Accurate Quantal Studies of Ion-Atom Collisions Using Finite-Element Techniques

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Methods have been developed to solve the time-dependent Schrödinger equation with Coulomb interactions, and applied to H^+ and C^{+6} collisions with H in the energy range 8–84 keV/amu. Total charge-transfer cross sections agree well with experiment, while ionization cross sections are higher than previous estimates at low energies. The phenomenon of "cusp asymmetry" is verified. Examination of charge-density plots reveals unexpected structures.

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One of the primary tasks set before atomic collision theorists is to perform accurate calculations on the simplest systems, e.g., a bare nucleus scattered by a hydrogen atom. Apart from the continuing intrinsic interest of this system, accurate calculations provide tests of models and approximations. Though benchmark calculations are now available[1,2] for the simplest cases of H^+ and $He^{++}+H$, such results are not yet available for more highly stripped projectiles: In many cases the best estimates come from classical trajectory studies.[3] Despite the attractiveness of direct numerical integration of Schrödinger's equation only one study (of a head-on collision) has been published.[4] This Letter describes the first successful calculations for nonzero impact parameters and highly stripped projectiles. The power of the numerical technique is illustrated by a sampling of results on $H^+ + H$ and $C^{+6} + H$ collisions: I can shed light on old aspects of these systems and even predict new phenomena.

Suppose a hydrogen nucleus is initially at rest at the origin of coordinates in the laboratory. The projectile is a bare nucleus of charge $+q$ moving uniformly with velocity $\vec{v}$ on a straight-line trajectory of impact parameter b; at time t the Cartesian coordinates of its position $\vec{R}$ may be taken as $X=b$, $Y=0$, and $Z=vt-Z_0$. I express the Hamiltonian H in a rotating frame $Oxyz$ such that $Oy=OY$ and Oz is the internuclear axis. Cylindrical coordinates ρ and φ represent the distance from Oz and the angle around Oz measured from the OZX plane, respectively. Then

$$H=H_{\rm rot}+H_{\rm Cor}, \quad H_{\rm rot}=T_\rho+T_z+V(\rho,z), \tag{1}$$

where $H_{\rm rot}$ is the axially symmetric Hamiltonian in $Oxyz$ and $H_{\rm Cor}$ contains all terms depending on φ, including Coriolis terms; T_ρ and T_z are components of the kinetic energy and V is the potential energy. Full expressions are found in many places.[1,2]

The detailed results were obtained with the "axial decoupling" (two-dimensional, 2D) approximation in which only $H_{\rm rot}$ is retained in Eq. (1), so that φ may be entirely ignored. Earlier work[5] supports the suggestion that this is often a reasonable approximation and indeed we shall find good agreement with experiment and with preliminary 3D calculations. The method used to integrate the time-dependent Schrödinger equation has already been described.[6,7] In the 2D approximation the Peaceman-Rachford[8] propagator for a single time step is defined by (in atomic units)

$$\psi(t+\tau)=L_\rho^{-1}L_z^{-1}L_z^*L_\rho^*\psi(t), \tag{2}$$

where

$$L_w=1+\tfrac{1}{2}i\tau(T_w+\tfrac{1}{2}V), \quad w=\rho \text{ or } z. \tag{3}$$

When ψ is discretized by expanding in finite elements (in fact, "tent" functions) Eq. (2) becomes a matrix equation in which L_z and L_ρ are tridiagonal matrices. The Coulomb singularities in Eq. (2) are properly taken into account and judicious use is made of variable step sizes.[6,7] The present (2D) results were all obtained with 94 functions in the z coordinate and 44 functions in the ρ, the ranges of z and ρ being $36a_0$ and $16a_0$, respectively. Each collision was integrated from $Z=-Z_0=-12a_0$ to $Z=12a_0$. For a single impact parameter and velocity the temporal integration requires <1 min on a Cray-1.

I have chosen to investigate the systems $H^+ + H$ and $C^{+6}+H$, the former as the most fundamental ion-atom process and the latter as the prototype of collisions with highly stripped projectiles. The energy range investigated was 8–84 keV/amu where theory is most lacking, though the present method is tractable at both lower and higher energies.

