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Theory of collisional angular-momentum mixing of Rydberg states*

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A theory for the collisional angular-momentum mixing of the Rydberg states of sodium atoms in rare gases is presented. The theory involves a coupled-state calculation based on a pseudopotential interaction between the valence alkali-metal electron and the rare-gas atom. The theory is in good agreement with experiment.

I. INTRODUCTION

Recently Gallagher, Edelstein, and Hill[1] measured cross sections for the collisional angular-momentum mixing of the Rydberg states of sodium atoms in rare-gas environments. The cross sections for the d states were observed to be large and roughly proportional to the geometric cross section of the excited sodium atom. In addition, the magnitude of the cross section was found to be more or less independent of the particular type of rare gas employed. The goal of this paper is to understand these results.

This type of experiment is similar in many respects to experiments involving the collisional quenching of metastable hydrogen atoms.[2] A theoretical interpretation of such experiments has been offered in terms of a coupled-state calculation involving the degenerate $n = 2$ manifold.[3] In the quenching problem the atom starts out in the 2S state and the effect of the collision is to redistribute the population among all the nearly degenerate $n = 2$ states. In the collisional angular-momentum experiments[1] the degenerate manifold consists of those states with $l > 1$. Owing to the presence of a non-Coulombic core and fine-structure interactions the S and P states are decoupled from this degenerate manifold by a frequency difference which is large compared with the inverse duration of a collision. The experimentally accessible parameter is the cross section for transfer out of the nd state.

II. MODEL

In a Rydberg state with principal quantum number n the size of the atom is roughly $r_n = n^2$ and the orbital speed is approximately $v_n = 1/n$, where we are employing atomic units ($\hbar = m = e = 1$). The rare-gas atom, whose radius will be on the order of unity, is thus small relative to typical valence electronic wavelengths. We will approximate the electron–rare-gas-atom interaction by a Breit-Fermi pseudopotential

$$H_1 = 2\pi a \delta(\vec{r} - \vec{R}) \frac{\partial}{\partial r} r \rightarrow 2\pi a \delta(\vec{r} - \vec{R}) , \qquad (1)$$

where a is the zero-energy scattering length, $\boldsymbol{R}$ is the location of the rare-gas atom, and $\vec{r}$ is the electron's coordinate.

The following assumptions will be made. (i) Since we shall be interested in large n ($n > 3$) and states with $l > 1$, we shall treat the atom as a highly excited hydrogen atom, i.e., the unperturbed Hamiltonian is simply

$$H_0 = \tfrac{1}{2} p^2 - 1/r . \qquad (2)$$

Core effects will be neglected altogether. (ii) The rare-gas atom will be regarded as a classical particle following the straight-line trajectory:

$$\vec{R} = \vec{b} + \vec{v} t , \qquad (3)$$

an approximation which is appropriate to inelastic atom-atom collisions. (iii) Excitation transfer to the rare-gas atom is energetically forbidden in this problem. Transitions involving $\Delta n \neq 0$ in the sodium atom are expected to be very small because of their nonadiabatic character. Thus if we compute a typical energy difference involving $\Delta n = 1$ we find $\Delta\epsilon_n$ on the order of n^{-3}. The typical duration of a collision is $\tau = n^2/v$; thus

$$\tau \Delta\epsilon_n \sim 1/nv . \qquad (4)$$

This number is on the order of several hundred for typical cases to be considered, and so such collisions will be expected to have very low cross sections. (iv) The fine- and hyperfine-structure intervals associated with the $l > 1$ states are all small compared to the transit frequency v/n^2, and hence such splittings will be neglected.

III. THEORY

Our goal will be to calculate the average cross section for a transition from an nd state to all nl states with $l > 2$:

$$\bar{\sigma} = \frac{1}{5} \sum_{m'} \sigma_{m'} = \frac{1}{5} \sum_{m'} \sum_{lm}{}' \int d^2 b \, |c_{lm}^{m'}(\infty)|^2 , \qquad (5)$$

where $c_{lm}^{m'}(\infty)$ is the amplitude for the transition from the state $|n, 2, m'\rangle$ to the state $|n, l, m\rangle$. It is obtained by solving the time-dependent Schrödinger equation

$$(H_0+H_1)|\psi\rangle = i\frac{\partial}{\partial t}|\psi\rangle , \tag{6}$$

where the state is expanded as

$$|\psi\rangle = {\sum_{lm}}' c^{m'}_{lm}(t)\, e^{-i\epsilon_n t}\,|nlm\rangle \tag{7}$$

and the initial condition is

$$c^{m'}_{lm}(t)|_{t=-\infty} = \delta_{m'm}\delta_{l,2} \, . \tag{8}$$

For convenience we may define $\epsilon_n = 0$.

