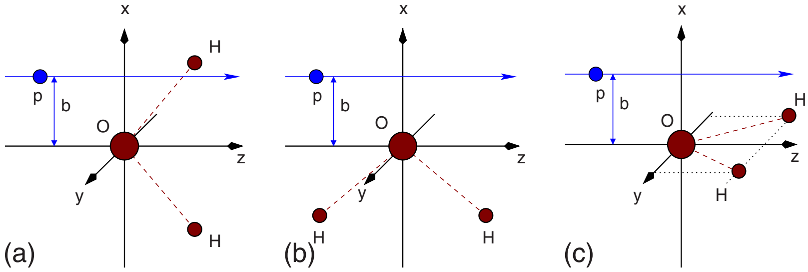

FIG. 1. (Color online) Geometries of the p-H_2O collision system. (a) (0,0,0) configuration; (b) (0,270,0) configuration; (c) (90,0,0) configuration.

Scenario (b) is obtained from the basic configuration by a 270° rotation about the y axis [i.e., by $(\alpha,\beta,\gamma)=(0,270,0)$], and scenario (c) by a 90° rotation about the z axis [i.e., $(\alpha,\beta,\gamma)=(90,0,0)$]. In principle, all such geometries have to be taken into account when calculating cross sections for total electron transfer and ionization since the orientation of the molecule with respect to the projectile beam direction is normally not fixed in experiments, i.e., orientation-averaged cross sections are measured.

Before we discuss the calculation of an appropriate orientation average let us address the problem of solving the single-particle equations (1) for a *given* orientation. Our approach involves several steps. First, we expand the solutions $|\psi^{\Gamma}_{\alpha\beta\gamma}(t)\rangle$ in a basis set $\{|\chi_j\rangle\}$,

$$|\psi^{\Gamma}_{\alpha\beta\gamma}(t)\rangle = \sum_j a^{\Gamma}_j(t)|\chi_j(t)\rangle, \tag{5}$$

which yields the coupled-channel equations

$$i\sum_{j=1} \dot{a}^{\Gamma}_j(t)\langle\chi_k|\chi_j\rangle = \sum_{j=1} a^{\Gamma}_j(t)\langle\chi_k|\hat{h}^{MO}_{\alpha\beta\gamma}+v_P(t)-i\partial_t|\chi_j\rangle \tag{6}$$

for the expansion coefficients. Note that we have neither assumed orthogonality nor stationarity of the basis states. The coupled equations have the same form as those of ion-atom collision problems, but they involve the multicenter matrix element $M_{kj}\equiv\langle\chi_k|\hat{h}^{MO}_{\alpha\beta\gamma}|\chi_j\rangle$, which cannot be evaluated by standard ion-atom techniques. This matrix element, and to a lesser extent the representation of the initial conditions $|\Gamma_{\alpha\beta\gamma}\rangle$, are the bottlenecks of the molecular collision problem.

In order to deal with them we work with the spectral representation of the molecular Hamiltonian $\hat{h}^{MO}_{\alpha\beta\gamma}=\Sigma_\Lambda\varepsilon_\Lambda|\Lambda_{\alpha\beta\gamma}\rangle\langle\Lambda_{\alpha\beta\gamma}|$ and expand the MOs in an orthonormal single-center basis $|\Lambda_{\alpha\beta\gamma}\rangle=\Sigma_s d^{\Lambda}_s|s\rangle$. This yields the expression

$$M_{kj} = \sum_{\Lambda}\sum_{su}\varepsilon_\Lambda\langle\chi_k|s\rangle d^{\Lambda}_s d^{\Lambda}_u\langle u|\chi_j\rangle, \tag{7}$$

in which multicenter terms no longer appear explicitly. They have been broken up and replaced with a combination of molecular energy eigenvalues ε_Λ, overlap matrix elements $\langle\chi_k|s\rangle$ of basis states and expansion coefficients d^{Λ}_s, which characterize the linear combinations of single-center states used to represent the MOs. Making use of the linearity of the time-dependent Schrödinger equation, we propagate the basis states $|s\rangle$ in the basis $\{|\chi_j\rangle\}$ rather than the MOs. This yields solutions $|\psi^{s}_{\alpha\beta\gamma}\rangle$ that are combined to generate the solutions $|\psi^{\Gamma}_{\alpha\beta\gamma}\rangle$ of Eq. (1),

$$|\psi^{\Gamma}_{\alpha\beta\gamma}(t)\rangle = \sum_s d^{\Gamma}_s|\psi^{s}_{\alpha\beta\gamma}(t)\rangle = \sum_{sj} d^{\Gamma}_s a^{s}_j(t)|\chi_j(t)\rangle. \tag{8}$$

The coefficients $a^{s}_j(t)$ are obtained from solving the coupled-channel equations (6) for the initial conditions $|s\rangle$, making use of expression (7) for the multicenter matrix element. Except for this term the problem is now similar to a standard ion-atom collision problem, and well-tested and established methods can be applied.

