Relativistically Enhanced Ionization Rates at Stark-Effect Level Crossings in Hydrogen

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Relativistic coupling terms at crossings between hydrogen Stark levels are computed with numerical Stark wave functions. Over a small interval of the electric field at crossings between a slowly and a rapidly ionizing state, the ionization rate of the former is increased. The effect is calculated to be observable with available techniques at more than thirty crossings between two $m_L = 0$ levels in the range 7 to 140 kV/cm, $n = 7$ to 16.

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Eigenfunctions of the nonrelativistic Schrödinger equation for a hydrogen atom in an electric field are characterized by two exact quantum numbers (e.g., n_1 and m_L) as well as energy, so that states of the same m_L originating from different principal quantum number n can cross exactly. The operator that distinguishes the two crossing states is the z component of a generalized Runge-Lenz vector.[1] This symmetry is broken by relativistic effects, which produce small coupling elements between states that otherwise would cross. Fine-structure splittings at zero field are an example of such anticrossing structure. At high-field crossings between states that are effectively discrete (i.e., do not ionize within an experimental time scale), coupling elements computed by methods described below are so small that the anticrossing occurs over a very small fraction ($< 5\times10^{-6}$) of the electric field. A more dramatic manifestation of relativistically induced symmetry breaking in the hydrogen Stark effect occurs at crossings beyond the classical saddle-point energy, when one level is rapidly ionizing in the nonrelativistic case. At such crossings, even small effects can couple a slowly ionizing state with a rapidly ionizing state so as to increase drastically the ionization rate of the former. This Letter presents a first survey of relativistically enhanced ionization (REI) rates at Stark-effect level crossings in hydrogen.

This study is timely now in view of recently developed techniques for measuring ionization rates in hydrogen,[2] and proposed experiments to observe the hydrogen Stark effect in fields of 1–5 MV/cm at the Clinton P. Anderson Meson Physics Facility (LAMPF).[3]

Anticrossings between discrete Stark levels have been observed in alkali atoms,[4] where the ion core breaks the Coulomb symmetry. The sharp change of ionization rate at level crossings between unstable Rydberg Stark states has been reported for sodium[5] and more recently for helium atoms.[6] In view of its recent successful application to the theory of Stark effects in nonhydrogenic atoms,[7] quantum defect theory might also be applicable to the much smaller effects due to relativistic terms in hydrogen. However, the present study is based on a direct evaluation of relativistic terms between Stark levels. Previous calculations[8] of the fine structure of hydrogen Stark levels did not deal with ionization phenomena.

The Hamiltonian for hydrogen in an electric field contains the nonrelativistic Stark effect (H_0) plus relativistic terms (H_1) from the Foldy-Wouthuysen transformation.[9] The terms that are nonzero between two degenerate states are the relativistic mass correction, the spin-orbit term, and the Darwin term, which is proportional to $\delta(\vec{r})$. A major part of the Lamb shift may also be represented by a term proportional to $\delta(\vec{r})$.[10] Nuclear spin hyperfine structure is neglected. In atomic units, the terms in the above order are therefore

$$H_1 = -\frac{\alpha^2}{2}(E+\Phi)^2 + \frac{\alpha^2}{4}\frac{\vec{\sigma}\cdot\vec{L}}{r^3} + \frac{\alpha^2}{4}\delta(\vec{r})\{1+C_L\}, \qquad (1)$$

where $\Phi = 1/r - Fz$ (F is the electric field), and $C_L = 0.045$ is the ratio of the $\delta(\vec{r})$ Lamb-shift term to the Darwin term (0.99 GHz vs 21.9 GHz for diagonal $n=2$ elements).

In this brief survey, only $m_L = 0$, $\Delta n = 1$ crossings are used to illustrate the discussion. Corresponding elements of H_1 for $\Delta n > 1$, $\Delta m_L = \pm 1$, and $m_L \neq 0$ crossings are at least one-third smaller. Within the $m_L = 0$ manifold, spin-orbit elements are zero, and the two $m_S = \pm\frac{1}{2}$ components are essentially degenerate except very near zero field.

