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Sum rules and expansion formula for Stark radiative transitions in the hydrogen atom

David R. Herrick*
Bell Laboratories, Murray Hill, New Jersey 07974
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An expansion formula for Stark effect transition probabilities is derived in terms of field-free (spherical) transition probabilities. Expansion coefficients are squares of Clebsch-Gordan coefficients from the $SO(4) = SU(2) \times SU(2)$ description of the hydrogen atom. The method provides new sum rules for Stark transitions which explain regularities in previous calculations. Accurate formulas for average Stark transition probabilities obtain from application of the method to an empirical model for field-free transition probabilities. The approximation permits estimation of Stark lifetimes in the large-n regime.

I. INTRODUCTION

In this paper we investigate radiative transitions from Stark states of the hydrogen atom. Numerical values for transition decay probabilities for both the field-free (spherical coordinates) and Stark (parabolic coordinates) states have been reported by Hiskes, Tarter, and Moody[1] for levels up to $n = 25$, and dipole matrix elements for spherical states up to $n = 60$ are available.[2] These calculations and their extension to higher Rydberg states present no formal difficulty, since Gordon[3] derived closed-form expressions for the necessary hydrogenic matrix elements. The situation concerning the interpretation of the behavior of Stark lifetimes with respect to variations in the quantum numbers n_1, n_2, and m is less satisfactory, in contrast to the familiar dependence of the spherical lifetimes on the azimuthal quantum number l. For discussion of the Stark energies, quantum numbers, and lifetimes, we refer the reader to Bethe and Salpeter.[4]

We resolve this situation by showing that each Stark transition probability expands as a finite sum of field-free transition probabilities over the range $l = |m|, |m|+1, \ldots, n-1$. Interpretation of the Stark lifetimes then follows *a fortiori* from analysis of the expansion coefficients. In addition, the method gives a new sum rule for the Stark transitions which shows that the lifetimes of states with $m = 0$ are closely related to those having $m \neq 0$.

A brief description of the Stark states appears in Sec. II, and investigation of the dipole transitions follows in Sec. III. A key feature of the method is that the Stark transitions are determined uniquely by the distribution of spherical transitions over l. In Sec. IV, we illustrate the behavior of the Stark transitions for a simple empirical formula representing the spherical transition probabilities. The resulting equations accurately reproduce the Stark transition probabilities of Ref. 1, explicitly illustrating the dependence of the radiative transitions on the Stark quantum numbers.

II. STARK STATES

The electric field Fz mixes the degenerate field-free hydrogen-atom states $|nlm\rangle$ of different l to give Stark states $|nkm\rangle$, which are the zero-order (in F) solutions of the Schrödinger equation in parabolic coordinates. In terms of the usual parabolic quantum numbers n_1 and n_2, we have set $k = n_2 - n_1$ corresponding to the electric quantum number used by Pauli.[5] The energy to second order in field intensity depends on n, k, and m in the following way[4]:

$$E_2 = -1/2n^2 - \tfrac{3}{2}Fnk - \tfrac{1}{16}F^2n^4(17n^2 - 3k^2 - 9m^2 + 19)\,, \tag{1}$$

so that states having more positive values of k lie lower in energy. For fixed n and m, k ranges over the values $n-|m|-1, n-|m|-3, \ldots, -n+|m|+1$, giving a total of $n-|m|$ nondegenerate states. For fixed n and k, there are $n-|k|$ states corresponding to $m = n-|k|-1, n-|k|-3, \ldots, -n+|k|+1$, all of which are degenerate to first order in F.

The two sets of hydrogenic states are related by the orthogonal transformation

$$|nkm\rangle = \sum_{l=|m|}^{n-1} |nlm\rangle C(nk, lm)\,. \tag{2}$$

General expressions for the $C(nk, lm)$ have been derived by Rojansky[6] using an expansion technique, and more recently by Tarter[7] using direct evaluation of the overlap $\langle nlm|nkm\rangle$. As Park[8] noted, however, the $C(nk, lm)$ are in fact Clebsch-Gordan coefficients for the pseudo-spin angular momentum $SU(2) \times SU(2)$ decomposition of the four-dimensional rotation group $SO(4)$ associated with the hydrogen atom degeneracies.

We therefore define the parabolic states (2) in

terms of a 3-j coupling coefficient as follows:

$$C(nk,lm)=(-)^m[2l+1]^{1/2}\begin{pmatrix}\frac{n-1}{2} & \frac{n-1}{2} & l\\ \frac{m-k}{2} & \frac{m+k}{2} & -m\end{pmatrix}. \quad (3)$$

This choice of coefficients is consistent with a set of normalized hydrogenic radial functions which behave as $(-r)^l$ near the origin.

