Dependence of electron-capture probabilities on the initial-state magnetic quantum numbers in ion-atom collisions

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(Received 9 August 1993)

Close-coupling calculations have been carried out for ion-atom collisions to show that electron-capture probabilities depend strongly on the magnetic quantum number of the initial target state if *the quantization axis is chosen to be perpendicular to the scattering plane.* In the *natural frame* of reference, the probability for electron capture is largest for $m_i = -l$ substates and decreases rapidly with increasing m_i, while states with positive values of m_i have negligible probabilities. This propensity rule results from the rotation of the electron cloud with the internuclear axis in the collision. We have shown further that this propensity rule can be interpreted classically and have carried out classical-trajectory Monte Carlo calculations to confirm the same qualitative results.

PACS number(s): 34.10.+x, 34.60.+z

I. INTRODUCTION

In recent years there has been an increasing number of experiments studying the collision of photons, electrons, and ions with laser-excited target atoms. In particular, there have been many experimental and theoretical studies of the collisions between ions and laser-excited Na($3p$) atoms [1–13]. In a number of these experiments, the dependence of electron-capture cross sections on the orientation or the alignment, or, in general, the magnetic substates of the target atom is examined. In referring to magnetic substates, a space-fixed quantization axis has to be chosen. For collisions where the direction of the scattered particles is not determined, the collision system has cyclindrical symmetry and the quantization axis is conveniently chosen to be along the direction of the incident beam. The determination of magnetic substate cross sections with respect to the beam axis provides information about the *alignment* of an excited atom. Meanwhile, for each collision event, the direction perpendicular to the scattering plane can also serve as a convenient quantization axis. This choice, which is used in the so-called natural frame [14], is convenient for describing the *orientation,* or the circulation property, of an excited atom.

In collisions between ions and target atoms in the ground state, certain propensity rules have been found for the orientation of the excited final states formed by direct excitation as well by electron-capture processes [14–16]. No evidence of propensity rules has been found for the alignment parameters. Experiments for collisions between ions and laser-excited target atoms indicate that no propensity rule exists for the dependence of total electron-capture cross sections on the alignment of the initial state [1,2]. There is a number of differential measurements for the collisions between protons and sodium atoms in the $3p$ states where the dependence of electron-capture cross sections on the orientation of the initial $3p$ state was measured [3,12]. Theoretical calculations based on the close-coupling expansion method have been carried out [6–9] and it has been shown that these calculations are in good agreement with experimental observations. All of these calculations were carried out for specific collision systems and have been limited to excited target atoms where the electron is in the $2p$ or $3p$ excited states [1–13,17]. It is the goal of this paper to address the general aspect of the dependence of electron-capture probabilities on the magnetic substates of the target atom and to draw the conclusion that a propensity rule exists if *the quantization axis is chosen to be perpendicular to the scattering plane.* It is emphasized that this propensity rule does not apply if the conventional quantization axis is used. The latter often refers to the direction of the incident beam.

The result is also of particular importance in the theoretical study of collisions with high-l Rydberg atoms [18] where the propensity rule permits a significant reduction in the number of magnetic substates needed in the close-coupling calculations or in any other models.

In this paper we report specific calculations on electron-capture probabilities from the different magnetic substates of H($4f$) by protons. The calculations and the results, the origin of the propensity rule, as well as the results from the classical-trajectory Monte Carlo (CTMC) calculations are addressed in Sec. II. Section III gives a summary and a discussion of the experimental confirmation of the propensity rule.

II. METHODS OF CALCULATIONS AND RESULTS

We have carried out specific calculations for the collisions between protons and H atoms in the $4f$ initial states using the close-coupling expansion method where

the time-ependent electronic wave function is expanded in terms of traveling atomic orbitals on the two collision centers. This is a well-established theoretical approach [19] and we use this method to obtain results for analysis since we do not expect experiments for such a system to be done in the near future. We chose $4f$ initial state so that the target atom can be set at a number of different initial magnetic substates. We carried out close-coupling calculations by including all hydrogenic atomic orbitals from n=1 to n=5 states on both collision centers. These atomic orbitals are expanded in terms of Gaussian orbitals such that all one- and two-center matrix elements can be evaluated in closed forms and the quantization axis can be referred to any direction [20]. We concentrate only in the energy regime where the projectile velocity is near the orbital velocity of the $4f$ electron, which is 0.25 a.u. In this energy region electron capture occurs at large impact parameters and the cross sections are large. In this velocity region the basis set we have used is expected to be adequate.

