

Classical model for angular momentum mixing of Rydberg states

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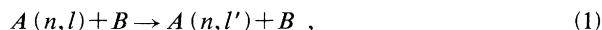
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A classical model for l mixing of Rydberg states in atomic collisions is described. The primary assumption of the model is that l changing occurs in a single hard-sphere collision between the Rydberg electron and the perturbing atom which is represented by the zero-energy scattering length L . Predictions of the model, which are in the form of cross sections as functions of principal quantum number n , are compared with data for l mixing of Na(nd) and Rb(nf) by rare-gas atoms. Agreement is, in most cases, quite good, comparable with that of other, more sophisticated, models. It is shown that, because the calculation must be carried out in the reference frame of the ion core, the energy deficit between low angular momentum states and the nearest hydrogenic manifold can be made up in a single collision between the Rydberg electron and the perturbing atom, an effect that is analogous to the gravitational slingshot effect used to alter the orbits of a spacecraft under the influence of the Sun's gravitational field. Comparison of data for l mixing by ground-state Rb atoms with model calculations in which L is treated as a free parameter leads to an estimate of 10 a.u. for the zero-energy scattering length of Rb.

INTRODUCTION

Collisions between atoms in high Rydberg states and atoms in the ground state have been studied extensively, both experimentally and theoretically.¹ These collisions differ from those involving atoms in lower states because, in the highly excited case, a three-body approach to their description, Rydberg electron, ion core, and ground-state atom can be employed. Because it is possible, using laser excitation, to produce Rydberg atoms in a given state, experiments can yield data that are quite state specific. Perhaps the most often studied of these processes is angular momentum mixing



where $A(n, l)$ is a Rydberg atom in a state characterized by principal quantum number n and angular momentum quantum number l , and B is a ground-state perturber atom, usually of a different species than A . Since l mixing may be viewed as the simplest inelastic process that can occur, models of this process constitute a first step toward the description of more complex inelastic collisions. Furthermore, because l -mixing rates for Rydberg atoms can be quite high,² reliable estimates of these rates are important when interpreting data for any experiment involving Rydberg atoms.

Many of the theoretical treatments of l mixing of Rydberg states have indeed employed the three-body approach.³ Frequently the electron is assumed to be free, as first suggested by Fermi in 1934.⁴ All of these models employ quantal calculations. The model that we describe is a purely classical one and, as such, presents a physically appealing picture of the process. Furthermore, in agreement with measured cross sections, the energy deficit between initial and final l states is made up in a single electron-perturber collision, the effect being analo-

gous to the boost supplied to an interplanetary spacecraft upon encounter with a Jovian planet—the gravitational slingshot effect.

MODEL

We treat the electron and the perturber B as particles, with the electron bound to the A^+ core. As in available data, the electron is in a low angular momentum state. It therefore executes a highly eccentric elliptic orbit about the ionic core. The perturber, assumed to follow a straight-line trajectory, presents a hard-sphere cross section to the electron given by

$$\sigma_e = 4\pi L^2, \quad (2)$$

where L is the zero-energy scattering length^{5,6} for B . We use atomic units in the calculations. The semimajor axis a of the orbit of the Rydberg electron about the ionic core is given by

$$a = n^2 \quad (3)$$

and, using Kepler's third law, the period is

$$\tau = 2\pi a^{3/2} = 2\pi n^3. \quad (4)$$

Figure 1 is a diagram of the collision. The impact parameter b is the impact parameter for the $A^+ - B$ collision. The velocities are in the frame of reference of A^+ , the ionic core. We wish to calculate $P(b, n)$, the probability that the electron in Keplerian orbit characterized by n collides with B as B drifts through the Rydberg orbit. A single $e - B$ encounter is assumed to produce l changing. The probability per electron orbit that B encounters the electron is equal to twice the fractional area presented to the electron by B , that is