Equation (6) is actually a set of n^2-4 coupled equations which must be integrated numerically to obtain the desired transition amplitude. This integration could be rather costly for large n; therefore we adopt the following alternate, but less desirable, approach: For large b the interaction will be weak enough for perturbation theory to be applicable. The amplitude will then be given by the expression

$$c^{m'}_{lm}(\infty) = -i\int_{-\infty}^{\infty} dt\,\langle nlm|H_1|n2m'\rangle \, . \tag{9}$$

For small b this integral is expected to be very large, and hence Eq. (9) is not at all reliable. At small impact parameters there will be a strong mixing of the states in the degenerate manifold. We assume that the probability for not returning to the d states upon collision is proportional to the relative population of the non-d states:

$$F = (n^2-9)/(n^2-4) \, . \tag{10}$$

Let us define an impact parameter b_0 such that for $b < b_0$ the states are thoroughly mixed, while for $b > b_0$ perturbation theory may be used. The cross section is then

$$\bar{\sigma} = \pi b_0^2 F + \frac{2\pi}{5}{\sum_{lmm'}}'\int_{b_0}^{\infty} db\, b\left|\int_{-\infty}^{\infty} dt\,\langle nlm|H_1|n2m'\rangle\right|^2 . \tag{11}$$

The parameter b_0 is to be determined from the condition

$$\frac{1}{5}{\sum_{lmm'}}' |c^{m'}_{lm}(\infty)|^2 = F \, . \tag{12}$$

This condition guarantees that there is no discontinuity in the transition probability as a function of b when one crosses from the strong-coupling regime to the perturbation-theory regime.

Evaluation of the matrix element appearing in Eq. (11) is trivial because of the δ function, i.e.,

$$\langle nlm|H_1|n2m'\rangle = 2\pi a\varphi^*_{nlm}(\vec{\mathrm{R}})\,\varphi_{n2m'}(\vec{\mathrm{R}}) \, . \tag{13}$$

We employ hydrogen-atom wave functions in Eq. (13),

$$\varphi_{nlm}(\vec{\mathrm{R}}) = N_{nl}R_{nl}(R)\,Y_{lm}(\hat{R}) \, , \tag{14}$$

where the radial wave function is

$$R_{nl}(r) = e^{-r/n}(2r/n)^l L^{2l+1}_{n+l}(2r/n) \tag{15}$$

and the normalization constant is

$$N_{nl} = -\{(2/n)^3(n-l-1)!/2n[(n+l)!]^3\}^{1/2} \, . \tag{16}$$

In evaluating Eq. (11) we must average over all orientations of the collision frame relative to the laboratory frame. Let the collision frame be chosen so that the trajectory follows the orbit $x=b,\ y=vt,\ z=0$. The transformation from the collision frame to the laboratory frame is accomplished through a Wigner rotation matrix,

$$Y_{lm}(\hat{r}) = \sum_{\mu} Y_{l\mu}(\tfrac{1}{2}\pi, \phi)\,D^{(l)}_{\mu m}(\alpha,\beta,\gamma) \, , \tag{17}$$

where α, β, γ are the Euler angles of the rotation and $\tan\phi = vt/b$. Insertion of Eq. (17) into Eq. (11) and making use of the unitarity of the D matrices allows us to simply evaluate Eq. (11) in the collision frame. Thus we finally obtain the expression

$$\bar{\sigma} = \pi F b_0^2 + \frac{8\pi^3 a^2}{5}{\sum_{lmm'}}' N^2_{nl}N^2_{n2}|Y_{ln}(\tfrac{1}{2}\pi,0)|^2|Y_{2m'}(\tfrac{1}{2}\pi,0)|^2 \times\int_{b_0}^{\infty} db\, b\left|\int_{-\infty}^{\infty} dt\, e^{-2r/n}(2r/n)^{l+2}L^{(2l+1)}_{n+l}(2r/n)\,L^{(5)}_{n+2}(2r/n)e^{i(m'-m)\phi}\right|^2 , \tag{18}$$

where $r = (b^2+v^2t^2)^{1/2}$. In evaluating Eq. (18) it is more convenient to introduce ϕ as the integration variable. This results in σ being manifestly a function of the parameter a/v.

IV. RESULTS

The integrals appearing in Eq. (18) were performed using a brute-force numerical integration scheme. Following Gallagher *et al.*[1] we compute v from the relation $v = (8kT/\pi\mu)^{1/2}$, where μ is the reduced mass. The temperature was taken to be $T = 430\,^\circ$K. For helium the scattering length used was $a = 1.1$, and for argon it was $a = -1.65$. This gives the values $a/v = 1480$ and -4570, respectively, for these noble gases.

