Theory of collisional quenching of fast metastable ions*

Joel I. Gersten
Department of Physics, City College of the City University of New York, New York, New York 10031

(Received 16 June 1976)

A perturbation theoretic calculation of the quenching of fast metastable ions by collision with rare-gas atoms is developed. The quenching is caused by transitions resulting from the interaction with the electrostatic potential of the target atom. A comparison with experimental data is given.

I. INTRODUCTION

The collisional quenching of metastable atoms and ions has been a topic of interest for some time.[1] Past studies have centered primarily on the situation where the atomic velocities are slow compared with electronic speeds. Recently Matthews, Fortner, and Bissinger[2] have measured total quenching cross sections for the $1s2p\ ^3P_1$ metastable x-ray-emitting state in a fast beam of helium-like fluorine ions (F^{7+}). The cross sections for quenching by rare-gas atom collisions were found to be roughly geometric in size. In this paper a theoretical interpretation of these results is provided.

The basic restriction to be made is that the speed of the ion is small compared with the speed of light but large compared with typical valence-electron speeds of the target atom. The former condition allows us to employ a nonrelativistic formalism, while the latter condition allows us to make several simplifying assumptions.

First we shall treat the electrons in the target atom as being frozen in space for the duration of the collision. This is a valid approximation for the valence electrons but is not accurate for the inner core. The net cross-sectional area of the core, however, is but a small fraction of the geometric size of the atom so the core corrections are likely to be negligible. Thus the target atom presents a static charge distribution to the impinging ion. This charge distribution will be taken to be that appropriate to the ground state of the target atom.

Secondly we shall treat the ion as a classical particle traveling at constant velocity. The internal dynamics of the ion, of course, must be treated quantum mechanically.

We are interested in the $1s2p\ ^3P_1$ metastable state of the ion. Since the $1s$ electron is more tightly bound, it is less susceptible to perturbations than the $2p$ electron. We may therefore restrict our attention to the $2p$ electron and treat the ion as if it had only a single active electron. Exchange effects are thus patently ignored, but are expected to be small.

II. THEORY

The Hamiltonian for the system, in atomic units ($\hbar = m = e = 1$) is

$$H = H_0 - \Phi(\vec{R} + \vec{r}), \tag{1}$$

where H_0 is the internal Hamiltonian governing the ion and Φ is the electrostatic potential produced by the target atom. The ion coordinate has been denoted by $\vec{R}$ and its electronic coordinate by $\vec{r}$. By our assumption, $\vec{R} = \vec{b} + \vec{v}t$, where $\vec{b}$ is the impact parameter and $\vec{v}$ is the velocity of the ion.

Let the initial state of the ion be $|i\rangle$ and the final state be $|f\rangle$. The quenching probability, from first-order perturbation theory, is

$$P = \sum_f{}' \left| \int_{-\infty}^{\infty} dt\, e^{-i\omega_{fi}t} \langle f | \Phi(\vec{R} + \vec{r}) | i \rangle \right|^2, \tag{2}$$

where the state $|f\rangle = |i\rangle$ is omitted from the summation. We are neglecting the possibility of an excited state cascading back to the original state following this transition because it is improbable. The cross section for quenching is determined by integrating over all impact parameters:

$$\sigma_Q = \int d^2b\, P. \tag{3}$$

For sufficiently fast projectiles we have $\omega_{fi} b / v \ll 1$; so the exponential appearing in Eq. (2) may be replaced by unity. The closure relation then leads to

$$\sigma_Q = \int d^2b \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \left[\langle i | \Phi(\vec{R} + \vec{r}) \Phi(\vec{R}' + \vec{r}) | i \rangle - \langle i | \Phi(\vec{R} + \vec{r}) | i \rangle \times \langle i | \Phi(\vec{R}' + \vec{r}) | i \rangle \right], \tag{4}$$

where $\vec{R}' = \vec{R}(t')$. Let us Fourier-analyze the potential:

$$\Phi(\vec{r}) = \int d\vec{q}\, \varphi(\vec{q}) e^{i\vec{q}\cdot\vec{r}}. \tag{5}$$

