Coriolis coupling effects in time-dependent Hartree-Fock calculations of ion-atom collisions

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Effects on the collision dynamics due to the inclusion of the Coriolis term in the time-dependent Hartree-Fock Hamiltonian are investigated for the $He^{2+}+He$ colliding system both at low and high incident energies. Whereas at low energies these effects are perturbative, Coriolis terms produce drastic reductions in charge-exchange cross sections at high energies.

INTRODUCTION

In a series of previous publications,[1-3] we have discussed the feasibility of the application of the time-dependent Hartree-Fock (TDHF) approximation to rearrangement ion-atom collisions. The various merits of using a coordinate representation to solve the dynamical equations over the basis expansion methods have also been discussed. The calculations reported were of a preliminary nature, the emphasis being on testing the accuracy of the method. They were also restrictive, the restrictions being (1) the imposition of axial symmetry about the rotating internuclear axis, and (2) the assumption of spin degenerate single-particle orbitals. Whereas reasonable agreement with the experimental data was obtained for incident velocities that are low compared to the characteristic velocities of electrons in the He atom, at higher energies the results were unphysical. The neglect of the nonaxial effects prevent a realistic treatment of the inability of electrons to follow the projectile nucleus.

Symmetry-breaking effects in the case of a one-electron system, $p+H$, have been investigated by Grün, Mühlhans, and Scheid.[4] In this paper, we discuss these effects in many-electron systems. We have also studied collisions with relative velocities that are greater than the characteristic velocity of the bound electrons, where one expects the Coriolis effects to be nonperturbative. We do find dramatic changes in the dynamics of the collision.

THEORY

In the impact parameter formulation, the Hamiltonian for the many-electron system is

$$H=H_0+V \ , \tag{1}$$

where

$$H_0=\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2-\frac{Z_1e^2}{|\vec{r}_i-\vec{R}_1|}+\frac{1}{2}\sum_j\frac{e^2}{|\vec{r}_j-\vec{r}_j|}\right) \ ,$$

$$V=-\sum_{i=1}^{N}\frac{Z_2e^2}{|\vec{r}_i-\vec{R}_2|} \ .$$

$\vec{R}_1$ and $\vec{R}_2$ are the position vectors of target and projectile nuclei. These are calculated assuming a Coulomb trajectory for point charges Z_1 and Z_2. The corresponding TDHF equations (the details of the derivation of these equations are given in Refs. 1–3) are

$$\mathscr{H}\psi_\lambda=i\hbar\dot{\psi}_\lambda \ , \tag{2}$$

where the TDHF Hamiltonian $\mathscr{H}$, in the coordinate representation, is given by

$$\mathscr{H}(\vec{r}\sigma,\vec{r}'\sigma')=\delta(\vec{r}-\vec{r}')\delta_{\sigma\sigma'}\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{Z_1e^2}{|\vec{r}-\vec{R}_1|}-\frac{Z_2e^2}{|\vec{r}-\vec{R}_2|}+\int\frac{\hat{\rho}(\vec{r}'',t)\,d\vec{r}''}{|\vec{r}-\vec{r}''|}\right)+\cdots \ , \tag{3}$$

where the ellipsis represents exchange terms. σ's are the spin coordinates and the density

$$\hat{\rho}(\vec{r},t)=\sum_\lambda\psi_\lambda^*(\vec{r},t)\psi_\lambda(\vec{r},t) \ . \tag{4}$$

For the two-electron systems we will be dealing with in the present work, the exchange terms are just one-half of the direct term,[2] under the restriction of spin degeneracy. We continue to use this restriction. Center-of-mass coordinates are used throughout.

For nonzero impact parameter collisions, the most convenient coordinate system to use for the solution of (2) is the one rotating with the internuclear axis. The corresponding set of TDHF equations in this system are

$$(\mathscr{H}-\omega l_y)\psi_\lambda=i\hbar\dot{\psi}_\lambda \ , \tag{5}$$

where the angular velocity ω, in terms of the impact parameter b, incident energy $E_{\text{c.m.}}$, and the internuclear distance R is given by

$$\omega=\left(\frac{2E_{\text{c.m.}}}{\mu}\right)^{1/2}\left(\frac{b}{R^2}\right) \ . \tag{6}$$