III. DIPOLE TRANSITION PROBABILITIES

A. General formulas

The total transition probability from the state $|nlm\rangle$ to all states within the level n' is[4]

$$A(nlm,n')=w(n,n')\sum_{l',m'}|\langle nlm|\vec{r}|n'l'm'\rangle|^2, \quad (4a)$$

with

$$w(n,n')=(4e^2a_0^2/3\hbar c^3)[n^{-2}-(n')^{-2}]^3. \quad (4b)$$

$A(nlm,n')$ is independent of m. For parabolic states, the analogous probability for $|nkm\rangle$ is

$$B(nkm,n')=w(n,n')\sum_{k',m'}|\langle nkm|\vec{r}|n'k'm'\rangle|^2, \quad (5)$$

where we assume only zero-field contributions to the energy factor $w(n,n')$. Total transition probabilities to lower levels are then

$$A(l)=\sum_{n'=l+1}^{n-1}A(nlm,n') \quad (6)$$

and

$$B(k,m)=\sum_{n'=|m|+1}^{n-1}B(nkm,n'), \quad (7)$$

where the initial level n is assumed. Corresponding radiative lifetimes are $\tau(nl)=A(l)^{-1}$ and $\tau(nkm)=B(k,m)^{-1}$.

The orthogonal transformation (2) suggests a "partial-wave" expansion of $B(k,m)$ in terms of $A(l)$. Substitution of (2) into (5) and (6) leads directly, upon application of standard angular-momentum theory, to the desired result:

$$B(k,m)=\sum_{l=|m|}^{n-1}A(l)D(nk,lm), \quad (8a)$$

$$D(nk,lm)=[C(nk,lm)]^2. \quad (8b)$$

The absence of interference terms in Eq. (8a) simplifies the interpretation of $B(k,m)$ considerably. Symmetry properties of the $C(nk,lm)$ show that

$$B(k,m)=B(-k,m)=B(k,-m). \quad (9)$$

B. Sum rules

Summation of Eq. (8) over k gives conservation of the total transition probability from all states having the same m value in the two sets of states:

$$\sum_k B(k,m)=\sum_{l=|m|}^{n-1}A(l). \quad (10)$$

Summation over both k and m also recovers conservation of the total transition probability from level n:

$$T(n)\equiv\sum_{l=0}(2l+1)A(l) \quad (11a)$$

$$=\sum_{k,m}B(k,m). \quad (11b)$$

These results, (10) and (11), are, of course, well known.[1,4]

A more stringent sum rule, which to our knowledge has not been previously noted, follows from summation of (8) over values of k and m so that either $k+m$ or $k-m$ is held constant. The result, which by virtue of (9) can be expressed in terms of values of $m\geq 0$, is

$$n^{-1}T(n)=B(k,0)+\sum_{m=1}^{\frac{1}{2}(n-1-k)}B(k+m,m)+\sum_{m=1}^{\frac{1}{2}(n-1+k)}B(k-m,m). \quad (12)$$

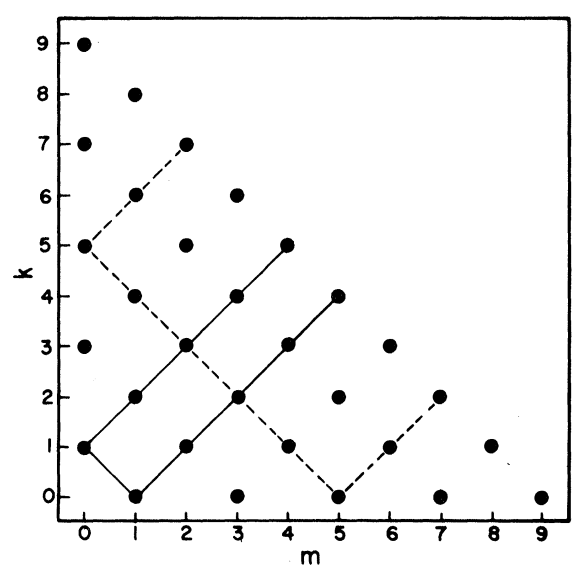

FIG. 1. Illustration of summation pathways over Stark states in Eq. (12) for $k=5$ and $k=1$ at $m=0$ within the $n=10$ level. Only states having $k,m\geq 0$ appear here.

