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Relativistic two-photon decay rates of $2s_{1/2}$ hydrogenic ions

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Rates are calculated for the decay of metastable $2s_{1/2}$ ions to the ground state by the simultaneous emission of two photons. The calculation includes all relativistic and retardation effects, and all combinations of photon multipoles which make significant contributions up to $Z = 100$. Summations over intermediate states are performed by constructing a finite-basis-set representation of the Dirac Green's function. The estimated accuracy of the results is ± 10 ppm for all Z up to 100. The decay rates are about 20 $(\alpha Z)^2$ % larger than an earlier calculation by Johnson owing to the inclusion of higher-order retardation effects. The general question of gauge invariance in two-photon transitions is discussed.

I. INTRODUCTION

The simultaneous emission of two electric dipole ($E1$) photons is the dominant decay mechanism to the ground state for the $2s_{1/2}$ state of hydrogen. A number of previous calculations for this process have been made, beginning with the early estimates of Breit and Teller.[1] More accurate non-relativistic calculations were done by a number of authors,[2-4] culminating in the work of Klarsfeld.[4] The two-photon decay of neutral hydrogen is difficult to measure because the rate is only 8.229 sec^{-1}. However, the emission has been observed in an experiment by O'Connel *et al.*[5]

In recent years, interest has centered on two-photon transitions in heavier hydrogenic ions. Since the decay rate increases as Z^6 along the isoelectronic sequence, accurate atomic-beam measurements of the decay rates become feasible. Such measurements have been performed for He$^+$, Li^{2+}, O^{7+}, F^{8+}, S^{13+}, and Ar^{17+} (see Table V for references). An accurate value of the two-photon decay rate is required in experiments to derive the Lamb shift from the electric-field quenching rate of the $2s_{1/2}$ state in ions such as Ar^{17+}.[6]

For these high-Z ions, relativistic corrections become important. The first relativistic calculation of the decay rates was done by Johnson.[7] His calculation, in effect, replaces the usual summations over intermediate states by a numerical evaluation of the relativistic Green's function for the electron. The major computational step in his work is the numerical solution of inhomogeneous Dirac equations at each frequency for the emitted photons. In the present paper, we apply a relativistic finite-basis-set method described previously[8] to perform directly the summations over intermediate states. Except for matrix diagonalizations, the entire calculation is done analytically. The method therefore has the advantages

of being very efficient and easy to apply. We also include some higher-order corrections to the radiative transition operators which are not contained in Johnson's work. Our results, therefore, differ from his at high Z. The new value for Ar^{17+} alters by a small but significant amount the recent Lamb-shift measurements in Ar^{17+} by Gould and Marrus.[6]

II. THEORY OF TWO-PHOTON TRANSITIONS

In this section, we obtain in a computationally convenient form a general expression for the two-photon emission rate for arbitrary combinations of electric and magnetic multipoles, and for an arbitrary choice of gauge for the electromagnetic potentials. The basic expression for the differential emission rate is[9] (in atomic units)

$$\frac{dw}{d\omega_1} = \frac{\omega_1 \omega_2}{(2\pi)^3 c^2} \left| \sum_n \frac{\langle f|\vec{A}_2^*|n\rangle\langle n|\vec{A}_1^*|i\rangle}{E_n - E_i + \omega_1} + \frac{\langle f|\vec{A}_1^*|n\rangle\langle n|\vec{A}_2^*|i\rangle}{E_n - E_i + \omega_2} \right|^2 d\Omega_1 d\Omega_2 , \quad (2.1)$$

where i and f denote the initial and final states, ω_j is the frequency, and $d\Omega_j$ the element of solid angle for the jth photon. The summation over n includes integrations over the continua for both positive and negative energy solutions to the Dirac equation. The photon frequencies satisfy the energy-conserving requirement

$$E_i - E_f = \omega_1 + \omega_2 . \quad (2.2)$$

For photon plane waves with propagation vector $\vec{k}_j$ and polarization vector $\hat{e}_j$ ($\hat{e}_j \cdot \vec{k}_j = 0$), the operators $\vec{A}_j^*$ in (2.1) are given by

$$\vec{A}_j^* = \vec{\alpha} \cdot (\hat{e}_j + G\hat{k}_j)e^{-i\vec{k}_j \cdot \vec{r}} - Ge^{-i\vec{k}_j \cdot \vec{r}} , \quad (2.3)$$

where G is an arbitrary gauge parameter controlling the contribution from fictitious longitudinal and scalar photon states. One would expect the final results to be independent of

G from the general requirement of gauge invariance. It is explicitly demonstrated in the Appendix that (2.1) is in fact independent of G, provided that the set of intermediate states labeled by n is complete and exact. One can even use different G's for different photons. The degree to which the results depend on G is therefore a check on the accuracy of the calculation.