Here, μ is the reduced mass of the nuclei. Equation (5) can be reduced to a set of coupled two-dimensional equations in cylindrical coordinate system by expanding ψ_λ as

$$\psi_\lambda(\rho,z,\phi)=\sum_m\chi_{\lambda m}(\rho,z)e^{im\phi} \ . \tag{7}$$

Insertion of this expansion in (5) gives

$$\sum_{m'}[\mathscr{H}_{mm'}-\omega(l_y)_{mm'}]\chi_{\lambda m'}=i\hbar\dot{\chi}_{\lambda m} \ , \tag{8}$$

where

$$\mathscr{H}_{mm'} = -\frac{\hbar^2}{2m}\left(\nabla^2_{\rho,z} - \frac{m^2}{\rho^2}\right)\delta_{mm'} + \Phi_{m-m'}(\rho,z) \ , \tag{9}$$

$$(l_y)_{mm'} = \frac{i\hbar}{2}\left[\left(\rho\frac{\partial}{\partial z} - z\frac{\partial}{\partial \rho} + \frac{Z}{\rho}m'\right)\delta_{m'm-1} + \left(\rho\frac{\partial}{\partial z} - z\frac{\partial}{\partial \rho} - \frac{Z}{\rho}m'\right)\delta_{m'm+1}\right] \ . \tag{10}$$

Φ_η is the self-consistent potential obeying the differential equation

$$(\nabla^2_{\rho z} - \eta^2/\rho^2)\Phi_\eta = -2\pi e^2\hat{\rho}_\eta(\rho,z) \ , \tag{11}$$

with

$$\hat{\rho}_\eta = \sum_m \chi^*_{\lambda\eta}\chi_{\lambda\eta+m} \ , \tag{12}$$

where we have used the notation

$$\nabla^2_{\rho,z} = \frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial^2}{\partial z^2} \ .$$

At $t=0$, the wave function ψ_λ, in the coordinate system rotated such that the Z direction is along the internuclear axis, is

$$\psi_\lambda(\rho,z,\phi) = \hat{\psi}_\lambda(\rho,z)e^{im_\lambda\phi}e^{-i\vec{k}\cdot\vec{r}} \ , \tag{13}$$

where $\hat{\psi}_\lambda$ are the static HF orbitals and $\vec{k}$ the electron translational momentum (i.e., static wave functions boosted to the correct center of mass velocity). Using

$$e^{-i\vec{k}\cdot\vec{r}} = e^{-ikz}\sum_\mu (i)^\mu J_\mu\left(\frac{bk}{R}\rho\right)e^{i\mu\phi} \ , \tag{14}$$

we get

$$\psi_\lambda(\rho,z,\phi) = \sum_m \hat{\psi}_\lambda(\rho,z)J_{m-m_\lambda}\left(\frac{bk}{R}\rho\right)e^{im\phi} \ .$$

This sets up the initial conditions for $\chi_{\lambda m}$'s as

$$\chi_{\lambda m} = \hat{\psi}_\lambda(\rho,z)J_{m-m_\lambda}\left(\frac{bk}{R}\rho\right) \ . \tag{15}$$

Calculations of Grün *et al.*[4] for the $p+H$ system show that the predominant contribution to the collision process arises from the terms $m = m_\lambda$, $m_\lambda \pm 1$ in the expansion (7). In the present work we, therefore, restrict the summation in (7) to these terms. This restriction is simply for ease of computation and can be lifted as needed. Checks are available to ensure that this truncation is adequate and that the larger m terms are small.

RESULTS AND DISCUSSION

The calculations were carried out for the $^3He^{2+} + He$ colliding system at laboratory energies of 30 and 250 keV. (The energy corresponding to the characteristic velocities of electrons in a He atom is ~ 198 keV.) The numerical methods and techniques for the time integration of the TDHF equations are discussed in detail in earlier publications.[1-3] The mesh parameters are $\delta\rho = \delta z = 0.1$ Å and the number of mesh points in the ρ and z directions are 40 and 130, respectively. The time step Δt is varied such that the coefficient $\omega\Delta t$ in the Coriolis term remains approximately a constant throughout the collision. This procedure was chosen so as to ensure the same degree of accuracy of the solutions as in the previous calculations.[3] This results in substantial increase in the required number of time steps, especially near the distance of closest approach, but is necessary to ensure reasonable accuracy.