At Stark-effect level crossings of interest here, a narrow, slowly ionizing level of principal quantum number n (denoted level a) crosses a broader Stark level (denoted level b) originating from $n+1$. The nonrelativistic width of level b, Γ_b, is normally 10^6 to 10^{13} times that of level a, Γ_a. A typical crossing is shown in Fig. 1(a). Relativistic effects mix these two levels so as to appreciably broaden the narrow one. This situation is analogous to the well known variation in radiative decay rate induced by electric field coupling between two levels of different radiative lifetime (e.g., H 2s and 2p).[11] Because the coupling element, V, is much smaller than Γ_b, Lamb's formula in the limit of small V describes phenomenologically the relativistic ionization rate near a crossing:

$$\Gamma_{\text{ion}}^R \cong \Gamma_a + \frac{|V|^2\Gamma_b}{(E_a-E_b)^2+\hbar^2\Gamma_b^2/4}, \qquad (2)$$

where E_α is the energy of level α. Figure 1(b) shows the relativistically enhanced ionization rate for the narrow level, $n, n_1, m_L = 12, 8, 0$ of Fig. 1(a). In this example, the nonrelativistic rate at the crossing, 4 s^{-1}, is completely negligible on the scale of Fig. 1(b).

Methods for computing V are discussed below.

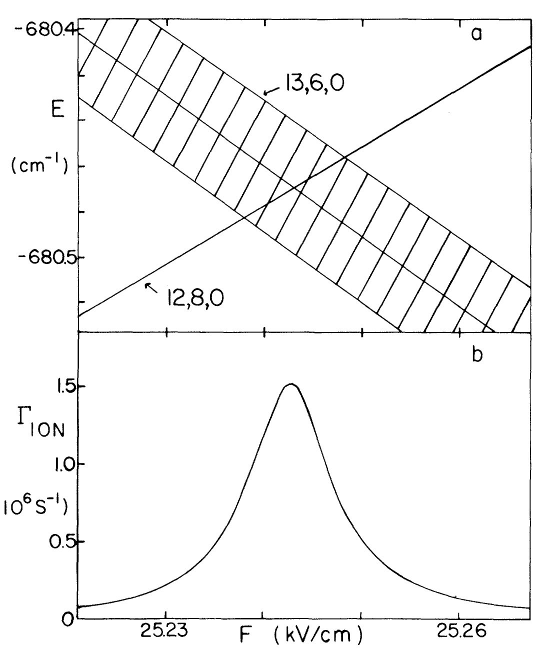

FIG. 1. (a) A level crossing between hydrogen Stark states $(n,n_1,m)=(12,8,0)$ and (13,6,0). The boundaries of the shaded region denote half-maximum points in the density-of-states function of the latter state. (b) The enhanced ionization rate of the (12,8,0) state due to relativistic coupling terms over the crossing region.

In summary, one finds that $V=-4.0\times10^{11} \times(n_{1a}-n_{1b})^{-1}(n_a n_b)^{-3/2}$ Hz fits the results for $n=7$–16 to 20% or so. [For two $m_L=0$ levels, the $\delta(\vec{r})$ term alone varies as $(n_a n_b)^{-2}$, but the r^{-2} term dominates.] At the crossing in Fig. 1, for example, where $\Gamma_b/2\pi = 1.8$ GHz, this estimate gives $V=-10.3$ MHz and a peak Γ_{ion}^R value of $1.4\times10^6\ \text{s}^{-1}$, in good agreement with Fig. 1(b). This indicates how a small symmetry-breaking term can remarkably enhance the ionization rate (in this case by $>10^5$) for propitious values of Γ_a and Γ_b.