Summation of (12) over the n values $k=n-1$, $n-3$, ..., $-(n-1)$ gives Eq. (11) once again. The sum rule (12) has strong implications in the interpretation of Stark lifetimes, since $T(n)$ is independent of k and m. Thus, the distribution of transition probabilities at $m=0$ is determined uniquely by the corresponding distribution for $m\neq 0$.

In Fig. 1, we illustrate summation pathways of Eq. (12) for $k=5$ and $k=1$ within the $n=10$ level. The values of m and k shown represent only one quadrant of the full spectrum of n^2 states. The pathways indicated are projections of equivalent pathways corresponding to negative values of m and k.

C. Average values of $B(k,m)$

Hiskes *et al.*[1] noted that for $n\leq 25$, the $B(k,m)$ are very nearly independent of k for fixed $m\neq 0$. We therefore define an average value of $B(k,m)$ for each m as follows:

$$\overline{B}(m)=(n-|m|)^{-1}\sum_k B(k,m) \tag{13a}$$

$$=(n-|m|)^{-1}\sum_{l=|m|}^{n-1} A(l)\,. \tag{13b}$$

Inversion of Eq. (13b) allows for solution of $A(l)$ in terms of the $B(k,l)$ and $B(k,l+1)$, but we shall not pursue this relation.

Since to good approximation $B(k,m)=\overline{B}(m)$ for $m\neq 0$, we can use the sum rule of Sec. III B to estimate Stark transition probabilities for $m=0$. We define the probabilities $B^0(k,0)\simeq B(k,0)$ as follows:

$$B^0(k,0)=n^{-1}T(n)-\sum_{m=1}^{\frac{1}{2}(n-1-k)}\overline{B}(m)-\sum_{m=1}^{\frac{1}{2}(n-1+k)}\overline{B}(m)\,. \tag{14}$$

For $k=n-1$, this reduces to

$$B^0(n-1,0)=n^{-1}T(n)-\sum_{m=1}^{n-1}\overline{B}(m)\,. \tag{15}$$

Values for $k<n-1$ then generate from the recursion relation:

$$B^0(k-2,0)=B^0(k,0)-\overline{B}(\tfrac{1}{2}(n+1-k))+\overline{B}(\tfrac{1}{2}(n-1+k))\,. \tag{16}$$

Thus, given the distribution $A(l)$, exact Stark transition probabilities of course obtain directly from Eq. (8). Good estimates of $B(k,m)$ for $m\neq 0$ follow, however, from setting $B(k,m)\simeq\overline{B}(m)$ and $B(k,0)\simeq B^0(k,0)$. The advantage of this approximation is that it avoids the necessity of evaluating the coefficients $D(nk,lm)$.

D. k dependence of $B(k,0)$

We limit the discussion in this section to values of $m,k\geq 0$. As a direct result of the familiar decreasing behavior of $A(l)$ for increasing $l=1,2,\ldots,n-l$; $B(k,m)$ and $\overline{B}(m)$ also decrease in magnitude as m increases. Note, for instance, that at $m=n-1$, $B(0,n-1)=\overline{B}(n-1)=A(n-1)$. This behavior for $m\neq 0$ is sufficient, by virtue of the sum rule (12), to determine the variations of $B(k,0)$ with respect to k. In general, the summations in (12) consist of a total of $n-1$ terms, which are weighted towards smaller values of m as k decreases in magnitude (cf. Fig. 1). Thus, $B(k,0)$ grows smaller as k decreases from $k=n-1$, reaching a minimum value at $k=0$ or 1 for $n=$odd or even, respectively. From the recursion relation (16) we also have immediately

$$B^0(k-2,0)<B^0(k,0)\,. \tag{17}$$

While this behavior is perhaps not surprising on the basis of physical characteristics of the states,[4] of interest here is that mathematically it is a direct consequence of the sum rule (12). Additional interpretation of the $B(k,0)$ appears in the following section.

E. Characteristics of the $D(nk,lm)$

Numerical evaluation of the $D(nk,lm)$ presents no difficulty, and we discuss here only general properties of the coefficients relevant to the interpretation of $B(k,m)$. Analytic evaluation for $m>0$ shows that coefficients with $l=m$ and $l=m+1$ are, respectively, slowly decreasing and increasing functions as k increases. With the fact that $A(m)>A(m+1)$, this behavior explains the near constancy of $B(k,m)$ for fixed $m>0$, due to a favorable addition of leading-order terms in Eq. (8). A rigorous proof of this approximate invariance awaits a general derivation of the $A(l)$ in a form suitable to interpretation (i.e., in some leading-order approximation) via Eq. (8).