(i) Low-energy results. The evolution of the one-body density, which is representative of the most probable collision processes, is displayed in Fig. 1, in a fixed reference frame. Note the molecular-type orbital formation at close distances ($R \sim 0.8$ Å). The densities at the edges of the box are of the order of 10^{-6} times the central density. The effect of reflections of small components of the wave function from the edges of the box, on the charge transfer probabilities are negligible. This was tested using a complex potential on the boundaries of the box,[3] which considerably reduces reflections. A measure of asymmetry with respect to the internuclear axis is the contribution of $\chi_{\lambda m = m_\lambda \pm 1}$ components to the norm. This quantity, which is also a measure of the population of the $2p\pi_u$ molecular orbital through the rotational coupling to the $2p\sigma_u$ orbital, increases to a value of 0.25 ($\sim 12\%$ of the total norm) as the

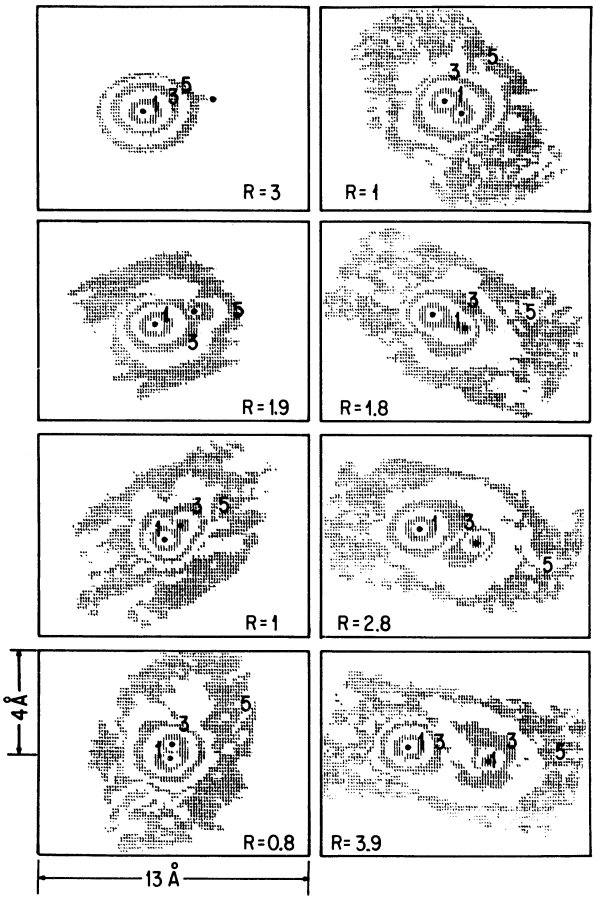

FIG. 1. Evolution of one-body density in a fixed coordinate system for $E_{He^{2+}} = 30$ keV and $b = 0.8$ Å. The numbers 1,3,5 indicate the negative powers of 10 times the central density. The relative distances (R) are in angstroms.

nuclei approach each other. A maximum is reached at the closest distance of approach and a depopulation occurs as the nuclei separate, finally reaching a constant value ~ 0.05. This final value is just $\sim 3\%$ of the total norm.

The inclusive double and single charge-transfer probabilities P_2 and P_1 are calculated by projecting the asymptotic TDHF state ($R \geq 4$ Å) on to the respective traveling atomic states.[3] These are plotted as functions of impact parameters in Fig. 2. The oscillations with respect to b (or the incident velocity) are well known to be the result of interference due to the fact that more than one channel is available to the electrons during the collision. In particular, in an independent particle, adiabatic molecular orbital formulation of the problem, Lichten[5] has proposed approximate expressions for double and single charge-transfer probabilities at low velocities which are

$$P_2 = \cos^4\left[\int_{-\lambda}^{\lambda} \frac{E_u - E_g}{4v\hbar}\, dz\right] ,$$
$$P_1 = \tfrac{1}{2}\sin^2\left[\int_{-\lambda}^{\lambda} \frac{E_u - E_g}{2v\hbar}\, dz\right] , \tag{16}$$

where $E_g(R)$ and $E_u(R)$ are the energies of the molecular states $(1\sigma_g)^2$ and $(1\sigma_u)^2$, respectively; λ is an interaction distance [with $R = (b^2+z^2)^{1/2}$] and v the incident velocity.