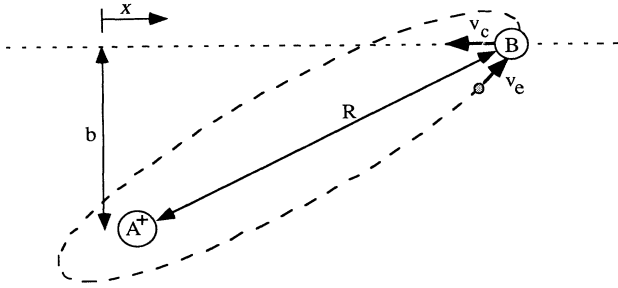


FIG. 1. Diagram of the collision and definition of parameters. The velocities are in the frame of reference of A^+ , the ionic core.

$$2 \frac{\sigma_e}{4\pi R^2},$$

where the factor of 2 arises because there are two chances per orbit for an e - B collision. The number of orbits executed by the electron as B moves a distance dx is $(dx/v_c)\tau^{-1}$ so that the probability that an e - B collision occurs in dx is given by

$$P(b, n, x) dx = 2 \left[\frac{\sigma_e}{4\pi R^2} \right] \left[\frac{dx}{v_c \tau} \right], \quad (5)$$

where $P(b, n, x)$ is the probability per unit length. We have then

$$P(b, n) = \int_{-(4n^2 - b^2)^{1/2}}^{+(4n^2 - b^2)^{1/2}} P(b, n, x) dx, \quad (6)$$

where the symmetric limits of integration result from a uniform distribution of orientations of the elliptic orbit with respect to the trajectory of B , as occurs in experiments. These limits of integration are appropriate for $n \gg l$, otherwise they are

$$\pm \left[\left[n^2 \left[1 + \left[1 - \frac{4l^2}{n^2} \right]^{1/2} \right] \right]^2 - b^2 \right]^{1/2}.$$

Integration of Eq. (6) leads to

$$P(b, n) = \frac{\sigma_e}{\pi b v_c \tau} \tan^{-1} \left[\frac{(4n^4 - b^2)^{1/2}}{b} \right], \quad (7)$$

which exceeds unity for small b because at some value of b , roughly $\sigma_e/(2v_c\tau)$, more than one e - B encounter can occur. We specify therefore that $P(b, n) \equiv 1$ for $b < \sigma_e/(2v_c\tau)$. A typical opacity function $P(b)$ is shown in Fig. 2 for $A(n=10)$ -Ar collisions. From the opacity function, the l -mixing cross section σ can be obtained by numerical integration since

$$\sigma = 2\pi \int_0^\infty P(b) b db. \quad (8)$$

The above discussion shows that the n dependence of σ will be determined largely by the behavior of the opacity function. We consider two regions of n , low and high. The maximum n for which the term "low n " applies increases with increasing scattering length, thus reflecting the nature of the perturbing atom. If n is indeed low, the multiple-collision region [for which $b < \sigma_e/(2v_c\tau)$ and

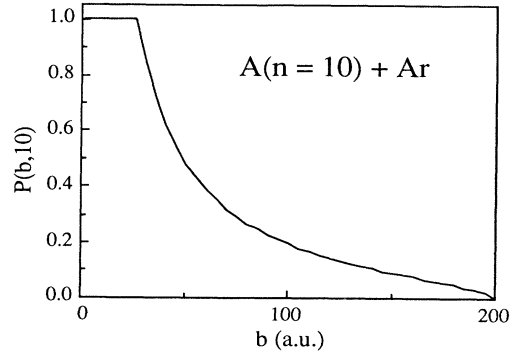


FIG. 2. Opacity function $P(b, 10)$ for collisions between an atom in an $n=10$ state and argon atoms calculated under the assumptions of the model. The zero-energy scattering length L was taken to be -1.7 a.u. (Ref. 6).

$P \equiv 1$] will be a substantial fraction of the Rydberg electron orbit. For this estimate we take $L \approx 1$ a.u. so that, in atomic units, $\sigma_e \approx 10$. Also in atomic units, $v_c \approx 10^{-4}$ and $\tau \approx n^3$ so that $b = \sigma_e/(2v_c\tau) \approx 10^5/n^3$. For $n < 10$ this is roughly the extent of the orbit of the Rydberg electron [see Eq. (3)]. Thus the l -mixing cross section will increase roughly as the geometric size of the Rydberg atom. For $n > 10$, however, the opacity function decreases because the rapidly increasing orbital period, with concomitant decrease in v_e , diminishes the probability of an e - B encounter. This permits B to "slip through" the Rydberg atom without encountering the electron, thus leading to a reduction of σ . In quantum-mechanical language⁷ this is analogous to a picture in which the decreasing density of the electron cloud with increasing n leads to a decrease in the interaction matrix element and a decrease in σ .

