[3]In fact, since the transfer is slightly endothermic ($\Delta E = -15$ cm^{-1}), it could lead by itself to an acceptor velocity distribution narrower than the thermal one. In a complementary linear absorption experiment (without saturating beam) performed on Xe atoms in the presence of Kr metastables, we indeed observed a slightly reduced width. However, in the nonlinear absorption experiment, this pure kinematic cooling effect can be neglected compared to the laser-induced narrowing effect.

[4]From the data of J. E. Velazco, J. H. Kolts, and D. W. Setser [J. Chem. Phys. 69, 4357 (1978)], this cross section can be estimated to be from 30 to 40 Å^2.

[5]We have also performed experiments with copropagating light beams. The two geometries yield the same line shapes, thus confirming the absence of the anisotropic coherence term in the expression of the signal.

[6]M. Borenstein and W. E. Lamb, Jr., Phys. Rev. A 5, 1311 (1972).

[7]J. Brochard and R. Vetter, J. Phys. B 7, 315 (1974).

[8]C. Bréchignac, R. Vetter, and P. R. Berman, J. Phys. B 10, 3443 (1977).

[9]Of course, these two widths depend on the temperature. We have made most observations at 77 K for reasons of experimental convenience.

[10]A usual kernel of the type $W(v_z \rightarrow v_z')$, connecting the initial and final velocities of the acceptors (Refs. 2 and 6), could also have been used. However, such a kernel seems less adapted to the present problem since its shape would depend on the donors' velocity distribution, and hence of the conditions specific to each experiment.

[11]See, e.g., J. Brochard and R. Vetter, J. Phys. (Paris) 38, 121 (1977).

Numerical Solution of the Time-Dependent Schrödinger Equation and Application to H^+-H

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The time-dependent Schrödinger equation for the motion of the electron in a H^+-H collision is solved numerically with a finite-difference method on an axially symmetric spatial mesh. Sample density distributions for $E_{lab} = 20$ keV are shown. The calculated charge-transfer probabilities at $E_{lab} = 3.92$, 7.69, and 20.1 keV are in good agreement with experiment.

The usual procedure in atomic collision problems is to expand the wave function in a basis set.[1] Even for velocities which allow a classical treatment of the nuclear motion,[2] the success of a calculation depends on the selection of a necessarily finite expansion basis. In principle one should be able to describe different effects like excitation, charge transfer, and ionization with the same basis set. Particularly, charge transfer involves a correct inclusion of the electron translational effects,[3] and ionization the knowledge of continuum functions for the two-center Coulomb problem.[4] Furthermore, the choice of a suitable basis set for the intermediate-velocity region, where neither an atomic expansion nor a molecular one is adequate, seems to be difficult.

For nulcear collision problems the numerical integration of the time-dependent Hartree-Fock equations was recently carried out and applied to heavy-ion scattering.[5-8] It seems worthwhile to try a similar method also in atomic physics in order to circumvent the difficulties sketched above. However, from the very beginning one should be aware of the different nature of the nuclear and atomic problem. All potentials in atomic physics are known to be of Coulombic type. Unlike the nuclear potentials, they have singularities at the positions of the charges and, further, have an infinite range which requires special numerical care. In the case of atomic collisions the difficulties in the calculation of the cross sections would be less stringent than in nuclear physics since the final states are more easily definable. Both theoretical fields have not yet fully answered the question to what extent a time-dependent Hartree-Fock theory gives the correct description of the collision process.

In order to gain experience in handling the atomic problem we start with the time-dependent one-electron problem and solve the Schrödinger equation of an electron in the Coulomb field generated by two moving nuclei. In the following we consider the H^+-H scattering. Then the Schrödinger equation is given by

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{r},t) - \left(\frac{e^2}{|\vec{r}-\vec{r}_1(t)|} + \frac{e^2}{|\vec{r}-\vec{r}_2(t)|}\right)\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t). \quad (1)$$

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The nuclear positions $\vec{r}_1(t)$ and $\vec{r}_2(t)$ are treated as externally prescribed parameters, which implies a classical motion of the nuclei. We neglect distortion of their orbits due to the electronic motion, which can be improved by computing the action of the electron on the nuclear motion.