These results are based on the assumption that all crossings are fully avoided and that the excitation energy of the $(1\sigma_u)^2$ state is twice that of the state $[(1\sigma_g 1\sigma_u) + (1\sigma_u 1\sigma_g)]/\sqrt{2}$, relative to the $(1\sigma_g)^2$ ground state. This latter assumption is consistent with an independent particle model and with the united-atom estimate of Lichten.[5]

Note that Eqs. (16) predict that the oscillation frequency in P_1 is twice that in P_2. Figure 2 shows that this is borne out in the present calculations as well.

The shift in the peaks of the probability curves can be understood as follows. In the absence of Coriolis term, the molecular states $2p\sigma_u$ and $2p\pi_u$ are degenerate. For small ω (small incident velocity), the first-order perturbation correction to the energy difference $E_u - E_g$, arising only from the coupling between σ_u and π_u states is $\hbar\omega$. This introduces an additional phase factor in the arguments of P_1 and P_2. This phase factor accounts for the shifts observed in the present calculations.

(ii) High-energy results. At 250 keV, considerable asymmetry in the system develops as the nuclei approach each other. This is also indicated by the increase in the contribution of the $\chi_{\lambda m_\lambda \pm 1}$ components to the norm ($\sim 21\%$ of the total norm). At high velocities, charge-transfer probabilities are considerably reduced due to the inability of the slow electrons in the target atom to follow the projectile ion. Imposing axial symmetry, however, forces the electron to follow the projectile nucleus, thus resulting in large spurious transfer probabilities. This is clearly indicated in Fig. 3 where bP_2 and bP_1 are plotted as functions of impact parameters. Note the drastic reduction in probabilities when the

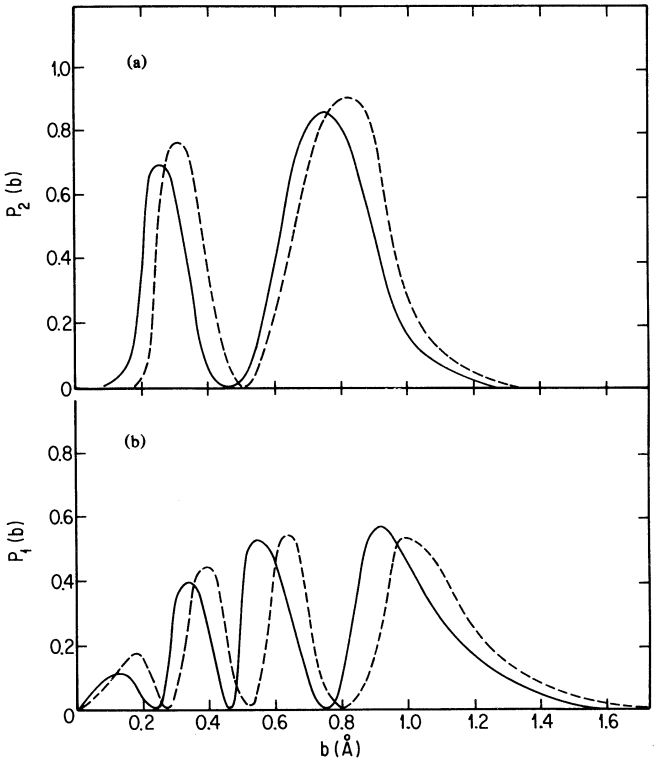

FIG. 2. (a) Double charge-transfer probability as a function of the impact parameter for $E_{He^{2+}} = 30$ keV. (b) Corresponding single charge-transfer probabilities.