The integrals over $\vec{k}_1$ and $\vec{k}_2$ in (2.1) are most easily evaluated by making use of the partial-wave expansions[10]

$$\hat{e}e^{-i\vec{k}\cdot\vec{r}} = \sum_{L,M,\lambda} [\hat{e}\cdot\vec{Y}_{LM}^{(\lambda)}(\hat{k})]\vec{a}_{LM}^{(\lambda)}* , \tag{2.4}$$

$$e^{-i\vec{k}\cdot\vec{r}} = \sum_{L,M} Y_{LM}(\hat{k})\Phi_{LM}^* , \tag{2.5}$$

where the $Y_{LM}^{(\lambda)}$ are related to the vector spherical harmonics by

$$\vec{Y}_{LM}^{(0)}(\hat{k}) = \vec{Y}_{L,L,M}(\hat{k}) , \tag{2.6}$$

$$\vec{Y}_{LM}^{(1)}(\hat{k}) = -i\hat{k}\times\vec{Y}_{LM}^{(0)}(\hat{k}) , \tag{2.7}$$

$$\vec{Y}_{LM}^{(-1)}(\hat{k}) = \hat{k}Y_{LM}(\hat{k}) , \tag{2.8}$$

and the coefficients $\vec{a}_{LM}^{(\lambda)}$ and Φ_{LM} are given by

$$\vec{a}_{LM}^{(0)} = g_L(kr)\vec{Y}_{L,L,M}(\hat{r}) , \tag{2.9}$$

$$\vec{a}_{LM}^{(1)} = \left(\frac{L}{2L+1}\right)^{1/2} g_{L+1}(kr)\vec{Y}_{L,L+1,M}(\hat{r})$$
$$+ \left(\frac{L+1}{2L+1}\right)^{1/2} g_{L-1}(kr)\vec{Y}_{L,L-1,M}(\hat{r}) , \tag{2.10}$$

$$\vec{a}_{LM}^{(-1)} = -\left(\frac{L+1}{2L+1}\right)^{1/2} g_{L+1}(kr)\vec{Y}_{L,L+1,M}(\hat{r})$$
$$+ \left(\frac{L}{2L+1}\right)^{1/2} g_{L-1}(kr)\vec{Y}_{L,L-1,M}(\hat{r}) , \tag{2.11}$$

$$\Phi_{LM} = g_L(kr)Y_{LM}(\hat{r}) , \tag{2.12}$$

$$g_L(kr) = 4\pi i^L j_L(kr) , \tag{2.13}$$

and $j_L(kr)$ is a spherical Bessel function. Terms with $\lambda = 1$ are electric multipoles and terms with $\lambda = 0$ are magnetic multipoles. The $\lambda = -1$ parts and Φ_{LM} are the longitudinal and scalar terms, respectively. Using the fact that

$$\hat{k}\cdot\vec{Y}_{LM}^{(-1)}(\hat{k}) = Y_{LM}(\hat{k}) , \tag{2.14}$$

the operator $\vec{A}_j^*$ has the partial-wave expansion

$$\vec{A}_j^* = \sum_{\lambda,L,M} [\hat{e}_j\cdot\vec{Y}_{LM}^{(\lambda)}(\hat{k}_j)]\vec{a}_{LM}^{(\lambda)}(r)* , \tag{2.15}$$

where $\hat{e}_j$ is now an arbitrary polarization vector (not necessarily transverse) and

$$\bar{a}_{LM}^{(\lambda)}* = \begin{cases} \vec{\alpha}\cdot\vec{a}_{LM}^{(\lambda)}*, & \lambda = 1,0 \\ G(\vec{\alpha}\cdot\vec{a}_{LM}^{(-1)}* - \Phi_{LM}^*), & \lambda = -1 . \end{cases} \tag{2.16}$$

As shown in the Appendix, the contribution from $\lambda = -1$ vanishes identically if exact wave functions are used, thereby ensuring gauge invariance separately for each partial wave, and nonvanishing contributions only from transverse polarization states.

Using these expressions, Eq. (2.1) for the differential emission rate becomes

$$\frac{dw}{d\omega_1} = \frac{\omega_1\omega_2}{(2\pi)^3 c^2} \sum_{\text{all }L,M,\lambda} (B_{L_1M_1\lambda_1}^{L_2M_2\lambda_2} + B_{L_2M_2\lambda_2}^{L_1M_1\lambda_1})(B_{L_1'M_1'\lambda_1'}^{L_2'M_2'\lambda_2'} + B_{L_2'M_2'\lambda_2'}^{L_1'M_1'\lambda_1'})* C_{L_2'M_2'\lambda_2'}^{L_2M_2\lambda_2} C_{L_1'M_1'\lambda_1'}^{L_1M_1\lambda_1} d\Omega_1 d\Omega_2 , \tag{2.17}$$

where

$$B_{L_1M_1\lambda_1}^{L_2M_2\lambda_2} = \sum_n \frac{\langle f|\bar{a}_{L_2M_2}^{(\lambda_2)}*|n\rangle\langle n|\bar{a}_{L_1M_1}^{(\lambda_1)}*|i\rangle}{E_n - E_i + \omega_1} , \tag{2.18}$$

$$C_{L_1'M_1'\lambda_1'}^{L_1M_1\lambda_1} = [\hat{e}_1\cdot\vec{Y}_{L_1M_1}^{(\lambda_1)}(\hat{k}_1)]*[\hat{e}_1\cdot Y_{L_1'M_1'}^{(\lambda_1')}(\hat{k}_1)] , \tag{2.19}$$

and similarly for $C_{L_2'M_2'\lambda_2'}^{L_2M_2\lambda_2}$. The C coefficients contain complete information on the polarization and angular correlation of the emitted photons for each combination of multipoles. The summation in (2.17) is over all superscripts and subscripts on the B and C coefficients.