For simplicity, the solution of Eq. (1) is restricted to axial symmetry, so that only head-on collisions can be treated without further approximations, although the results should also be meaningful for impact parameters small compared to the Bohr radius a_0. For the collision H^+-H the relative velocity is given by

$$\dot{R}(t) = \pm \left(\frac{4}{M}\right)^{1/2} \left(E_{\mathrm{c.m.}} - \frac{e^2}{|\vec{r}_1(t) - \vec{r}_2(t)|}\right)^{1/2}. \quad (2)$$

Here, M is the proton mass and $E_{\mathrm{c.m.}}$ the incident energy in the center-of-mass system. The nuclear centers are assumed to lie at the points $z_{1,2} = \pm R(t)/2$ and move with velocities $\dot{z}_{1,2} = \mp \dot{R}(t)/2$ along the z axis.

Equation (1) is solved in cylindrical coordinates z and ρ. The problem is independent of the azimuth angle φ because of the symmetry restriction. A spatial mesh was chosen with 160 and 40 points in the z and ρ directions, respectively, with a spacing of $\Delta z = \Delta\rho = 0.2a_0$. The mesh points are set at $\rho = (i - \frac{1}{2})\Delta\rho$ and $z = (j - 1)\Delta z$ with $i, j = 1, 2, \ldots$, so that there are no mesh points on the z axis where the nuclei lie. The numerical solution of (1) is carried out by using the decomposition of the time-development operator:

$$\exp[-i(H_z + H_\rho)\Delta t/\hbar] \approx \frac{1}{1 + i\Delta t H_\rho/2\hbar} \frac{1 - i\Delta t H_z/2\hbar}{1 + i\Delta t H_z/2\hbar} (1 - i\Delta t H_\rho/2\hbar). \quad (3)$$

The horizontal and vertical Hamiltonians H_z and H_ρ are defined by Koonin *et al.*[7] and by Varga.[9] The inversion of the operators in the denominator of Eq. (3) is calculated with the alternating-direction–implicit method (ADI), also called Peaceman-Rachford algorithm.[9] The time step Δt is chosen on the order of $\Delta t = 4\times10^{-18}$ sec in the calculations.

The initial distance between the protons is taken as $16a_0$, at which the calculation is started with the electron in an unperturbed $1s$ orbit around one of the two protons. Extensive tests were carried out to check the accuracy of the numerical methods. Some of the most important ones are as follows:

(a) The electron moves in the field of a proton at rest. This tests the overall conservation of energy and norm. We found energy conservation better than 0.05% during a time of $100\Delta t = 4\times10^{-16}$ sec. In this calculation the nucleus is assumed to be a point charge.

(b) The electron and proton move uniformly with the same velocity v_0. In this case, the electronic wave function is initially multiplied with a plane-wave factor $\exp(imv_0 z/\hbar)$. This is a much more stringent test than the previous case, as the proton with its singular potential on the z axis now comes into various positions with respect to the mesh points. We find that energy conservation becomes quite inadequate with a point-charge proton.

Extending the proton charge to a uniform distribution with radius $R_0 = 0.2a_0 (= \Delta z = \Delta\rho)$ we ensure conservation better than 2% during a time of $100\Delta t$. This is quite remarkable since in this case the potential is modified only at the closest neighboring points to the proton. It can be understood, however, from the nonanalytic behavior of the electronic $1s$ wave function at the origin. The extension of the proton charge smooths the wave function near the proton and, therefore, changes its differentiation properties so that the energy is conserved in time.