For $m=0$, representative terms in (8) are

$$B(k,0)=A(0)n^{-1}+A(1)\left(\frac{3k^2}{n(n^2-1)}\right)+A(2)\left(\frac{5(3k^2-n^2+1)^2}{4n(n^2-1)(n^2-4)}\right)+\cdots$$
$$+A(n-2)\left(\frac{k^2(n-1)(n-2)!^4}{2(2n-4)!\beta(k)}\right)+A(n-1)\left(\frac{(n-1)!^4}{(2n-2)!\beta(k)}\right), \tag{18}$$

with

$$\beta(k)=[\tfrac{1}{2}(n-1+k)]!^2[\tfrac{1}{2}(n-1-k)]!^2. \tag{19}$$

Other special cases are

$$D(n0,l0)=\frac{(2l+1)(n-l-1)!}{(n+l)!}\left(\frac{l![\frac{1}{2}(n-1+l)]!}{(\frac{1}{2}l)!^2[\frac{1}{2}(n-1-l)]!}\right)^2,\quad l+1,\ n=\text{odd only} \tag{20}$$

and

$$D(nn-1,l0)=\frac{(2l+1)(n-1)!^2}{(n+l)!(n-1-l)!}. \tag{21}$$

In general, the $D(nk,lm)$ vanish when $k=0$ if $n+l$ is an even integer. Since only odd values of n have $k=0$ states,

$$D(n0,lm)=0,\quad l=\text{odd integer}.$$

General features of the coefficients also obtain from the large-n limit, for which the 3-j symbols reduce to associated Legendre functions.[9] Thus, for large n and fixed l,

$$D(nk,l0)\approx\frac{2l+1}{n}[P_l(x)]^2,\quad n\gg l, \tag{22a}$$

$$x=k(n^2-1)^{-1/2}, \tag{22b}$$

where P_l is the Legendre polynomial. Equation (22) is exact for $l=0,1$, and gives good estimates of the high-n coefficients for values of l roughly $<n^{1/2}$.

Note in particular the large variation in the $l=1$ coefficient, behaving as k^2n^{-3}. This explains the qualitative behavior of the $B(k,0)$ for increasing k to the extent that the $A(1)$ contribution, which contains the $np\to 1s$ transition, dominates the expansion (18). The $A(0)$ contribution to (18) is constant with respect to k.

In the large-l regime, with $l=n-1-c$, values of $D(nk,l0)$ near $k=0$ behave as $n^{-1/2}$ or $n^{-3/2}$ for even and odd c, respectively. For large k, the coefficients are damped as 2^{-2n} times a power of n. These observations illustrate a shift in the concentration of larger $D(nk,l0)$ coefficients from the large-l region to the small-l region as k increases from zero. This explains the large variations in $B(k,0)$ with respect to k beyond just the $l=1$ contributions. The interpretation here is somewhat more detailed than that based on the sum rule in Sec. III D.

Although we have demonstrated that the coupling coefficients $D(nk,lm)$ are not essential to the determination of approximate values of the $B(k,m)$, Tarter[7] has noted their importance to the radiative attenuation of a beam of Stark Rydberg states resulting from an initial distribution of field-free states.[10]

IV. MODEL APPROXIMATION OF AVERAGE TRANSITION PROBABILITIES

A. Field-free distribution

To illustrate the behavior of the Stark transition probabilities $B(k,m)$ noted in the previous sections, we consider here the average probabilities $\overline{B}(m)$ and $B^0(k,0)$ determined from the following model for $A(l)$:

$$A^0(l)=A(1)[1+\alpha(l-1)]^{-2}. \tag{23}$$

Although this form is admittedly crude, it represents the general behavior of $A(l)$ for $l>0$ if α is chosen so that $A^0(n-1)$ reproduces the exact result $A(n-1)$. Analysis of the spherical probabilities in Ref. 1 shows surprisingly little variation in α over the range $3\leq n\leq 25$, with

$$\alpha=0.7148\pm 0.0004. \tag{24}$$

Using an asymptotic expansion for the exact[4] expression for $A(n-1)$ gives the following result for $l>0$:

$$A^0(l)=\left(\frac{1+\alpha(n-2)}{1+\alpha(l-1)}\right)^2\frac{(2n-1)(2n^2-n-1)}{n^6(n-1)^2}\times 2.6759\times 10^9\ \text{sec}^{-1}. \tag{25}$$

We find that $A^0(l)\leq A(l)$, with the largest deviations of several percent occurring for $l<\frac{1}{2}n$. Substitution of $A^0(l)$ into Eq. (11a) for $T(n)$ suggests that for large n the average transition probability from level n is $n^{-2}T^0(n)\approx n^{-5}\ln n$. This n dependence is slightly smaller than the statistical value $n^{-2}T(n)\approx n^{-4.5}$ usually quoted.[4,11]

Equation (25) is not applicable to the $l=0$ transition. For our purposes, we have fitted the exact[1] $A(0)$ for $10\leq n\leq 25$ as follows:

$$A^0(0)=[5.97/n^2(n+1.46)]\times 10^8\ \text{sec}^{-1}. \tag{26}$$

A more accurate fit is not justified at present.