The total decay rate is obtained by summing (2.17) over $\hat{e}_1$, $\hat{e}_2$ and integrating over $d\Omega_1$, $d\Omega_2$. This is easily accomplished by noting that

$$\int \sum_{\hat{e}_1} C_{L_1'M_1'\lambda_1'}^{L_1M_1\lambda_1} d\Omega_1 = \delta_{L_1,L_1'}\delta_{M_1,M_1'}\delta_{\lambda_1,\lambda_1'} \tag{2.20}$$

with the result that,

$$\frac{dW}{d\omega_1} \equiv \int\int \sum_{\hat{e}_1,\hat{e}_2} \frac{dw}{d\omega_1} d\Omega_1 d\Omega_2 = \frac{\omega_1\omega_2}{(2\pi)^3 c^2} \sum_{L_1,M_1,\lambda_1,L_2,M_2,\lambda_2} |B_{L_1M_1\lambda_1}^{L_2M_2\lambda_2} + B_{L_2M_2\lambda_2}^{L_1M_1\lambda_1}|^2 . \tag{2.21}$$

Cross terms involving different multipoles for the same photon are present in (2.17), but integrate to zero

in (2.21).

The reduction to radial integrals of the matrix elements in (2.18) has been discussed by Grant.[11] The general matrix element is

$$\langle \alpha | \bar{a}_{LM}^{(\lambda)*} | \beta \rangle = (-1)^{j_\alpha - m_\alpha} \begin{pmatrix} j_\alpha & L & j_\beta \\ -m_\alpha & M & m_\beta \end{pmatrix} (-i)^{L+\lambda-1} (-1)^{j_\alpha - 1/2} \left(\frac{4\pi}{2L+1} \right)^{1/2}$$

$$\times [j_\alpha, j_\beta]^{1/2} \begin{pmatrix} j_\alpha & L & j_\beta \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \bar{M}_{\alpha\beta}^{(\lambda, L)} , \tag{2.22}$$

where

$$\bar{M}_{\alpha\beta}^{(1,L)} = \left[\left(\frac{L}{L+1} \right)^{1/2} [(\kappa_\alpha - \kappa_\beta) I_{L+1}^+ + (L+1) I_{L+1}^-] - \left(\frac{L+1}{L} \right)^{1/2} [(\kappa_\alpha - \kappa_\beta) I_{L-1}^+ - L I_{L-1}^-] \right] ,$$

$$\bar{M}_{\alpha\beta}^{(0,L)} = \frac{(2L+1)}{[L(L+1)]^{1/2}} (\kappa_\alpha + \kappa_\beta) I_L^+ ,$$

$$\bar{M}_{\alpha\beta}^{(-1,L)} = -G[(2L+1) J^{(L)} + (\kappa_\alpha - \kappa_\beta)(I_{L+1}^+ + I_{L-1}^+) - L I_{L-1}^- + (L+1) I_{L+1}^-] ,$$

$$I_L^\pm = \int_0^\infty (g_\alpha f_\beta \pm f_\alpha g_\beta) j_L \left(\frac{\omega r}{c} \right) dr ,$$

$$J_L = \int_0^\infty (g_\alpha g_\beta + f_\alpha f_\beta) j_L \left(\frac{\omega r}{c} \right) dr ,$$

g_α and f_α are the large and small components of the radial Dirac wave function as defined by Grant, and ω is the photon frequency. The notation $[j, k, \ldots]$ means $(2j+1)(2k+1)\ldots$.

The results can be further simplified by extracting explicitly the summations over magnetic quantum numbers in (2.21) for intermediate states with total angular momentum j. For this purpose we define the radial integral part of (2.18) for a particular combination of multipoles to be

$$S^j(2,1) = \sum_{n_j} \frac{\bar{M}_{f,n_j}^{(\lambda_2, L_2)}(\omega_2) \bar{M}_{n_j,i}^{(\lambda_1, L_1)}(\omega_1)}{E_n - E_i + \omega_1} \Delta^j(2,1) , \tag{2.23}$$

where

$$\Delta^j(2,1) = \frac{4\pi [j_i, j, j_f]^{1/2}}{[L_1, L_2]^{1/2}} \begin{pmatrix} j_f & L_2 & j \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} j & L_1 & j_i \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}$$

together with the factor

$$\Theta(2,1) = (2j+1)^{1/2} \sum_{m_j} (-1)^{m_j + m_f + 1} \begin{pmatrix} j_f & L_2 & j \\ -m_f & M_2 & m_j \end{pmatrix} \begin{pmatrix} j & L_1 & j_i \\ -m_j & M_1 & m_i \end{pmatrix} . \tag{2.24}$$

The decay rate summed over m_f and averaged over m_i is then

$$\frac{d\overline{W}}{d\omega_1} = \frac{\omega_1 \omega_2}{(2\pi)^3 c^2 (2j_i + 1)} \sum_{L_1, M_1, \lambda_1, L_2, M_2, \lambda_2, m_f, m_i} \left(\sum_j [\Theta^j(2,1) S^j(2,1) + \Theta^j(1,2) S^j(1,2)] \right)^2 . \tag{2.25}$$