In Fig. 1 we present the results of the theoretical calculation and compare them to experiment.[1]

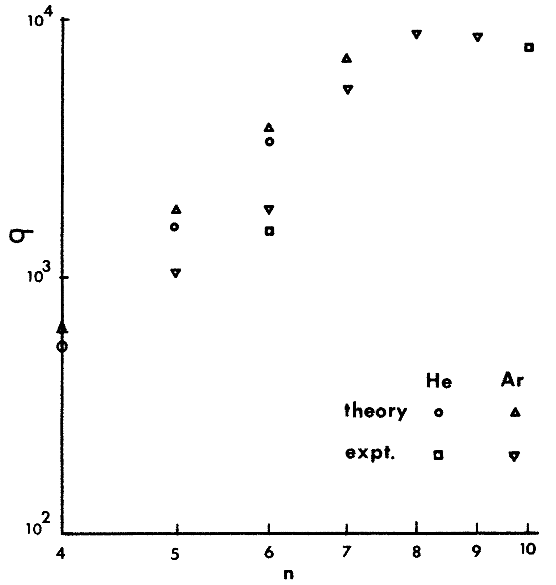

FIG. 1. Comparison of theoretical and experimental cross sections for collisional depopulation of the *nd* Rydberg states of sodium in He and Ar gas. The cross sections, in atomic units, are plotted as a function of the principal quantum number *n*.

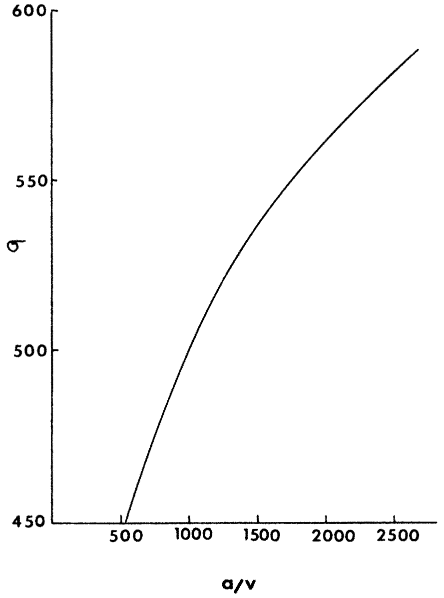

FIG. 2. The cross section σ as a function of the parameter $|a/v|$ for $n = 4$. The ordinate and the abscissa are in atomic units.

Theory and experiment are in quantitative agreement, given the large error bars associated with the experimental results.[1] The cross sections, when fitted to a power law, grow as $n^{4.5}$ for He and $n^{4.3}$ for Ar. We have calculated cross sections only for $n = 4$, 5, 6, and 7. For those cases studied it was found that between $\frac{1}{3}$ and $\frac{1}{2}$ of the total cross section was due to the last term in Eq. (18), with the remainder coming from close-impact parameters.

In this particular problem the interaction which brings about the collisional mixing is strong for small internuclear separations and falls off rapidly for large internuclear separations. It is thus qualitatively similar in nature to the problem of scattering from an inverse power-law potential of the form $V = c/r^n$, where $n \gg 1$. In such a problem it is known that the cross section behaves as $\sigma \sim (c/\hbar v)^{2/(n-1)}$ and is therefore a slowly varying function of both the speed and the strength of the coupling. We therefore expect a similar phenomenon to occur here.

In order to display the relative insensitivity of the cross section to rare-gas-type interactions we plot in Fig. 2 the variation of cross section with parameter $|a/v|$. One finds a slow variation of σ with this parameter. The results are presented for $n = 4$. A similarly slow variation was found for $n = 6$, indicating that it is not dependent on the magnitude of the electronic energy of the atom. Thus not only is the cross section a slowly varying function of the scattering length, it is also predicted to be a slowly varying function of velocity (or temperature or isotopic species). If it were possible to perform the collisional mixing experiments accurately a relative scale of scattering lengths could be established. One would simply have to find those temperatures for which the cross sections had a definite common value. One would then know that for the gases $1, 2, \ldots, N$, $a_1/v_1 = a_2/v_2 = \cdots = a_N/v_N$, and the ratios a_1/a_N, a_2/a_N, etc. would be fixed.

In summary we see that a coupled-state analysis involving a simple pseudopotential interaction allows us to understand the collisional mixing experiments of the Rydberg states or sodium atoms. The present theory is applicable to other alkali metals and predicts that the cross section is independent of the type of alkali-metal atom being used.

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