Projection of a numerical wave function onto a

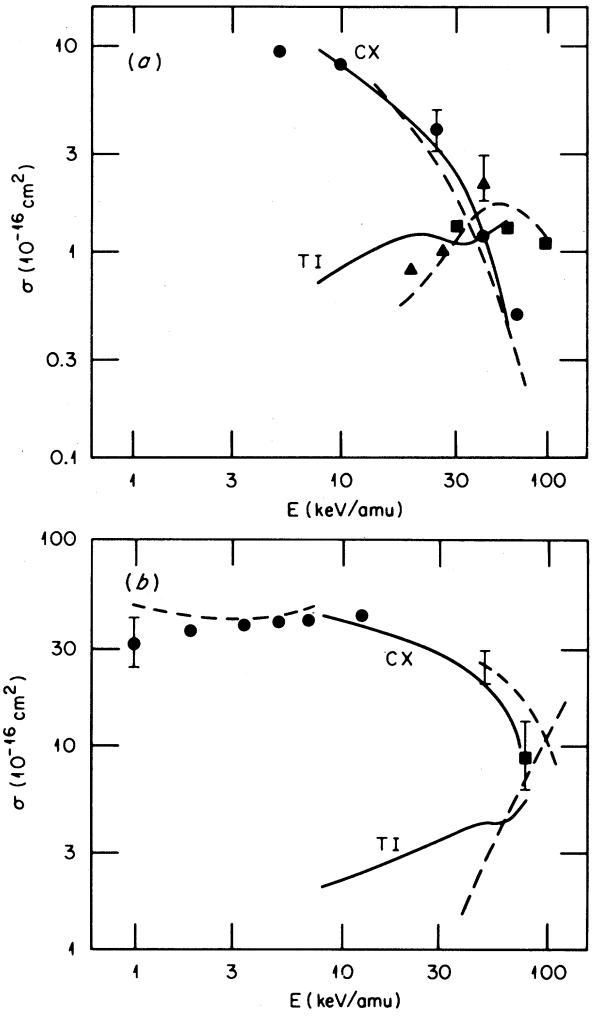

FIG. 1. Present results compared with other theory and experiment for (a) $H^+ + H$, (b) $C^{+6} + H$. Charge-exchange cross sections are labeled CX and ionization TI. Theory: full lines, this Letter; dashed lines, (a) Ref. 1 and (b) Refs. 3 and 11. Experiment: circles, (a) Ref. 9, (b) Ref. 11; triangles, Ref. 10; squares, (a) Ref. 10 and (b) Ref. 3.

complete set of eigenstates is far from straightforward, and so I have adopted a more empircal approach to the calculation of transition probabilities. It is desirable to separate four types of processes: (a) target excitation; (b) capture into bound states (CX); (c) direct ionization of the target (DI); and (d) ionization by capture into the continuum (CC). Inspection of charge-density plots (to be discussed in greater detail below) shows that at a late stage in the collision (a) and (c) are clearly separated from (b) and (d) by the median plane $z = \frac{1}{2}R$. The separation of (a) and (b) from (c), (d) is less clear but seems to take place around $\rho = 7a_0$ and I adopt this radius as my criterion. For most of the cases I considered, the cross section for (b) greatly exceeds that for (d) so that the method should lead to little uncertainty in the charge-exchange cross section.

Figure 1 compares total cross sections for charge exchange and ionization, calculated as just explained, with experimental results and other theories. Consider first the $H^+ + H$ results. The charge-exchange cross section is in excellent agreement with experiment,[9] and with the most elaborate close-coupling calculation.[1] The ionization agrees reasonably with experiment[10] and with close coupling above 25 keV, though it is larger than other theories below this energy. Turning to $C^{+6} + H$, we see that the charge-exchange cross section is in excellent agreement with measurements at high[3] and low[11] energies using O^{6+} projectiles, which in this energy range ought to be equivalent to C^{+6} for the same relative velocity.[12] The ionization cross section here can only be compared with a classical calculation and again the present value is much larger at low energies (<50 keV/amu). Large ionization cross sections in the energy range 20–60 keV/amu with projectiles of charges up to +5 have been observed by Shah and Gilbody.[13] In the present calculations low-energy ionization is almost entirely DI.

More insight is obtained by considering the variation of transition probabilities with impact parameter. Typical results (for $C^{+6} + H$ at 40 keV/amu) are shown in Fig. 2(a). They agree with earlier work[1] that in the energy range 25–50 keV/amu the cross sections for DI and CC are comparable; however, the mechanisms have different dependences on b.