We need to emphasize that the coordinate system used is the so-called *natural frame*, which is depicted in Fig. 1. In this frame, the xy plane is the collision plane where $+x$ is the direction of the incident beam and the projectile lies on the collision plane and on the $+y$ side. The quantization axis is perpendicular to the collision plane with the $+z$ direction chosen such that it forms a right-handed xyz Cartesian system. We calculated the scattering amplitudes in this frame; the scattering amplitudes with respect to any other quantization axis can be obtained by a simple rotation.

In Fig. 2 we show the total electron-capture probabilities vs impact parameter (on the collision plane) for different initial magnetic substates in $H^+ + H(4fm_i)$ collisions at v=0.2 a.u. In the upper frame, the quantization axis was referred to the natural frame and $m_i = -3, -2, ..., +3$. The probabilities are largest for $m_i = -3$ and decrease rapidly with increasing values of m_i. Note that the probabilities for $m_i = -3$ extend to large impact parameters and electron capture is possible for positive m_i only at small impact parameters where the collision is considered to be hard. This propensity rule in electron-capture probabilities is more pronounced if one compares the probabilities where the quantization axis is chosen to be along the direction of the incident beam which are shown in the lower frame. In this frame the cross sections depend only on the magnitude of the magnetic quantum number. The probabilities are all comparable, except for $|m_i| = 3$, which is somewhat smaller. Thus it is clear that the electron-capture probabilities show a strong propensity rule in the dependence on the magnetic quantum numbers if the quantization axis is chosen to be perpendicular to the scattering plane. There is no such propensity rule if the quantization axis is chosen to be along the direction of the incident beams. This is consistent with the general experimental evidence that the dependence of electron-capture cross sections on the alignment of the initial state varies from one system to another [1,2,16]. In most of the experimental studies the scattered particles are not measured, thus only the dependence on the alignment is available. One needs to remember that the amplitudes in the two frames are related by a rotation. The existence of a propensity rule for

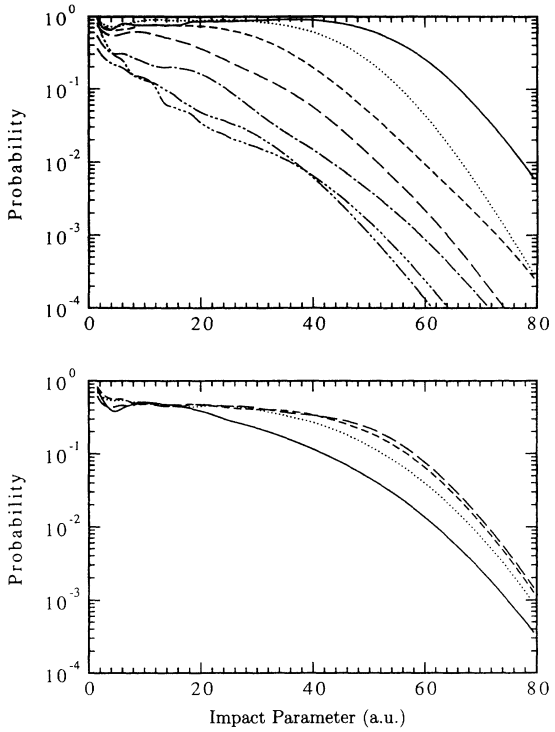

FIG. 2. Comparison of the total electron-capture probabilities vs impact parameter for different initial m_i's for $H^+ + H(4fm_i) \rightarrow H(\text{total}) + H^+$ at $v = 0.2$. In the upper frame the quantization axis is perpendicular to the scattering plane; in the lower frame the quantization axis is parallel to the direction of the incident beam. Note that the probabilities and the range of impact parameters for electron capture decrease rapidly with increasing values of m_i in the upper frame, but not as much in the lower frame. The m_i's for the upper frame, in the order of decreasing probability at large impact parameters, are $-3, -2, ..., +3$. For the lower frame the probability depends only on $|m_i|$, and in order of decreasing probabilities at large impact parameters they are 0, 1, 2, and 3.