The replacement of the point charge by an extended charge distribution of radius $0.2a_0$ of course leads to a shift of 0.24 eV in the energy of the electronic ground state. If higher accuracy for the binding energy as well as for energy conservation during the collision should be desired, the step sizes $\Delta\rho$ and Δz may be decreased. As an example, for the time evolution of the electronic wave function during a H^+-H collision we show results for $E_{\mathrm{lab}} = 20$ keV. Figure 1 contains isodensity lines for the electron distribution at different times. In the initial stage of the collision the electron merely follows the proton. As the two protons approach each other, the electron starts to feel the attraction by the other proton and moves faster in that direction. When the protons get very close, the electronic distribution "shoots over," i.e., its center of mass moves outside the region between the two protons, and then begins to oscillate back and forth between the protons. Meanwhile, however, the wave function shows increasingly complicated patterns. As the two protons separate finally, the electronic wave function also breaks up and the probabil-

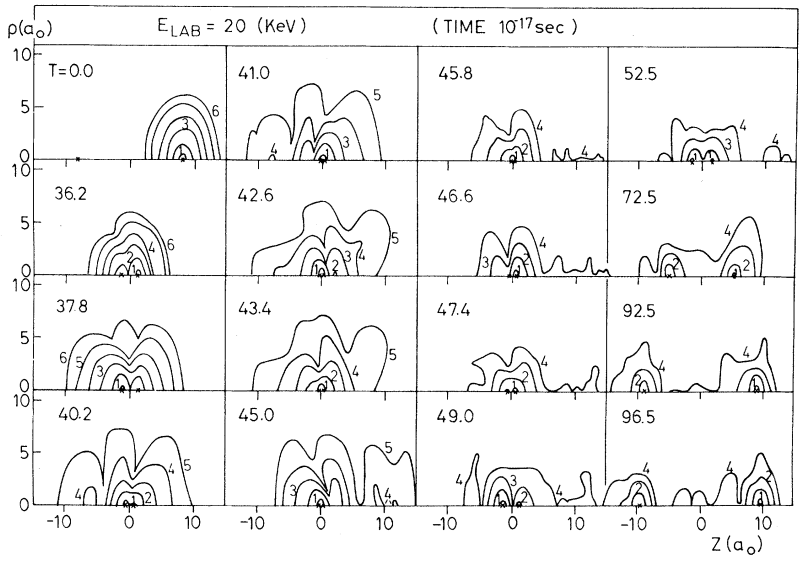

FIG. 1. Contour maps of the electron density in a head-on H^+-H collision at $E_{lab} = 20$ keV. The collision is shown in the center-of-mass frame. Because of the rotational symmetry about the z axis the electron density is drawn only in the z-ρ plane. The positions of the nuclei are indicated by crosses. The elapsed times for each frame are given on the upper left in units of 10^{-17} sec. From one contour line to the next the density changes by a factor 10, indicated by the numbers for the negative exponents in the figure.

ity of staying with each of the two protons can be calculated by integrating the probability distribution over the appropriate half-space. Thus one obtains the probability for charge transfer. After the protons have reached a separation of $16a_0$, this probability remains stationary, so that the charge transfer seems to be reasonably well defined in this calculation.

We have computed the charge-transfer probability for several incident energies in order to compare it with experimental data[10] measured at a laboratory angle of 3° at energies $E_{lab} = 0.5$–50 keV. In that case we took the charge-transfer probability as the probability that the electron is localized near the proton that emerges in beam direction. This approximation is justified since the impact parameters for 3° scattering in the energy region considered are small compared with the mesh size used in the calculation.[11] In Fig. 2 the results are shown together with the experimental data and a pseudostate-expansion calculation.[12] Apparently the results are in good agreement with the experimental data.