Then the $\vec{b}$, t, and t' integrations may be performed leading to the result

$$\sigma_Q = \frac{(2\pi)^4}{v^2} \int d^2q_\perp |\varphi(q_\perp)|^2 [1 - |\langle i| e^{i\vec{q}_\perp\cdot\vec{r}} |i\rangle|^2], \tag{6}$$

where $\vec{q}_\perp = q_x\vec{i} + q_y\vec{j}$ and $\vec{v} = v\vec{k}$. If use is made of Poisson's equation, this may be reexpressed in terms of the charge form factor of the target atom

$$\sigma_Q = \frac{256\pi^6}{v^2} \int \frac{d^2q_\perp}{q_\perp^4} |\rho(q_\perp)|^2 (1 - |\langle i| e^{i\vec{q}_\perp\cdot\vec{r}} |i\rangle|^2). \tag{7}$$

Note that charge neutrality allows the integral to avoid a divergence at small values of $q_\perp$. Equation (7) is to be averaged over all three orientations of the magnetic quantum number of the electron.

Let us employ a hydrogenic $2p$ wave function for the state $|i\rangle$. Thus

$$\langle \vec{r}|i\rangle = \left(\frac{\sqrt{8\epsilon}}{24}\right)^{1/2} r e^{-r\sqrt{2\epsilon}} Y_{1m}(\theta, \phi), \tag{8}$$

where $\epsilon = (Z-1)^2/8$, including the $1s$ screening effect. The ionic integrals may then be carried out with the result that

$$\sigma_Q = \frac{256\pi^7}{12v^2\epsilon} \int_0^\infty dy\, y \left|\rho\left(\frac{\sqrt{8\epsilon}}{Y}\right)\right|^2 \times \left[3 - 2\left(\frac{Y^2}{1+Y^2}\right)^6 - \left(1 - \frac{5}{Y^2}\right)^2 \left(\frac{Y^2}{1+Y^2}\right)^8\right], \tag{9}$$

where we have let $q_\perp = (8\epsilon)^{1/2}/Y$. The charge density of the atom is obtained from

$$\rho(\vec{r}) = Z\delta(\vec{r}) - \sum_{i\alpha} 2|\varphi_{i\alpha}(\vec{r})|^2, \tag{10}$$

where Z is the nuclear charge and $\varphi_{i\alpha}$ is the wave function for orbital i with magnetic quantum number α. The wave functions are taken from the tables of Clementi and Roetti[3] and are of the form

$$\varphi_{i\alpha} = \sum_p C_{ip} R_{\lambda p}(r) Y_{\lambda\alpha}(\theta, \phi), \tag{11}$$

where $R_{\lambda p}$ are normalized Slater orbitals. We find the following formula for the charge form factor for a closed-shell atom

$$\rho(q) = \frac{Z}{(2\pi)^3} - \frac{1}{(2\pi)^4} \sum_i (2\lambda_i + 1) \sum_{pp'} \frac{C_{i\lambda p} C_{i\lambda p'}}{[(2n_{ip})!(2n_{ip'})!]^{1/2}} (2\zeta_{ip})^{n_{ip}+1/2} (2\zeta_{ip'})^{n_{ip'}+1/2} S_{n_{ip}+n_{ip'}-2}(q, \zeta_{ip} + \zeta_{ip'}), \tag{12}$$

where

$$S_n(q, \sigma) = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} r^n e^{-\sigma r}, \tag{13}$$

is an integral which is obtainable analytically. The parameters n_{ip}, ζ_{ip}, λ_i, and $C_{i\lambda p}$ are defined in Ref. 3.

In summary Eq. (9) is our final formula for the total quenching cross section. The y integration has been performed numerically using the expression given in Eq. (12).

III. RESULTS AND DISCUSSION

In summary we have developed a theory for the collisional quenching of fast metastable ions by atomic impact. The quenching is brought about by electrostatic fields of the target atom. As the metastable ion passes the target, it is subjected to a transient electric field pulse which possesses a rich assortment of Fourier components. These Fourier components induce transitions to the excited states of the ion—both bound and continuum states, with the result that the metastable state is depopulated.