Using the sum rules

$$\sum_{M_1, M_2, m_f, m_i} \Theta^j(2,1) \Theta^{j'}(2,1) = \delta_{j,j'} \tag{2.26}$$

and

$$\sum_{M_1, M_2, m_f, m_i} \Theta^j(2,1) \Theta^{j'}(1,2) = [j, j']^{1/2} (-1)^{2j' + L_1 + L_2} \begin{Bmatrix} j_f & j' & L_1 \\ j_i & j & L_2 \end{Bmatrix} , \tag{2.27}$$

the final expression for the decay rate is

$$\frac{d\overline{W}}{d\omega_1} = \frac{\omega_1 \omega_2}{(2\pi)^3 c^2 (2j_i + 1)} \sum_{L_1, \lambda_1, L_2, \lambda_2, j} \left[[S^j(2,1)]^2 + [S^j(1,2)]^2 \right.$$

$$\left. + 2 \sum_{j'} (-1)^{2j' + L_1 + L_2} [j, j']^{1/2} \begin{Bmatrix} j_f & j' & L_1 \\ j_i & j & L_2 \end{Bmatrix} S^j(2,1) S^{j'}(1,2) \right] . \tag{2.28}$$

The form of Eq. (2.28) is completely general and applies to any two-photon transition between states with definite total angular momenta j_i and j_f. For transitions in nonhydrogenic systems, only the definitions of the radial integrals need be altered.

III. COMPUTATIONAL METHOD

Since the initial- and final-state solutions to the Dirac equation are known exactly, the major computational difficulty is the summation over complete sets of intermediate states with angular momentum j in the definition of $S^j(2,1)$ [Eq. (2.23)]. We replace the infinite summations (including integrations over the positive and negative-energy continua) by finite summations over variationally determined sets of discrete pseudostates. The method has been described in detail previously,[8] and is only briefly summarized here, as follows.

For convenience, we define a real two-component radial spinor by

$$\Phi(r) = \begin{pmatrix} g(r) \\ f(r) \end{pmatrix}, \tag{3.1}$$

with the corresponding radial Dirac Hamiltonian (in atomic units)

$$H_r = -i\sigma_y \frac{d}{dr} + \sigma_x \frac{\kappa}{r} + \frac{\sigma_z}{\alpha} - \frac{\alpha Z}{r}, \tag{3.2}$$

such that

$$H_r \Phi = \alpha E \Phi. \tag{3.3}$$

In the variational procedure, the ith eigenvector Φ_i is written in the form

$$\Phi_i(r) = r^{\gamma-1} e^{-\lambda r} \sum_{j=1}^{N} r^j \left[a_{i,j} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + b_{i,j} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right], \tag{3.4}$$

with $\gamma = (\kappa^2 - \alpha^2 Z^2)^{1/2}$ and λ is an adjustable parameter. For a given i, the $a_{i,j}$'s and $b_{i,j}$'s are $2N$ linear variational parameters determined by the conditions

$$\int_0^\infty \Phi_i^\dagger \Phi_j \, dr = \delta_{i,j}, \tag{3.5}$$

$$\int_0^\infty \Phi_i^\dagger H_r \Phi_j \, dr = \alpha \epsilon_i \delta_{ij}, \tag{3.6}$$

in analogy with the usual nonrelativistic variational procedure.[12] We have shown[8] that for a Coulomb potential, the ϵ_i provide bounds on the Dirac spectrum, and the Φ_i satisfy a number of sum rules to high accuracy. The discrete variational basis set therefore provides an accurate description of the complete Dirac spectrum that systematically improves as the basis set is enlarged. These basis sets are used in place of the actual Dirac spectrum in the summation over intermediate states in (2.21). Only a single diagonalization step is required for each Z and j for all photon frequencies and combinations of multipoles. All integrals over spherical Bessel functions can be evaluated analytically by use of the formula

$$\int_0^\infty e^{-\lambda r} r^\gamma j_l(kr) \, dr = \frac{(\pi/2k)^{1/2} (k/2\lambda)^{l+1/2} \Gamma(\gamma+l+1)}{\lambda^{\gamma+1/2} \Gamma(l+\frac{3}{2})} \, _2F_1 \left[\frac{\gamma+l+1}{2}, \frac{\gamma+l+2}{2}; l+\frac{3}{2}; -\left(\frac{k}{\lambda}\right)^2 \right]. \tag{3.7}$$

IV. RESULTS

Although the summations over multipoles and j,j' in (2.28) are in principle, infinite, only the first few terms make significant contributions, even for high Z. The terms included and the approximate magnitude of their contributions to the total decay rates are shown in Table I. The numerical values give the leading term in an expansion in powers of $(\alpha Z)^2$. The values for $2E1$ and $2M1$ agree with those obtained previously.[4,7] The others have not been calculated before.