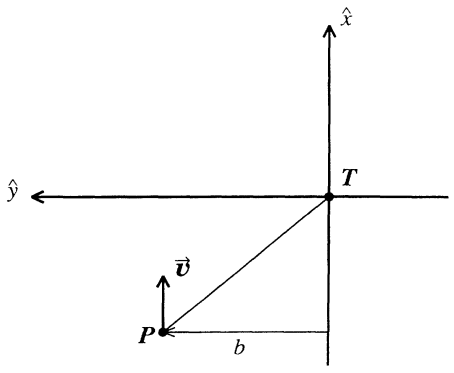

FIG. 1. The natural frame of reference for atomic collisions. The $+z$ axis is pointing out of the plane and the two other axes are as shown.

electron-capture probabilities with respect to one frame implies the lack of a propensity rule with respect to the other frame. The results in Fig. 2 indicate that it is advantageous to choose the axis perpendicular to the scattering plane as the quantization axis in atomic collisions.

The results in Fig. 2 are typical of collisions where the collision speed is near the orbital speed of the electron. Qualitatively, the results can be understood as follows. In our definition of the collision geometry (see Fig. 1), the impact parameters lie on the collision plane such that the internuclear axis rotates clockwise during the collision. Thus a target electron with negative m_i has the same sense of rotation as the rotation of the internuclear axis with time. The propensity rule displayed in Fig. 2(a) indicates that *electron capture is more likely if its initial sense of rotation is identical to that of the internuclear axis during the collision.* This appears to be an intuitively obvious result. This preservation of the circulation of the electron cloud also implies that negative values of m_f of final states are more likely populated by the electron-capture process (see below).

The results in Fig. 2(a) also show that electron capture probabilities decrease rapidly when m_i increases from -3 to -2, -1, and 0. We interpret this as a consequence of the electron density distribution of the different magnetic states near the scattering plane. For the $4f$ state, the electron density for $m_i = -3$ is localized near the scattering plane. As m_i changes to -2, -1, and 0, the electron density near the collision plane decreases rapidly. This is illustrated in Fig. 3 where we show the polar density plots of the spherical harmonics $|Y_{3m}|^2$ for $|m| = 3$ and 1. For $|m| = 3$, the density is concentrated immediately above and below the collision plane; for $|m| = 1$, the middle section is smaller, with a total integrated density of only 0.304. We speculate that the "fraction" of the electron localized near the scattering plane contributes mostly to the electron-capture process. Thus the large difference in the electron-capture probabilities, say between $m_i = -3$ and -1, is attributed to the difference in electron density near the collision plane. Note that there is no such simplification if the quantization axis is chosen to be along the beam axis.

The interpretation above also implies the existence of propensity rules for the final magnetic substate distributions. In Fig. 4 we examine the variation of electron-capture probabilities vs impact parameters for the collision $H^+ + H(4fm_i) \rightarrow H(4fm_f) + H^+$. If m_i is negative, electron-capture probabilities are large at large impact parameters and the propensity rule is $m_f = m_i$. If m_i is positive, electron capture occurs only at small impact parameters where negative values of m_f are still predominately populated and the propensity rule is $m_f = -|m_i|$. This implies that electron density distribution with respect to the collision plane remains more or less the same throughout the collision. At small impact parameters, where the electron experiences a larger Coulomb attraction from the projectile nucleus, the electron can be switched from a counterclockwise rotation to a clockwise one. If the initial and final values of l's are not identical, the final magnetic states which have similar density distributions with respect to the scattering plane will be predominantly populated. Our results show that electron capture to $4d_{-2}$ and $4p_{-1}$ are the dominant substates populated among the $4d$ and $4p$ manifolds for the system considered.

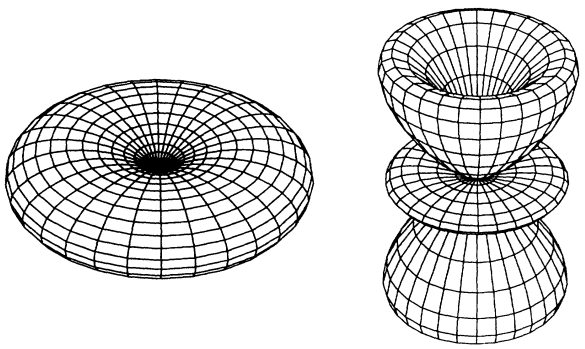

FIG. 3. Density plots of $|Y_{3m}|^2$ for $m = \pm 3$ and $m = \pm 1$.