To the approximation that Stark wave functions consist of a constant spatial part times an amplitude that varies as a Lorentzian over a resonance, elements of V in (2) may be computed by normalizing each wave function to unity over the Coulomb well, as if it were a discrete state. Previously described procedures are used here to obtain the wave functions.[12,13] Briefly, the ordinary differential equations obtained by separating H_0 in parabolic coordinates (ϵ,η,ϕ) are integrated by the Numerov method. The separation constant Z_1 (the eigenvalue for the equation in ξ) is found by iteration. The width parameter is obtained from the energy variation of the amplitude at the origin when Ψ is normalized to an outgoing wave of constant amplitude $1/2\pi$. Resulting nonrelativistic energies and widths agree with published values.[13,14]

For a more rigorous and general approach, Fano's analysis[15] of the coupling between a discrete state and a continuum is easily modified to apply to a quasidiscrete state and a continuum. To obtain the coupling parameter $|V_E|^2$, one again assumes that the matrix element at energy ϵ, $|\langle a\epsilon|H_1|b\epsilon\rangle|^2$, has a Lorentz form with a full width $\hbar\Gamma_a$ and a maximum $|V_{ab}|^2$ at $\epsilon=E_a$. Since the integral over the Lorentzian is $\pi|V_{ab}|^2\hbar\Gamma_a/2$, the Fano width parameter is

$$\Gamma_{\text{ion}}^R = 2\pi|V_E|^2\hbar^{-1} = \pi^2|V_{ab}|^2\Gamma_a. \qquad (3)$$

It is found that the effective V in (2) is constant over the crossing region to a few percent or better. When $\Gamma_{\text{ion}}^R \cong \Gamma_a$, as for example, far from the crossing center, Eq. (2) must be used rather than (3). Further details of the calculations will be given in a longer report.[16]

Systematics of Stark-level crossings are illustrated in Fig. 2. Figure 2(a) shows the energy-level diagram for $m_L=0$, $n=10$ and 11. It is useful to classify crossings by $\Delta n_1 = n_{1a}-n_{1b}$ (n_1 is the number of nodes in the ξ function). Figure 2(a) shows that crossings between n and $n+1$ for a given Δn_1 occur over a small range of field values. Relativistic and nonrelativistic ionization rates, Γ_{ion}^R and Γ_{ion}^{NR}, for

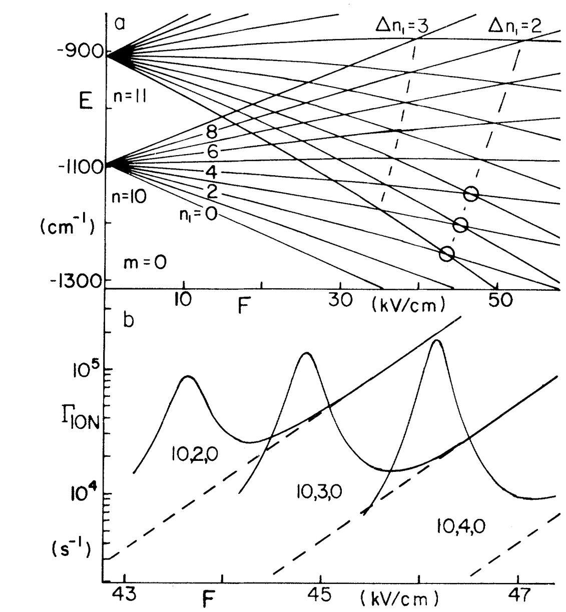

FIG. 2. (a) Stark energy levels for $m=0$, $n=10$ and 11 illustrating level crossings. (b) Ionization rates for $m=0$, $n=10$, $n_1=2$–4 levels in the vicinity of the crossings that are circled above. Solid lines are relativistic rates, including crossing effects; dashed lines are nonrelativistic ionization rates.

$n=10$ levels near three $\Delta n_1=2$ crossings are plotted in Fig. 2(b). Even for these relatively broad crossing regions, the ionization rate at $E_a=E_b$ is at least a factor of 10 greater than the nonrelativistic rate.