Experiments on continuum capture usually focus on the now famous "cusp" which appears on a plot of ejected electron yield versus laboratory electron energy[14] [cf. Fig. 2(b), inset]. With highly stripped projectiles a clear backward-forward asymmetry is observed between the numbers of electrons trailing and leading the projectiles [marked B and F in Fig. 2(b), inset]. This effect has been explained by the second Born approximation,[15] though some controversy persists.[14,16] To study the asymmetry let us monitor the amount of probability in two hollow cylinders bounded by $\rho = 7a_0$, $14a_0$ and $z = R$, $R \pm 4a_0$. At large times these quantities reach fairly constant values, suggesting that we are indeed tracking continuum capture. The ratio $\mathfrak{A}$ of probability in the backward and forward cylinders is plotted in Fig. 2(b)

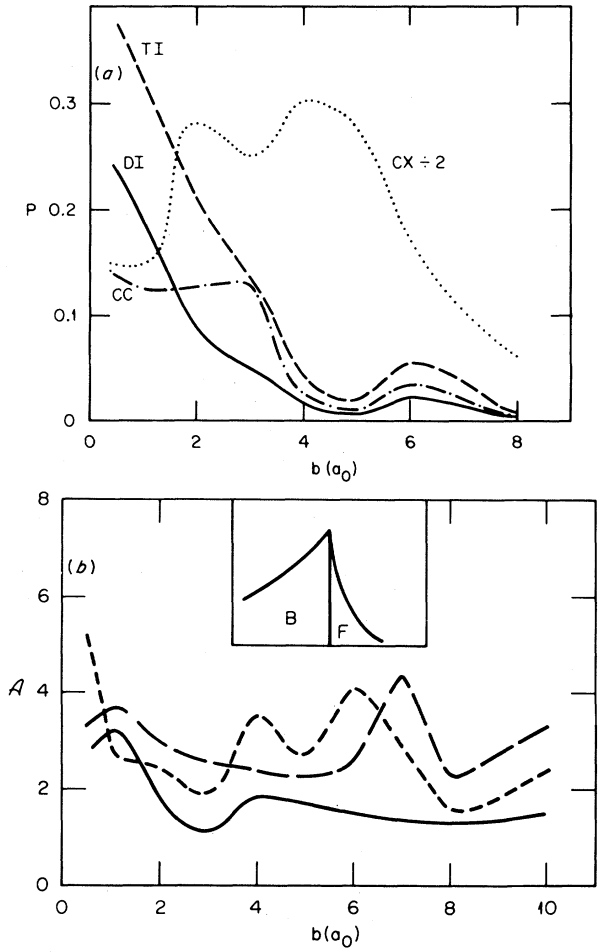

FIG. 2. (a) Variation of transition probabilities with impact parameter for C^{+6}+H at 25 keV/amu: dotted line, charge exchange divided by 2; dashed line, total ionization; full line, direction ionization; dot-dashed line, continuum capture. (b) Variation of the cusp asymmetry parameter defined in the text with impact parameter for C^{+6}+H: full line, 25 keV/amu; short-dashed line, 40 keV/amu; long-dashed line, 65 keV/amu. The inset shows the appearance of the "cusp" on a plot of ejected electron yield vs electron energy in the laboratory.

versus b for C^{+6}+H collisions at three energies. In all cases $\mathcal{A}>1$. The observed asymmetry, obtained by integrating the forward and backward yields over b, increases from 1.9 to 2.6 for C^{+6}+H over the energy range considered. Smaller asymmetries are predicted by the H^++H calculations.

Figure 3 displays charge-density contour plots at a series of times during the collision for two cases. Figure 3(a) pertains to H^++H at 40 keV and $b=1.5a_0$, the same case for which density