It is interesting that in this classical picture of the collision, a single e - B encounter, as is assumed in the model calculations, can lead to sufficient energy transfer to the electron to make up the deficit ΔE that exists between the nl initial state and the nl' final state. This is because the change in kinetic energy of the electron in an elastic collision with B can cause a substantial change in the energy of the electron relative to the A^+ core. If the electron were free of the core prior to the e - B encounter, this change in A^+ - e relative energy would be of no consequence. It is consequential, however, because the internal energy state of the A atom changes upon perturbation by B . The energy exchange is analogous to that between a planet and a spacecraft that is bound to the Sun. This is frequently referred to as the slingshot effect. The encounter can change the orbit of the spacecraft about the Sun by adding or subtracting energy from the spacecraft. This corresponds to state-changing in the atomic case. The spacecraft can also extract enough energy from the planet to escape the Sun's gravitational field, thus the name slingshot effect. The atomic analog of this escape is of course ionization.

It is important to note that the slingshot effect occurs for any type of interaction, not just an attractive $1/r$ potential. It can either add or subtract energy from the spacecraft (electron), and will even occur if the interac-

tion is repulsive. The assumed hard-sphere interaction is therefore consistent with state-changing in a single collision as a result of the slingshot effect.

To examine the magnitude of this effect in l -changing collisions we compare the energy transfer in two contrasting situations, free electron or bound electron. The amount of energy ΔE that must be converted from translational energy of the A - B system to internal energy of this system is the difference between the energy of the low angular momentum state l and of the hydrogenic manifold of states. That is,

$$\Delta E \approx \frac{\delta_l}{n^3}, \quad (9)$$

where δ_l is the quantum defect for the Rydberg series of angular momentum l . For example, if $nl = 10d$ then $\delta_l = 0.014$ and $\Delta E \approx 3 \text{ cm}^{-1}$. If $\delta_l > 1$, ΔE to the nearest hydrogenic manifold is given by Eq. (9) with $\delta_l = \delta_l(\text{mod } 1)$.

Consider first the e - B collision as if the electron were free. To do this we ignore the ionic core and perform calculations in the e - B center-of-mass system. The maximum value of the kinetic-energy transfer ΔT occurs for a head-on e - B elastic collision and is approximately

$$\Delta T \approx 4 \left[\frac{m}{M} \right] T_e, \quad (10)$$

where m is the mass of the electron, M is the mass of the atom B , and T_e is the kinetic energy of the electron. Accordingly, l mixing by He perturbers should be more efficient than by more massive perturbers. Experiments show the reverse to be the case. Furthermore, if we take T_e to be the average orbital kinetic energy $\langle T_e \rangle = 1/2n^2$, then, from Eq. (10), $\Delta T \approx 0.5 \text{ cm}^{-1}$ for He, but only 0.05 cm^{-1} for Ar. Thus, while the He case is marginal, the energy transfer in a single (most efficient) e -Ar encounter is too low by about an order of magnitude. Of course we could consider an e - B encounter at a position in the electronic orbit at which T_e exceeds $\langle T_e \rangle$ so that ΔT would be greater, but this must occur closer to the core and the cross section would be lower.

Because the electron was considered to be free, the above calculation of ΔT was performed in the e - B center-of-mass reference frame. To account for the fact that the electron is bound to A^+ we must compute ΔT in the rest frame of this core, taking account of the relative motion of A^+ and B , as well as of A^+ and the electron. We obtain

$$\Delta T \approx 4 \left[\frac{v_c}{v_e} \right] T_e, \quad (11)$$

where v_e is the electronic orbital velocity and v_c is, as before, the velocity of B . Equation (11) yields considerably larger values, ~ 34 and 15 cm^{-1} at 450 K, for He and Ar, respectively, suggesting that ΔE can be made up in a single e - B encounter using a model such as the present one in which the three-body nature of the collision is preserved.