The solutions are then analyzed by projection onto appropriate asymptotic states. These are traveling bound projectile states for the evaluation of electron transfer probabilities p^{Γ}_{pro}, and bound (molecular) target states, again represented in the single-center basis, for the probabilities that an electron remains bound to the target p^{Γ}_{tar}. Applying unitarity, ionization probabilities p^{Γ}_{ion} are obtained from $p^{\Gamma}_{\text{ion}}=1-p^{\Gamma}_{\text{pro}}-p^{\Gamma}_{\text{tar}}$.

The outlined scheme involves three expansions: (i) for the propagation, (ii) for the representation of the MOs, and (iii) for the molecular Hamiltonian. In practice, they are all finite. For the dynamics, we use the basis generator method (BGM) [18] in its two-center (TC) implementation [19]. A TC-BGM basis includes sets of atomic orbitals (AOs) placed on a center that represents the target (the oxygen atom in our case) and the projectile. The AOs are endowed with the appropriate translation factors to ensure Galilean invariance. In addition, pseudostates are included, which are constructed by the repeated application of a regularized projectile potential onto the target states. These states allow for an adaptation to the dynamics of the system and account for ionization and for quasimolecular effects at low collision velocity.

For the results presented below we have used a set of atomic oxygen orbitals obtained from a density-functional-theory structure calculation within the so-called exchange-only limit of the optimized potential method [20]. All AOs of the *KLM* shells are included in the basis. On the projectile center all eigenstates of the *KLMN* shells of atomic hydrogen are taken into account and 22 pseudostates are added to describe ionization. We have checked that this basis produces well-converged results for the proton-oxygen ion-atom collision system [21].

The oxygen AOs are then used to describe the water molecule. We follow the minimal-basis-set Hartree-Fock calculation of Ref. [22] and represent the five ground-state MOs originally given in terms of Slater-type orbitals placed on the three atomic centers in this AO basis. This representation is not perfect and yields total norm integrals $0.9\leq\Sigma^{KLM}_{s}|\langle s|\Gamma_{\alpha\beta\gamma}\rangle|^2<1$. Finally, we limit the spectrum $\{|\Gamma_{\alpha\beta\gamma}\rangle\}$ in the representation of the target Hamiltonian to

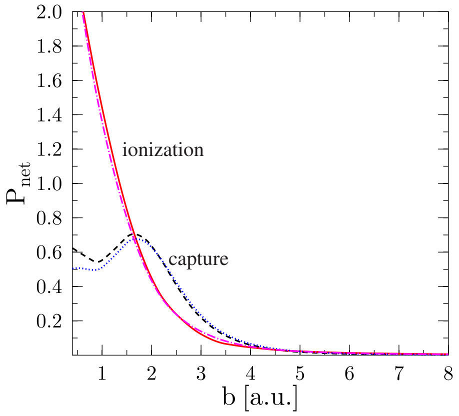

FIG. 2. (Color online) Net capture and ionization probabilities as functions of the impact parameter for the p-H_2O collision system at $E_P=30$ keV. Full and dashed curves: averages in the scattering plane; chain and dotted curves: averages in the azimuthal plane.

these initially occupied MOs and neglect contributions from excited and continuum states. This approximation may be drastic, but it is consistent with the previous assumptions since it would be pointless to try to describe the latter states within a limited single-center basis. We have also checked that taking them into account globally in terms of a closure approximation does not change the results of the collision calculations significantly.