The accuracy of the calculations was checked by investigating the dependence of the results on both the size of the basis set and the gauge parameter. Equation (2.28) for the decay rate, which was derived from the plane-wave photon states, depends only quadratically on G since cross terms between different L, M, λ states for the same photon integrate to zero in (2.20). However, a different gauge transformation can be applied instead, directly to the spherical photon states[11] by defining matrix elements

$$\overline{\mathfrak{M}}_{\alpha,\beta}^{(1,L)} = \overline{M}_{\alpha,\beta}^{(1,L)} - \overline{M}_{\alpha\beta}^{(-1,L)}, \tag{4.1}$$

$$\overline{\mathfrak{M}}_{\alpha,\beta}^{(0,L)} = \overline{M}_{\alpha,\beta}^{(0,L)}, \tag{4.2}$$

$$\overline{\mathfrak{M}}_{\alpha,\beta}^{(-1,L)} = 0, \tag{4.3}$$

TABLE I. Terms included in the multipole expansion of the two-photon decay rate.

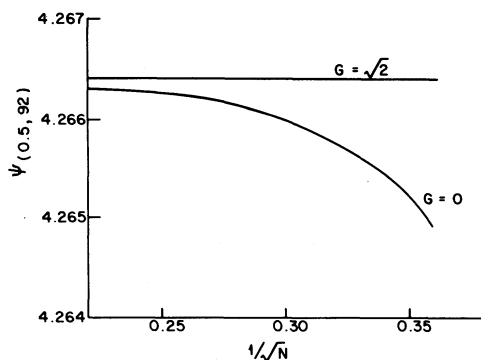| Multipoles	Intermediate states	Nonrelativistic contribution (sec^{-1})
$2E1$	$p_{1/2}, p_{3/2}$	$8.229 \, Z^6$
$E1$-$M2$	$p_{3/2}$	$2.537 \times 10^{-10} Z^{10}$
$2M1$	$s_{1/2}, d_{3/2}$	$1.380 \times 10^{-11} Z^{10}$
$2E2$	$d_{3/2}, d_{5/2}$	$4.907 \times 10^{-12} Z^{10}$
$2M2$	$p_{3/2}$	$4.089 \times 10^{-22} Z^{14}$
$E2$-$M1$	$d_{3/2}$	$1.638 \times 10^{-23} Z^{14}$

FIG. 1. Variation of the integrated decay rate with the size of the basis set at $Z=92$ for two different values of the gauge parameter G.

FIG. 2. Variation of the integrated decay rate with λ at $Z=40$ with a 2×14 term basis set. The value of λ is obtained from Eq. (4.5) for a given n.

and using the $\overline{\mathfrak{M}}$'s in place of the $\overline{M}$'s in (2.28). Since $\overline{M}_{\alpha,\beta}^{(-1,L)}$ is linear in G, the final results also now contain terms linear in G. Since the choices $G=0$ and $G=\sqrt{2}$ reduce to the dipole velocity and length forms in the nonrelativistic limit,[11] all calculations were done with the $\overline{\mathfrak{M}}$ matrix elements. The exact results remain independent of G since

$$\vec{\mathfrak{a}}_{LM}^{(-1)} = -\frac{ic}{\omega}\vec{\nabla}\Phi_{LM} \qquad (4.4)$$

(see the Appendix).

Figure 1 shows the dependence of the differential decay rate on the size of the basis set at $Z=92$ for $G=0$ and $G=\sqrt{2}$. Since the $G=\sqrt{2}$ results are more rapidly convergent, this value was used in all the calculations. With a 2×14 term basis set, the differences between the two sets of values slowly increase from $\sim10^{-5}\%$ at $Z=1$ to $5\times10^{-3}\%$ at $Z=92$. The convergence test suggests that the $G=\sqrt{2}$ values are more accurate than these differences would indicate. The estimated uncertainty arising from convergence of the basis set is about ±10 ppm.

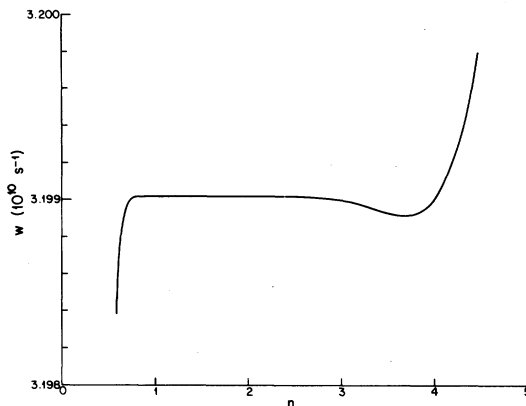The results also depend on the parameter λ in (3.4). For an exact eigenfunction, λ is related

to the principal quantum number n by

$$\lambda(n) = \frac{Z}{[n^2 - 2(n-|\kappa|)(|\kappa|-\gamma)^{1/2}]^{1/2}}. \qquad (4.5)$$

However, a single representative λ must be chosen for the complete spectrum of intermediate states. By varying λ, we find a broad region of stability centered around $\lambda(1.5)$ for the s and p sets of intermediate states, and $\lambda(2)$ for the d set. Figure 2 is a typical curve showing how the integrated decay rate depends on λ.