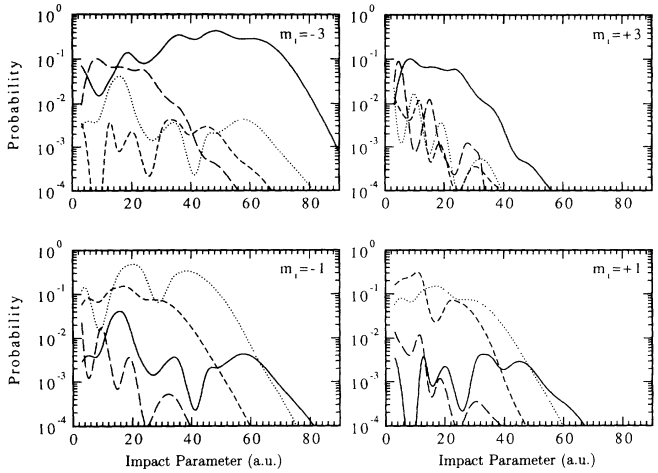

FIG. 4. Electron-capture probabilities vs impact parameters for $H^+ + H(4fm_i) \rightarrow H(4fm_f) + H^+$ at $v = 0.1$ for $m_i = -3, -1, +1$, and $+3$. The quantization axis is chosen to be perpendicular to the scattering plane. Symbols: solid lines, $m_f = -3$; dotted lines, $m_f = -1$; short-dashed lines, $m_f = +1$; long-dashed lines, $m_f = +3$. Note that the propensity rule states that the dominant final magnetic substate populated in the electron-capture process is $m_f = -|m_i|$. Also note that the probabilities and range of impact parameters for electron capture decrease rapidly with increasing values of m_i.

To investigate the velocity dependence of the propensity rule, we show in Fig. 5 the "electron-capture cross sections σ_m," defined by the integral $\sigma_m = 2\pi \int P(b) b db$, where $P(b)$ is the probability referred to a fixed chosen scattering plane. Note that σ_m is not directly related to experimentally measurable cross sections since the present choice of the quantization axis is not space-fixed and changes with each collision plane. In Fig. 5 we note that the total cross sections decrease rapidly with increasing values of m_i, illustrating the validity of the propensity rule. We also note that the propensity rule does not work as well at $v = 0.05$. At low velocities the

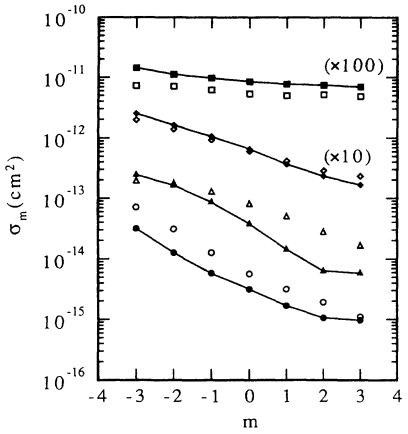

FIG. 5. Comparison of the total electron-capture cross sections from the different magnetic substates (see text) calculated using the close-coupling method (symbols connected by lines) and the CTMC method (symbols only). The results for $v = 0.05$ and 0.1 have been multiplied by 100 and 10, respectively, for easier reading. Symbols: squares, $v = 0.05$; diamonds, $v = 0.1$; triangles, $v = 0.2$; circles, $v = 0.4$.

electron has time to oscillate between the two collision centers and the propensity rule becomes less valid.

The propensity rule observed above has been interpreted classically. It is interesting to see whether the same conclusion is obtained if the collision is described using classical physics. In Fig. 5 we also show results obtained from CTMC calculations (shown by symbols without a line connecting them). The cross sections calculated classically also show the same propensity rule, although the magnitudes are somewhat different. This illustrates that the interpretation of the propensity rule using classical physics is at least qualitatively sound. In obtaining the CTMC results, we used a microcanonical ensemble for the phase-space distribution of the electrons in the initial state; we define the classical orbital angular momentum $l = 3$ to be in the range $3 \leq l < 4$ and the classical magnetic quantum number m in the range $(m - 0.5)$ to $(m + 0.5)$. We mention that the present conclusion is consistent with the results obtained for p+Na($3p$) collisions where it was shown that the CTMC calculations do give correct qualitative results [10].