We have performed such calculations for the geometries $(\alpha=0,\beta,\gamma=0)$ and $(\alpha,\beta=0,\gamma=0)$ from $E_P=20$ keV to $E_P=5000$ keV. The details of the calculations show a considerable dependence of capture and ionization probabilities on the orientation of the molecule, particularly at low energies. However, we have found that their averages in the scattering plane [i.e., the averages of the $(0,\beta,0)$ configurations over β] and the averages in the azimuthal plane [obtained by averaging the results of the (0,0,0) and (90,0,0) configurations] are quite similar. This is demonstrated in Fig. 2, which displays these averages for net capture and ionization at $E_P=30$ keV obtained by summing up the contributions from all initially populated MOs [23,24]. We have exploited this result in order to reduce the computational costs and have calculated TCSs for net capture and ionization according to

$$\sigma=\int P(b;\alpha,\beta=0,\gamma=0)d^2b \tag{9}$$

$$\approx\pi\int_0^\infty b\left[P(b;0,0,0)+P\left(b;\frac{\pi}{2},0,0\right)\right]db. \tag{10}$$

Using this expression involves the assumptions that (i) the fully orientation-averaged TCSs are well represented by these partial averages and (ii) the average of the (0,0,0) and (90,0,0) configurations approximates the TCS that corresponds to the integral of the results for the (0,0,0) configuration over the impact-parameter plane [25].

Our results are presented in Fig. 3. We observe very good agreement with experimental data for both net capture and ionization. For capture, the present cross sections are the only ones which reproduce the experimental impact energy dependence correctly over the entire range. Note that the CTMC results of Refs. [13,14] are not for net, but for *single* capture and ionization. For net ionization, our method agrees with the other methods at high energies, while a small discrepancy remains with the experimental data. At intermediate energies only the CTMC calculations of Ref. [13] appear to be competitive. Compared to experiment, the present calculation leaves a room for corrections due to dynamical changes in the effective target potential [27]. Such response effects may be significant since at small energies and impact parameters the present calculations predict net ionizations considerably larger than 1 (cf. Fig. 2), which implies substantial multiple ionization.

In summary, we have presented an approach for the theoretical description of ion-molecule collisions. It is based on a spectral representation of the molecular Hamiltonian, a single-center expansion of the ground-state molecular orbitals, and the basis generator method for orbital propagation. We have addressed the p-H_2O collision system and have calculated cross sections for net capture and ionization. It is interesting to note that it takes a nonperturbative, quantum-mechanical method to achieve satisfactory agreement with the measurements.

In the future, we will extract more detailed information from our calculations, such as charge-state correlated cross sections. Also, it would be interesting if experimental data

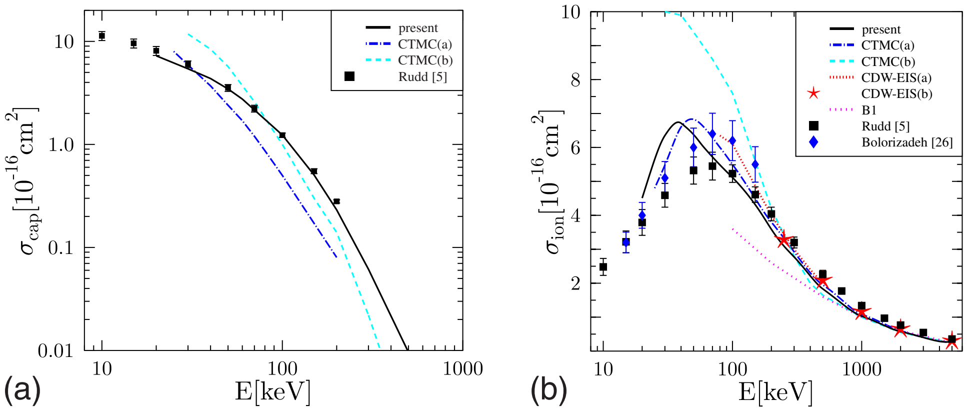

FIG. 3. (Color online) (a) Net capture and (b) ionization cross sections as functions of the impact energy for the p-H_2O collision system. Present calculations according to Eq. (10). Previous calculations: CTMC(a) [13], CTMC(b) [14], CDW-EIS(a) [11], CDW-EIS(b) [12] and B1 [10]; experiments: Rudd *et al.* [5] and Bolorizadeh and Rudd [26].

sensitive to the orientation of the molecule would become available since our method allows for studies of the orientation dependence of cross sections.

The approach is not restricted to collisions from water molecules. It can be applied to any target, for which a one-center expansion of the ground-state orbitals can be obtained. Previous work shows that this is possible, e.g., for small hydrocarbon molecules [28]. It will be interesting to apply our method to such systems.

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