To present the results, we express the differential decay rate in the standard form[2]

$$\frac{d\overline{W}}{dy} = Z^6\left(\frac{9\alpha^6}{2^{10}}\right)\psi(y,Z)\,\mathrm{Ry}\,, \qquad (4.6)$$

where y is the fraction of the energy carried by one of the two photons. Values of $\psi(y,Z)$ are given in Table II for a number of ions. All of the contributions listed in Table I are included in these figures. Figure 3 shows the shape of the spectral distribution at $Z=1$ and $Z=92$. Relativistic corrections make the curve more shar-

TABLE II. Frequency distribution of the two-photon decay rate. The function $\psi(y,Z)$ in Eq. (4.6) is tabulated.

| $y\backslash Z$	1	20	40	60	80	92
0.0625	2.032 39	1.944 67	1.714 63	1.418 42	1.125 09	0.963 67
0.1250	3.157 92	3.085 15	2.878 08	2.567 69	2.191 90	1.947 84
0.1875	3.844 52	3.786 28	3.615 38	3.343 25	2.983 40	2.728 39
0.2500	4.284 35	4.238 31	4.100 84	3.874 04	3.557 33	3.319 77
0.3125	4.569 58	4.533 08	4.422 73	4.236 02	3.964 68	3.752 29
0.3750	4.748 55	4.718 85	4.628 21	4.471 88	4.237 60	4.048 05
0.4375	4.847 32	4.821 68	4.742 97	4.605 39	4.394 88	4.220 70
0.5000	4.878 92	4.854 64	4.779 90	4.648 66	4.446 29	4.277 50
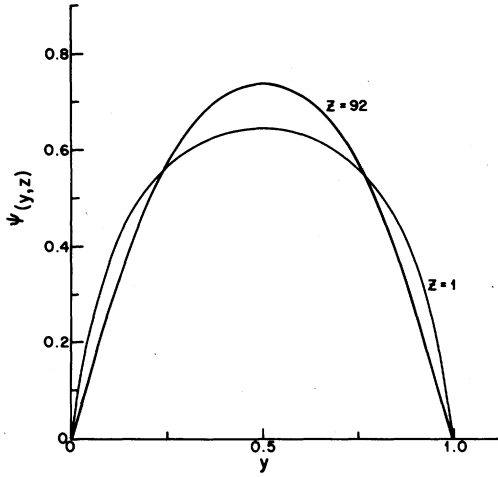
FIG. 3. Shape of the spectral distribution function $\psi(y)$ at $Z=1$ and $Z=92$. The areas under the curves are normalized to unity.

ply peaked at $y=0.5$, and reduce the integrated decay rate. The breakdown of the integrated decay rate $\overline{W}$ into contributions from different combinations of multipoles is shown in Table III for the same selection of ions. Finally, the total two-photon decay rates are given in Table IV for a large number of ions. The results are accurately approximated by the formula

$$\overline{W}=8.229\,43\,Z^6\frac{[1+3.9448(\alpha Z)^2-2.040(\alpha Z)^4]}{[1+4.6019(\alpha Z)^2]}\quad(4.7)$$

in units of $\sec^{-1}$ with an error of $\pm0.05\%$ in the range $1\leqslant Z\leqslant92$. This can be used to estimate the decay rates for ions not listed. The tabulated results do not include the reduced-mass correction factor $(1-m/M)$.

The $2E1$ contributions to the decay rates in Table III are larger than Johnson's[7] by about $20(\alpha Z)^2\%$. The reason is as follows. The $\mathfrak{M}_{\alpha\beta}^{(1)}$ matrix elements arise, after angular integrations, from the operator

$$\vec{a}_{LM}^{(1)*}=\vec{\alpha}\cdot\vec{a}_{LM}^{(1)*}-G(\vec{\alpha}\cdot\vec{a}_{LM}^{(-1)*}-\Phi_{LM}^{*}).\quad(4.8)$$

With the choice $G=[(L+1)/L]^{1/2}$, this reduces to

$$\vec{a}_{LM}^{(1)*}=\left(\frac{L+1}{L}\right)^{1/2}\Phi_{LM}^{*}-\left(\frac{2L+1}{L}\right)^{1/2}$$

$$\times g_{L+1}^{*}\left(\frac{\omega r}{c}\right)\vec{\alpha}\cdot\vec{Y}_{L,L+1,M}^{*}.\quad(4.9)$$

Johnson's calculation contains only the first term of (4.9). The second term, of relative order $(\alpha Z)^2$, accounts for the differences in the results. We were able to reproduce exactly Johnson's values by omitting the second term.

The measured decay rates of the $2s_{1/2}$ state also contain an additive contribution from single-photon $M1$ transitions to the ground state. These rates have been accurately calculated by Johnson.[7] For low Z, they are given by

$$\overline{W}_{M1}=2.496\times10^{-6}Z^{10}$$

in $\sec^{-1}$. The total decay rates, including Johnson's $M1$ values, are compared with the experimental data in Table V. All of the measurements are in agreement with theory, but are not accurate enough to be sensitive to the $20(\alpha Z)^2\%$ difference between the present results and Johnson's[7] calculation. For Fe^{25+}, the difference is 0.75%, which might be large enough to be measurable.