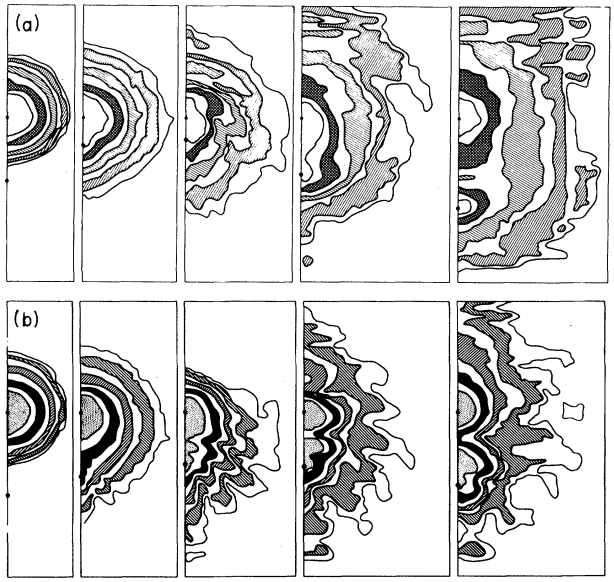

FIG. 3. Contour density plots at times 3.75, 7.35, 10.75, 14.55, and 18.15 during the collisions (a) H^++H, 40 keV, $b=1.5\,a_0$; (b) C^{+6}+H, 25 keV/amu, $b=6\,a_0$. In each frame the z axis is vertical and the ρ axis horizontal, the range of z being $36a_0$. On the z axis the upper dot is the target and the lower the projectile nucleus. Moving outward from the nuclei the shadings correspond to the following ranges of $-\log|\psi|^2$: (0, 1.5), (2, 2.5), (3, 3.5), and (4, 4.5); beyond the last contour, <5.

plots obtained by close coupling have been published.[1] The most striking feature of Fig. 3(b), which pertains to C^{+6}+H at 25 keV/amu and $b=6a_0$, are the fingerlike structures appearing at the last three times. Some structure can be discerned in Fig. 3(a) and even in the close-coupling results.[1] Systematic calculations have suggested a plausible mechanism for forming these "fingers," viz., excitation of the initial target state φ_A to a virtual state $\varphi_B \exp(i\vec{v}\cdot\vec{r})$ traveling with the projectile and hence to a continuum target state of *high angular momentum* φ_A'. Consideration of overlap integrals leads to a condition $l_f \lesssim bv$ consistent with the present results.

The last plot of Fig. 3(b) also reveals that the charge distribution in the bound states formed by capture is highly asymmetric and directed towards the target nucleus. The same effect is found over the whole energy range considered here. This distribution corresponds to a mixture of Stark states of the form $|n_1, n_2, m\rangle = |n-1, 0, 0\rangle$, which is already predicted by curve-crossing models[17] at much lower energies (<1 keV).

I have made preliminary 3D calculations on H^+

+H collisions using Eq. (1) and an extension[7] of Eq. (2). At moderate impact parameters [$b = (1 - 3)a_0$] the charge-transfer probabilities are very close to the 2D results, though they show considerable asymmetry with respect to φ. More detailed information than total-cross sections is probably required to establish effects peculiar to 3D calculations.

Without serous modification the methods used to obtain the present results can be applied to a vast range of problems. In addition to numerical studies, theoretical explanations must be sought for such apparently novel phenomena as the "fingers."

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[12]Compare Ref. 3. I have actually made some calculations on O^{+6}+H, using a model potential for the projectile. The difference between the C^{+6} and O^{+6} cross sections is about 1% at 25 keV/amu.

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Isotope-Selective Laser Analysis of the Electron-Impact Excited $6\,^1S_0 \rightarrow 6\,^1P_1$ Transition of Mercury: A Test of the Percival-Seaton Hypothesis

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An isotope-selective technique has been used to measure line polarizations in the range 7.5 to 12.0 eV for the electron-impact–excited 185-nm transition of atomic mercury. Measurements were made on the $I = 0$ and $I = \frac{1}{2}$ nuclear-spin isotopes. A stepwise excitation technique was used involving electron excitation followed by single-mode laser excitation. The results obtained indicate a breakdown in the Percival-Seaton hypothesis near threshold.

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In this Letter, we report on results obtained from an experiment in which a low-energy beam of electrons and single-mode laser radiation were used to excite mercury atoms stepwise according to the excitation scheme shown in Fig. 1(a). Fluorescence emitted following the stepwise excitation was analyzed to determine the line polarization of the electron-impact–excited transition. This technique allows several aspects of atomic collision physics to be studied in new detail. The narrow bandwidth of the laser radiation permits the fine and hyperfine structure of atoms to be resolved in the laser-excited transition, thus providing a means of studying the role of spin-orbit