The results and conclusions above are not limited to an initial $4f$ state. We have carried out calculations from different magnetic substates of H($4p$) and H($4d$) by protons for $v = 0.1 - 0.4$ a.u. The propensity rule derived above applies to these collisions as well.

The propensity rule derived in this article is quite general and we expect it to apply to any ion-atom collisions in the region where the projectile velocity is near the orbital velocity of the target electron. The propensity rule applies only when the magnetic substates are defined with respect to an axis perpendicular to the scattering plane. This propensity rule is similar to the one derived by Andersen and Nielsen [21] for the direct excitation process. Using the distortion approximation, they have shown that in the direct excitation from $s \rightarrow p$, the $m = -1$ state is predominantly populated in the velocity matching region. Their proof also shows that for the deexcitation process, the $m = +1$ state is predominantly populated. Thus the propensity rule depends on whether the transition is exoergic or endoergic. For the electron-capture processes investigated here, the propensity rule has been confirmed for the resonant capture to the $n = 4$ states. It has also been confirmed for the exoergic process for electron capture to the $n = 3$ states. We have checked for the electron-capture probabilities to the $n = 5$ states and found that the same propensity rule still applies. Thus the present propensity rule does not depend on the relative energies between initial and final states. This is consistent with our interpretation of the origin of the propensity rule in terms of the rotation of the electron cloud following the rotation of the internuclear axis. One must be cautioned, however, that electron capture to the nondominant states in general has smaller probabilities and the propensity rule may no longer be valid.

The present results also indicate that the experimental search for the propensity rules for atomic collisions should aim at measuring not the alignment but the orientation of the initial or the final states, despite that the former can be carried out more easily experimentally. Recall that the scattering amplitudes $\{a_m\}$ defined with respect to the beam axis and those $\{a_{m'}\}$ defined with respect to the axis perpendicular to the scattering plane are related by $a_m = \sum_{m'} D^l_{mm'}(\omega) a_{m'}$, where D is the rotation matrix and ω is the rotation angle. The existence of a dominant a'_m implies that many components of a_m will have nearly equal values. Thus the existence of a propensity rule for the orientation effect implies a lack of a propensity rule for the alignment effect.

The propensity rule derived in this article applies to collisions at large impact parameters. This makes the experimental test of the derived propensity rule less straightforward. At small scattering angles, the scattering amplitude at a given angle is obtained by carrying out a diffraction integral over the impact parameter plane. Thus the scattering amplitudes calculated and the propensity rule derived here cannot be applied to interpret experimental differential measurements directly. Instead, the amplitudes have to be convoluted to obtain differential cross section from which can then be compared to experiments. Such calculations have been carried out by Hansen *et al.* [22,23] in applications to the p+Na($3p$) collisions. We do not perform such calculations because such experiments are not possible in the near future.

III. CONCLUSIONS

In conclusion, we have shown that electron-capture probabilities depend sensitively on the magnetic quantum number of the initial state if the quantization axis is chosen to be perpendicular to the scattering plane. This dependence is summarized by a propensity rule which states that electron capture favors $m_i = -l$ substates and $m_f = -l'$ substates for any l' in the natural frame of reference. Electron capture from other m_i substates, especially from substates with positive values of m_i, do

not contribute significantly to the electron-capture process. In this paper we illustrated this propensity rule for the electron capture processes by protons from excited H($4f$) states. Similar conclusions have been obtained for electron capture processes in He^{2+} and Li^{3+} collisions with H($2p$) states [24]. Together with the numerous studies in protons colliding with Na($3p$) states, one can conclude the general validity of this propensity rule. This rule is useful in interpreting experimental results of the dependence of electron-capture cross sections on the orientation of the initial states. It is also useful in reducing the number of magnetic substates that are needed in the theoretical calculations for collisions in the velocity matching region. Furthermore, this rule is especially useful in future theoretical studies of collisions involving Rydberg atoms where this rule allows a substantial reduction in the number of magnetic states to be included in the calculation.

ACKNOWLEDGMENTS

This work was supported in part by the U.S.–Japan Cooperative Research Program. C.D.L. was also supported in part by the U.S. Department of Energy, Office of Energy Research, Office of Energy Sciences, Division of Chemical Sciences.

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