The new two-photon decay rate for Ar^{17+} has a small effect on the Lamb-shift measurement of Gould and Marrus.[6] They determine the Ar^{17+} Lamb shift from the rate at which the $2s_{1/2}$ state is quenched by a $\vec{v}\times\vec{B}/c$ electric field. To lowest order, the total measured decay rate is given by

$$W_{\text{tot}}=W_s+W_p|V|^2/[\hbar^2(S^2+W_p^2/4)],\quad(4.10)$$

where W_s and W_p are the natural $2s_{1/2}$ and $2p_{1/2}$ decay rates, S is the Lamb shift (in radians/sec) $V\simeq0.992\sqrt{3}\,eEa_0/Z$, and E is the field strength (in volts/cm). The experimental conditions are such that the two contributions to (4.10) are roughly equal in magnitude. For fixed W_{tot}, the

TABLE III. Contributions from different combinations of multipoles to the integrated decay rate $\overline{W}$ (in $\sec^{-1}$).

Z	$2E1$ $Z^{-6}\overline{W}$	$E1-M2$ $Z^{-10}10^{10}\overline{W}$	$2M1$ $Z^{-10}10^{11}\overline{W}$	$2E2$ $Z^{-10}10^{12}\overline{W}$	$2M2$ $Z^{-14}10^{22}\overline{W}$	$E2-M1$ $Z^{-14}10^{23}\overline{W}$
1	8.2291	2.5371	1.3804	4.9072	4.089	1.638
20	8.1181	2.5028	1.4046	4.8739	4.098	1.732
40	7.8096	2.4156	1.4778	4.7724	4.133	2.046
60	7.3446	2.3024	1.6005	4.5974	4.216	2.721
80	6.7440	2.1822	1.7737	4.3370	4.392	4.135
92	6.3097	2.1118	1.9030	4.1290	4.578	5.752

TABLE IV. Total two-photon decay rates in sec^{-1} for infinite nuclear mass.

Z	$\overline{W}^a$	Z	$\overline{W}$
1	8.2291	25	1.9672(9)
2	5.2661(2)	26	2.4850(9)
3	5.9973(3)	27	3.1111(9)
4	3.3689(4)	28	3.8628(9)
5	1.2847(5)	29	4.7592(9)
6	3.8347(5)	30	5.8217(9)
7	9.6654(5)	32	8.5405(9)
8	2.1525(6)	34	1.2236(10)
9	4.3612(6)	36	1.7164(10)
10	8.2010(6)	40	3.1990(10)
11	1.4518(7)	42	4.2651(10)
12	2.4451(7)	45	6.4003(10)
13	3.9491(7)	50	1.1869(11)
14	6.1547(7)	56	2.2980(11)
15	9.3017(7)	60	3.4282(11)
16	1.3686(8)	65	5.4387(11)
17	1.9668(8)	70	8.3139(11)
18	2.7682(8)	74	1.1404(12)
19	3.8242(8)	80	1.7701(12)
20	5.1956(8)	85	2.4824(12)
21	6.9530(8)	90	3.4021(12)
22	9.1785(8)	92	3.8361(12)
23	1.1966(9)	100	6.0045(12)
24	1.5423(9)	110	9.8152(12)

^{a} Numbers in parentheses are the powers of 10 by which the numbers are to be multiplied. Rates for ions not listed can be estimated from Eq. (4.7). For the finite nuclear-mass correction, multiply the results by $1-m/M$.

TABLE V. Comparison of theoretical and experimental total decay rates of the $2s_{1/2}$ state (in sec^{-1}).

Ion	Theory	Experiment
He$^+$	526.61	491^{+95}_{-140} [a]
		520 ± 21 [b]
		525 ± 5 [c]
O^{7+}	2.1552×10^6	$(2.21 \pm 0.22) \times 10^6$ [d]
F^{8+}	4.3699×10^6	$(4.22 \pm 0.28) \times 10^6$ [d]
S^{15+}	1.3964×10^8	$(1.37 \pm 0.13) \times 10^8$ [e]
Ar^{17+}	2.8590×10^8	$(2.82 \pm 0.20) \times 10^8$ [e]

^{a} C. A. Kocher, J. E. Clendenin, and R. Novick, Phys. Rev. Lett. 29, 615 (1972).

^{b} M. H. Prior, Phys. Rev. Lett. 29, 611 (1972).

^{c} E. A. Hinds, J. E. Clendenin, and R. Novick, Phys. Rev. A 17, 670 (1978).

^{d} C. L. Cocke, B. Curnutte, J. R. McDonald, J. A. Bednar, and R. Marrus, Phys. Rev. A 9, 2242 (1974).

^{e} R. Marrus and R. W. Schmieder, Phys. Rev. A 5, 1160 (1972).

fractional change in the calculated S resulting from a change in the value of W_s used is

$$\frac{\Delta S}{S} \simeq \frac{\hbar^2(S^2 + W_p^2/4)^2}{2|V|^2 S^2} \frac{W_s}{W_p} \frac{\Delta W_s}{W_s}$$

$$\simeq \frac{2.18 \times 10^{11}}{E^2} \frac{\Delta W_s}{W_s}$$

for Ar^{17+}. Since $\Delta W_s/W_s = 0.0034$ is the fractional correction to the two-photon decay rate, the correction to the Lamb shift ranges from 0.21% to 0.10% for the different field strengths used in the experiment. The average correction of 0.14% for all the runs alters the measured Lamb shift from 38.0 ± 0.6 THz to 38.1 ± 0.6 THz. This slightly improves agreement with the theoretical values 39.0 ± 0.16 THz (Ref. 13) and 38.25 ± 0.025 THz.[14]

V. DISCUSSION

Our results demonstrate that finite-basis-set methods applied to the Dirac equation provide a powerful method for performing exact relati-vistic calculations of atomic properties. We believe the results to be correct to the number of figures quoted within the framework of other approximations made. The most important corrections not included arise from finite nuclear size and quantum electrodynamic effects. These can probably also be treated by perturbation theory within the framework of finite-basis-set methods.