According to these estimates, l mixing of s states would

be very unlikely for principal quantum numbers in the vicinity of 10. For example, for sodium, the energy difference between the $10s$ state and the nearest hydrogenic manifold is $\sim 80 \text{ cm}^{-1}$, higher than the 34-cm^{-1} estimate for He. In fact, experiments show that, at these relatively low values of n , l mixing of s states does not occur.⁷ On the other hand, for $25s$, $\Delta E \approx 5 \text{ cm}^{-1}$ to the nearest hydrogenic manifold, and indeed, experiments performed with sodium s states in the vicinity of $n=25$ show that l mixing occurs at an easily observable rate.⁸ Although the model is clearly inapplicable for s states of low n because the relatively large values of ΔE require core interaction, it should be applicable for s states at higher quantum numbers.

In actuality, the long-range e - B interaction is due to the attractive charge induced dipole potential, while the shorter-range interaction is that of a hard sphere, as assumed in the model. While we have ignored the $1/r^4$ charge-induced dipole potential, it must affect the course of any collision involving Rydberg atoms. In fact, it has been suggested⁹ that this attraction effectively polarizes the $A(nl)$ - B system at long range, leading to a transitory A^+B^- configuration. The resulting Coulomb attraction then reduces R to values at which the electron clouds of A^+ and B overlap so that chemical bonding or electron exchange can occur. Such a mechanism could be responsible for the large cross sections for associative ionization¹⁰ and Penning ionization⁹ that have been measured for collisions involving Rydberg atoms.

RESULTS

We have applied the model to several alkali-metal-atom-rare-gas collision systems and compared calculated l -mixing cross sections as functions of n to measured cross sections. The calculations were performed using the average thermal speed of the A - B system for v_c . For the range of n considered here the cross sections are roughly proportional to $1/v_c$, thus making any average of the rate constant σv_c independent of the averaging process. Furthermore, thermal averaging would raise the calculation to a level that is inconsistent with the simplicity of the model.

Figures 3 and 4 show the data⁷ and the model predictions for collisions of $\text{Na}(nd)$ with He and Ar, respectively. Also included in Fig. 4 for reference are the theoretical results of Olson¹¹ and of de Prunelé and Pascale,¹² the latter of whom obtained upper and lower bounds to σ versus n . These earlier models are based on more sophisticated considerations than our model, but, as may be seen in the figure, the comparison is favorable. The calculations required for our purely classical model are, however, relatively easy to perform.

We emphasize that both the magnitude and the n dependence of σ are obtained from the model; no normalization of the model predictions to the data has been made. Note that, although the cross sections for l mixing by these rare-gas atoms differ by nearly an order of magnitude, the model yields values of σ that are close to the measured values. The only parameter for which any un-

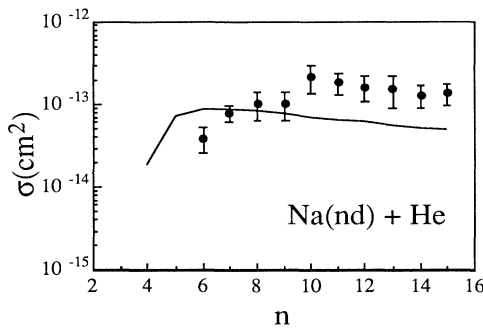


FIG. 3. Cross section σ for l mixing of $\text{Na}(nd)$ atoms by He perturbors. The data are those of Gallagher, Edelstein, and Hill (Ref. 7). The solid line is the model prediction using $L=1.2$ a.u. (Ref. 6).

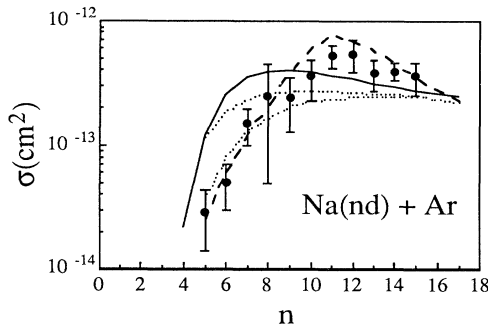


FIG. 4. Cross section σ for l mixing of $\text{Na}(nd)$ atoms by Ar perturbors. The data are those of Gallagher, Edelstein, and Hill (Ref. 7). The solid line is the model prediction using $L=-1.7$ (Ref. 6); the dashed line is the calculation of Olson (Ref. 11); the dotted lines are the upper and lower limits of the calculations of de Prunelé and Pascal (Ref. 12).