The collisions may be broken into two classes: close and distant. For the close collisions the metastable ion experiences the strong electrostatic fields characteristic of the interior of the target atom. Here the quenching is effective. For the distant collisions the ion experiences a weaker field with softer high-frequency components and the quenching is not very effective. Thus it seems plausible to expect a cross section which varies roughly as the geometric area of the target atom.

Let us apply the theory to the experimental results of Matthews, Fortner, and Bissinger.[2] For 30-MeV F^{7+} ions one has a speed of $v = 1.7 \times 10^9$ cm/sec. This exceeds the typical valence electron speeds estimated to be $< \alpha c$, but is still small compared with the speed of light. The results of our calculation for the rare-gas atoms appear in Table I along with the experimental results. Good

TABLE I. Comparison of theoretical and experimental[2] total quenching cross sections, in units of 10^{-16} cm^2.

Gas	σ_Q(theor.)	σ_Q(expt.)
He	0.026	
Ne	0.48	0.7 ± 0.2
Ar	1.51	1.5 ± 0.4
Kr	4.27	2.0 ± 0.6

agreement is obtained for Ne and Ar, and poor agreement is obtained for Kr. We do not understand the reason for this latter discrepancy.

Let us summarize the various approximations made in this paper. (a) The use of the nonrelativistic formalism requires, of course, that $v/c \ll 1$. (b) The neglect of the internal dynamics of the target atom is valid as long as the ionic speed exceeds typical electronic velocities, i.e., $v \gg c\alpha$. (c) The use of straight-line trajectories is justified as long as the kinetic energy of the ion exceeds typical potential energies, i.e., $Mv^2/2 > e^2/a_0$. (d) The classical path assumption works well when the orbital angular momenta involved are large, i.e., $Mvb \gg \hbar$. (e) Perturbation theory is justified when the typical phase evolution $\int V\,dt/\hbar$ is small. The duration of a collision is on the order of b/v, while the strength of the interaction is on the order of e^2/b. Thus we obtain the requirement that $(e^2/b\hbar)(b/v) \ll 1$. (f) Finally, the neglect of the frequency ω_{fi} is justified when it is smaller than the inverse duration of a collision. This leads to the criterion $(e^2/\hbar a_0)(b/v) \ll 1$. The above criteria may be subsumed by the concise statement that $1 \gg v/c \gg \alpha$.

The above analysis is not limited to F^{7+} ions or to rare-gas targets. Any ion system where a single electron is highly susceptible to having transitions induced in it may be substituted for F^{7+}. Similarly Eq. (7) may be employed with any type of target, such as other atoms, molecules, or thin-film solids.

---

*Research supported in part by the City University Faculty Research Award Program.

[1]L. R. Wilcox and W. E. Lamb, Jr., Phys. Rev. 119, 1915 (1960); E. M. Purcell, Astrophys. J. 116, 457 (1952); W. L. Fite, R. T. Brackman, D. G. Hummer, and R. F. Stebbings, Phys. Rev. 116, 363 (1959); 124, 2051 (1961); F. J. Comes and U. Wenning, Z. Naturforsch. 24a, 487 (1969); F. W. Byron, Jr., R. V. Krotkov, and J. A. Medeiros, Phys. Rev. Lett. 24, 88 (1970); V. Dose, V. Meyer, and M. Salzmann, J. Phys. B 2, 1357 (1969); R. S. Kass and W. L. Williams, Phys. Rev. Lett. 27, 473 (1971); J. I. Gersten, J. Chem. Phys. 51, 637 (1969); F. W. Byron, Jr. and J. I. Gersten, Phys. Rev. A 3, 620 (1971); Phys. Rev. Lett. 30, 115 (1973).

[2]D. L. Matthews, R. J. Fortner, and G. Bissinger, Phys. Rev. Lett. 36, 664 (1976).

[3]E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).