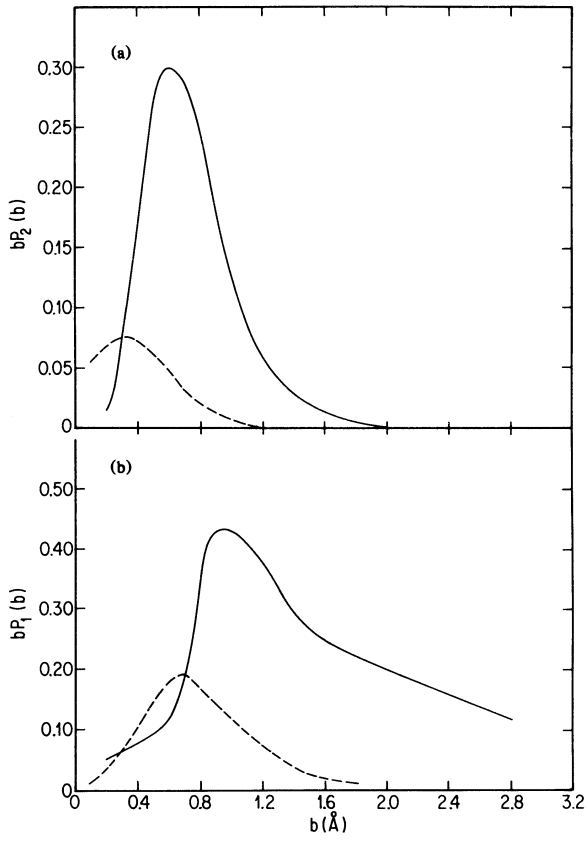

FIG. 3. (a) Comparison of the double charge-transfer probabilities times the impact parameter with and without the inclusion of Coriolis effects for $E_{He^{2+}} = 250$ keV. (b) Same as (a) for the corresponding single charge-transfer probabilities.

TABLE I. (a) Comparison of the TDHF inclusive single, double, and excited state charge-transfer cross sections with the molecular and atomic basis expansion calculations and experimental data for $E_{He^{2+}} = 30$ keV. (b) Same as in (a) for $E_{He^{2+}} = 250$ keV.

Cross section (10^{-16} cm^2)	TDHF	Molecular state (Harel and Salin)	Atomic state (Mukheriee *et al.*)	Experiment
(a) $E_{lab} = 30$ keV				
σ_1^{incl}	1.353	1.12	· · ·	1.4 ± 0.2[a] 1.13[b]
σ_2^{incl}	1.378	1.5	· · ·	1.7 ± 0.25[a] 1.385[b]
$\sigma_1^{exc.}$	0.294	0.92	· · ·	0.95[b]
(b) $E_{lab} = 250$ keV				
σ_1^{incl}	1.6	· · ·	1.35	2.0[c]
σ_2^{incl}	0.19	· · ·	0.26	0.30[c]

[a]Reference 6(a). [b]Reference 6(b). [c]Reference 6(c).

Coriolis effects are included.

Table I compares the inclusive single and double charge-transfer cross sections at 30- and 250-keV laboratory energies with the experimental data[6] and with the molecular[7] and atomic basis expansion[8] calculations. Good agreement for inclusive charge-transfer probabilities is obtained with the data of Berkner, Pyle, Stearns, and Warren[6(a)] at 30 keV and with that of Pivovar, Tubaev, and Novikov[6(c)] at 250 keV. Since in calculating the inclusive probabilities, we include only s and p states, the cross sections are slightly underestimated.

Experimental data of Afrosimov, Basalaev, Leiko, and Panov[9] show that for energies in the range 2–45 keV ($^3He^{2+}$ ions) the single charge transfer to excited states of the projectile dominates over the transfer to the ground state. The excited-state transfer probability decreases with increase in energy. However, even at 45 keV, about 60% of the single charge transfer is observed to be into the excited states of the projectile. This is also borne out in molecular configuration mixing calculations of Harel and Salin.[7] The total single charge-transfer cross sections to excited states at 30 keV, in the present calculations, are given in Table I, part (a). Even after the inclusion of Coriolis effects, single charge transfer to excited states never exceeds 10% of the total single charge-transfer cross section. Similar results have been reported by Stich, Ludde, and Dreizler[10] in the molecular basis TDHF calculations. A look at the correlation diagram by Lichten[5] shows that transfer to excited atomic states arises due to the crossing of the σ_u^2 level with a whole series of Rydberg states at large distances. Since the TDHF wave function, in principle, contains all one-particle one-hole excitations of the HF state, and since the initial state is a linear combination of σ_g^2, σ_u^2, and $(\sigma_g\sigma_u + \sigma_u\sigma_g)/\sqrt{2}$, the transfers to these states are not in principle ruled out. A careful examination of the excitated energy levels (particularly the σ_u^2 level) in the molecular HF approximation, is, however, necessary. If these states lie so high in energy that their population through potential coupling is reduced, or the crossing with the Rydberg states occur at very small internuclear distances, the cross sections for transfer to excited states will be reduced. Investigations in this regard are currently underway.

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