Nevertheless, the REI effect at $\Delta n_1=2$, $n=10$ crossings is not likely to be observed experimentally because the peak ionization rate is less than the radiative decay rate. To identify conditions under which REI does exceed radiative decay, one notes from (2) that the maximum rate, at $E_a=E_b$, is inversely proportional to Γ_b. The crucial role of Γ_b is illustrated by the crossings at low N (<7), which occur where level b is rapidly ionizing (large Γ_b) because Stark shifts are smaller and zero-field intervals larger for low n than for high n. Even though V varies as n^{-3}, REI rates for all crossings $n<7$ are much less than the radiative decay rate. For all $\Delta n_1=1$ crossings, Γ_b is too large for significant REI.

On the other hand, a crossing can occur over an interval of the electric field smaller than the experimental resolution if Γ_b is too small. The parameter of interest is the "fractional width," or full width at half maximum of the REI shape divided by the crossing field. Experimentally, electric field uniformities of 2 parts in 10^4 have been achieved in molecular beam work,[17] for example. All $\Delta n_1>3$ crossings above $n=6$ have fractional widths less than 5 ppm.

The crossings of interest therefore have $\Delta n_1=2$ and 3. Representative data are given in Table I. For given Δn_1, Γ_b decreases with n as well as with n_1, so that the REI rate ($\Gamma_{\rm ion}^R$) exceeds the radiative decay rate ($\Gamma_{\rm rad}$) at many $\Delta n_1=2$ crossings for $n>10$. The fractional width exceeds 2 parts in 10^4 in about thirty such cases, with $n=11$ to 16. Four $\Delta n_1=3$ crossings at fields of 80 to 140 kV/cm, $n=7$ and 8, also have fractional widths $>2\times10^{-4}$ and $\Gamma_{\rm ion}^R>\Gamma_{\rm rad}$. For all these selected cases, $\Gamma_{\rm ion}^R$ rates are within the range of previously measured hydro-

TABLE I. Typical parameters for level a at a crossing with broad level b in the hydrogen Stark effect.

n_a	n_{1a}	n_b	n_{1b}	Δn_1	Crossing field (kV/cm)	$\Gamma_{\rm ion}^{NR}$ ($\rm s^{-1}$)	$\Gamma_{\rm ion}^{R}$ [a] ($10^4\ \rm s^{-1}$)	$\Gamma_{\rm rad}$ [b] ($10^4\ \rm s^{-1}$)	Fractional Width
7	3	8	0	3	136.67	0.018 [c]	462	189	8.8×10^{-4}
8	3	9	0	3	82.30	0.008 [c]	1300	117	2.0×10^{-4}
12	2	13	0	2	21.64	1640	15	44	3.7×10^{-3}
12	6	13	4	2	23.87	61	52	23	1.1×10^{-3}
12	10	13	8	2	26.86	0.052 [c]	970	65	9.0×10^{-5}
14	2	15	0	2	11.93	336	26	27	1.2×10^{-3}
14	6	15	4	2	12.95	18	90	13	3.4×10^{-4}
14	10	15	8	2	14.25	0.12 [c]	1190	20	3.4×10^{-5}
16	4	17	2	2	7.35	20	85	11	2.0×10^{-4}

[a]Peak relativistically induced ionization rate.
[b]Radiative decay rate at zero field.
[c]Ionization rate obtained by extrapolation from slightly higher fields.

gen Stark ionization rates.[2]

Γ_{rad} values in Table I are for zero field and agree with plotted values of Hiskes, Tarter, and Moody.[18] Careful but preliminary calculations[16] using perturbation theory[19] as well as numerical integration indicate that the variation of Γ_{rad} from zero field to the crossing field is less than 40% for each case in Table I.

One concludes that when the width of the crossing region is sufficiently small, relativistically enhanced ionization competes successfully with radiative decay. Over a range of n values, this new relativistic effect in hydrogen is calculated to be large enough to be detected with available experimental techniques. Surprisingly, although the coupling element decreases as n^{-3}, most instances for which the effect is predicted to be observable occur not at the very high fields at which levels from low-n states cross, but at fields in the range 7–40 kV/cm where $n = 11$–16 levels cross components from the next higher n. Measurements of REI rates would provide stringent tests of the theory of the Stark effect.

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