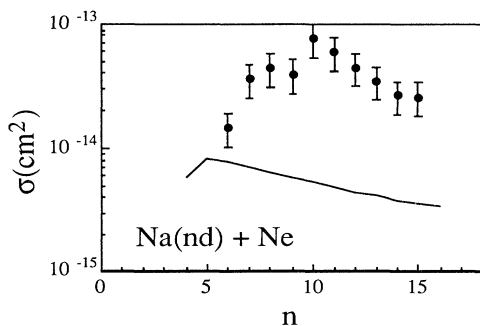


FIG. 5. Cross section σ for l mixing of $\text{Na}(nd)$ atoms by Ne perturbors. The data are those of Gallagher, Edelstein, and Hill (Ref. 7). The solid line is the model prediction using $L=0.24$ a.u. (Ref. 6).

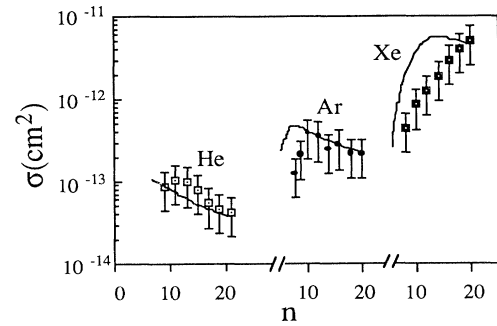


FIG. 6. Summary of the comparisons of the predictions of the model with data for l mixing of $\text{Rb}(nf)$ by the indicated rare gases. The data are those of Hugon *et al.* (Ref. 13). The values of L for He and Ar are the same as those used in the calculations for $\text{Na}(nd)$; for Xe $L=-6.5$ a.u. (Ref. 6) was used.

certainty might exist is the zero-energy scattering length L , for which we used the values of O'Malley.⁶

While there is general agreement on the values of L for both He and Ar, there is a wide range of reported values⁶ for Ne. Moreover, these values for Ne do not fit the pattern of increasing L with increasing atomic weight for the other rare-gas atoms; they are considerably lower. This of course indicates that the zero-energy scattering length, the leading term in the s -wave phase shift,⁵ does not accurately describe e -Ne scattering. Therefore any model that employs only this zero-energy term cannot be expected to produce agreement with data. Nevertheless, for completeness we show the comparison in Fig. 5.

We have also compared the model with data for l mixing of $\text{Rb}(nf)$ atoms.¹³ Figure 6 is a summary of these comparisons. The agreement is seen to be quite good for these three cases for which rare-gas data are available. It is encouraging that the model has the capability of matching experimental results with reasonable accuracy over nearly three orders of magnitude in the value of σ .

As a final application of the model, we calculate σ versus n for self- l -mixing of $\text{Rb}(nf)$ states, that is, l mixing of $\text{Rb}(nf)$ by ground-state Rb atoms. Because reli-

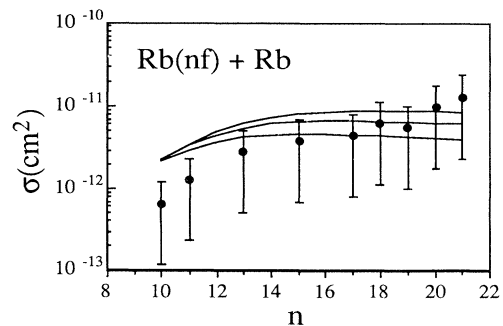


FIG. 7. Comparisons of data for self- l -mixing of $\text{Rb}(nf)$ states with the predictions of the model for three different values of L : 8, 10, and 12 a.u. from bottom to top, respectively. The data are those of Hugon *et al.* (Ref. 13).

able values of the zero-energy scattering length for ground-state Rb are not available, we treat this quantity as a free parameter and compare various model predictions with available data. Figure 7 shows the comparison for three values of L : 8, 10, and 12 a.u. On the basis of this comparison we conclude that 10 a.u. is a reasonable estimate of L for ground-state Rb atoms.

ACKNOWLEDGMENTS

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