B. Stark transitions

Substitution of $A^0(l)$ into Eq. (13b) gives reasonable estimates of the $\overline{B}(m)$, on the order of several percent below the exact values as determined from the data of Ref. (1). The error is compounded in

TABLE I. Comparison of $n=10$-level hydrogen-atom Stark-decay transition probabilities from approximation formulas in Sec. IV B with exact values. Units are 10^6 sec^{-1}.

i	$\bar{B}(i)$ Approx.[a]	$\bar{B}(i)$ Exact[b]	$\bar{B}(i,0)$ Approx.[a]	$\bar{B}(i,0)$ Exact[b]
1	1.0905	1.0871	0.4753	0.4806
2	0.5472	0.5523		
3	0.3623	0.3658	0.5666	0.5685
4	0.2703	0.2722		
5	0.2155	0.2163	0.7757	0.7706
6	0.1791	0.1794		
7	0.1532	0.1532	1.1891	1.1733
8	0.1338	0.1338		
9	0.1186	0.1188	2.1610	2.1473

[a]This paper, using Eqs. (14), (26)–(28).
[b]Reference 1.

the subsequent use of Eq. (14) for $B^0(k,0)$. Greater accuracy, and indeed more insight to the behavior of $\bar{B}(m)$, obtains from the leading-order, upper-bound integral approximation to Eq. (13b) for $m>0$:

$$\bar{B}^0(m) = (n-m)^{-1}A^0(m) + \frac{A^0(1)}{(n-m)}\frac{(n-1-m)}{[1+\alpha(m-\frac{1}{2})][1+\alpha(n-\frac{3}{2})]}. \tag{27}$$

Comparison of results from Eq. (27) with exact values of $\bar{B}(m)$ for $n=10$ appears in the first two columns of Table I. $T(n)$ can be determined from $\bar{B}^0(m)$ upon noting that Eq. (11) rearranges to the exact form

$$T(n) = A(0) + 3(n-1)\bar{B}(1) + 2\sum_{m=2}^{n-1}(n-m)\bar{B}(m). \tag{28}$$

Estimates of $B^0(k,0)$ thus obtain from substitution of Eqs. (27) and (28) into Eq. (14) or, equivalently, by use of Eqs. (15) and the recursion relation (16). Values calculated in this way appear in Table I for comparison with exact values from Ref. 1. The accuracy indicated in Table I is typical of that found over the range $2 \leq n \leq 25$, owing in part to a fortuitous cancellation of errors.

One feature of the present approximation is that it allows for the continuation of Stark transition probabilities into the higher-n regime with a minimum of effort. Of course, exact values can be determined from Eq. (8) once the distribution $A(l)$ is specified.

V. DISCUSSION

We have established the connection between the dipole transition probabilities of the hydrogen-atom Stark states and the field-free states, thus avoiding the explicit use of parabolic coordinates. Relative magnitudes of the Stark transition probabilities $B(k,m)$ for $m=0$ and $m\neq 0$ are determined in part by a new sum rule for the $B(k,m)$. Qualitative features of the Stark transition rates were illustrated by means of an approximation formula for the spherical transition rates $A(l)$.

While we have specifically considered only total radiative decay probabilities from a level n, it should be obvious that the key results in Eqs. (8) and (12) are independent of the distribution of final energy levels n'. They thus apply equally well to dipole excitation probabilities, oscillator strengths, and dipole matrix elements, for example. In each case the corresponding function $A(nlm,n')$ in Eq. (4) contains a different distribution function $w(n,n')$.

*Present address: Department of Chemistry, University of Oregon, Eugene, Oregon 97403.

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[10]Interpretation of data for experimental conditions somewhat different than those assumed in Ref. 7b provided the initial motivation for the present work.
[11]Note that if we set $n^{-5}\ln n \equiv n^{-a}$, then $a(n=10) = 4.64$, $a(n=100) = 4.67$.