As shown, it is straightforward to extract the charge transfer from the final wave function. The excitation cross sections can be calculated by taking the overlap with the known moving atomic states in question at the end of the collision. For ionization the situation is more complicated. A possible procedure is to calculate the quantum-mechanical flux out of a surface far enough away from the nuclei. The presented calculations are a first step towards the numerical integration of the scattering problem with many electrons. As the next step, the nonaxisymmetric one-electron

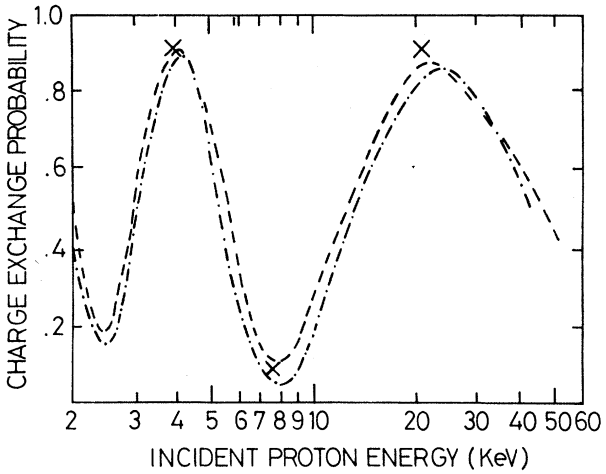

FIG. 2. Charge-transfer probability for the H^+-H collision at $\theta_{lab} = 3°$ as a function of incident proton energy in the laboratory system. Present theory, crosses; pseudo-state expansion (Ref. 12), dash-dotted line; experiment (Ref. 10), dashed line.

problem has to be solved, and finally the case of many electrons should be attacked within the framework of the Hartree-Fock method.

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Observation of Pure Rotational Transitions in the HBr^+ Molecular Ion by Laser Magnetic Resonance

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A molecular ion (HBr^+) has been observed for the first time by laser magnetic resonance spectroscopy. Pure rotational transitions have been detected with five different far-infrared laser lines. Assignment of the hyperfine patterns has produced values for the magnetic hyperfine constants.

Although optical emission spectra have been obtained for a fairly large number of molecular ions,[1] high-resolution spectroscopic techniques have been successfully applied to these species in only a few cases. H_2^+ was detected by Jefferts[2,3] in a rf-optical double-resonance experiment; several different isotopic forms of CO^+ (Ref. 4), HCO^+ (Ref. 5), and HNN^+ (Ref. 6) have been studied in live discharges with microwave spectroscopy by Woods and co-workers; Wing *et al.*[7] have observed vibration-rotation transitions in HD^+ by Doppler-tuning an ion beam into coincidence with an infrared laser; and, most recently, CO^+ (Ref. 8) and H_2O^+ (Ref. 9) have been detected by Carrington and co-workers, and O_2^+ by Tadjeddine *et al.*,[10] Moseley *et al.*,[11] and Carrington, Roberts, and Sarre[12] in the same manner using visible lasers. In this Letter we report the observation of pure rotational transitions for the HBr^+ molecular ion by far-infrared laser-magnetic-resonance (LMR) spectroscopy of a dc glow discharge contained inside the laser cavity.

The LMR spectrometer is similar to a previously described version[13] built in this laboratory. Briefly, it consists of a 7.6-cm-diam by 38-cm-long quartz far-infrared gain cell pumped transversely by a 2.3-m CO_2 laser with a 30-W output, and separated from the 5-cm-diam by 58-cm-long intracavity sample region by a 1.3-mm polypropylene beam splitter set at the Brewster angle. Instead of being located between the pole faces of a 15-in. magnet, as in Ref. 13, the sample region is centered inside the bore of a 5-cm-diam by 33-cm-long solenoid magnet cooled by liquid nitrogen, capable of providing field strengths up to 0.5 T with a homogeneity of 0.1% over a 15-cm length. The HBr^+ ions were generated within the laser cavity in a dc glow discharge through a flowing mixture of ~1% HBr in helium at 133-Pa (1-Torr) total pressure and near-ambient temperature. Pure rotational transitions in the paramagnetic $^2\Pi_{3/2}$ ground state of

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