APPENDIX

We consider here the gauge invariance of two-photon transitions. This topic has been previously disucssed by several authors,[15-22] but always within the nonrelativistic electric-dipole approximation. We show that the argument can be made completely general.

As is well known, gauge transformations of the vector and scalar potentials of the form

$$\vec{A}'(\vec{r}, t) = \vec{A}(\vec{r}, t) + \nabla\chi(\vec{r}, t), \tag{A1}$$

$$\phi'(\vec{r}, t) = \phi(\vec{r}, t) - \frac{1}{c} \frac{\partial}{\partial t} \chi(\vec{r}, t), \tag{A2}$$

where $\chi(\vec{r}, t)$ is an arbitrary gauge function, leave the electric and magnetic fields invariant. Assume that $\chi(\vec{r}, t)$ has the form

$$\vec{\chi}(\vec{r}, t) = \chi(\vec{r}) e^{-i\omega t}, \tag{A3}$$

where ω is the transition frequency $E_i - E_f$. After performing time integrations, the transition matrix element for spontaneous emission is

$$T = -i \langle \psi_f | \beta \gamma_\mu A_\mu^* | \psi_i \rangle, \tag{A4}$$

where $A_4 = i\phi$, and the ψ's are eigenfunctions of the Dirac Hamiltonian. The transition operator $t = -i\beta\gamma_\mu A_\mu^*$ can be written in the form

$$t = t_\perp + t_\chi, \tag{A5}$$

where

$$t_\perp = \vec{\alpha} \cdot \hat{e} e^{-i\vec{k}\cdot\vec{r}} \tag{A6}$$

is the transverse part and

$$t_\chi = \vec{\alpha} \cdot \vec{\nabla}\chi^*(\vec{r}) + \frac{i\omega}{c}\chi^*(\vec{r}) \tag{A7}$$

is the gauge-dependent part. Equation (2.3) of the text corresponds to the special choice

$$\chi^*(\vec{r}) = \frac{ic}{\omega} G e^{-i\vec{k}\cdot\vec{r}}. \tag{A8}$$

Matrix elements of t_χ vanish if $\omega = E_i - E_f$ since

$$\langle \psi_f | \vec{\alpha}\cdot\vec{\nabla}\chi^* | \psi_i \rangle = \frac{i}{c}\langle \psi_f | [H, \chi^*] | \psi_i \rangle$$

$$= -i\frac{(E_i - E_f)}{c}\langle \psi_f | \chi^* | \psi_i \rangle, \tag{A9}$$

which cancels the contribution from the second term of (A7). It follows from (A9) that an arbitrary matrix element of t_χ can be written in the form

$$(t_\chi)_{\alpha\beta} = \frac{i}{c}(E_\alpha - E_\beta + \omega)\langle \psi_\alpha | \chi^* | \psi_\beta \rangle. \tag{A10}$$

Two-photon transitions require the evaluation of quantities of the form

$$Q = \sum_n \left(\frac{\langle f | t^{(2)} | n \rangle \langle n | t^{(1)} | i \rangle}{E_n - E_i + \omega_1} + \frac{\langle f | t^{(1)} | n \rangle \langle n | t^{(2)} | i \rangle}{E_n - E_i + \omega_2} \right). \tag{A11}$$

In general, we can adopt different gauge functions χ_1 and χ_2 for different photons in the definitions of $t^{(1)}$ and $t^{(2)}$. Using (A5) and (A10), Q can immediately be written in the form

$$Q = \sum_n \left(\frac{\langle f | t_\perp^{(2)} | n \rangle \langle n | t_\perp^{(1)} | i \rangle}{E_n - E_i + \omega_1} + \frac{\langle f | t_\perp^{(1)} | n \rangle \langle n | t_\perp^{(2)} | i \rangle}{E_n - E_i + \omega_2} \right)$$

$$+ \frac{i}{c}\sum_n \left(\langle f | t_\perp^{(2)} | n \rangle \langle n | \chi_1^* | i \rangle - \langle f | \chi_1^* | n \rangle \langle n | t_\perp^{(2)} | i \rangle + \langle f | t_\perp^{(1)} | n \rangle \langle n | \chi_2^* | i \rangle - \langle f | \chi_2^* | n \rangle \langle n | t_\perp^{(1)} | i \rangle \right)$$

$$- \frac{1}{c^2}\sum_n \left[\langle f | \chi_2^*(E_f - H + \omega_2) | n \rangle \langle n | \chi_1^* | i \rangle - \langle f | \chi_1^* | n \rangle \langle n | (H - E_i + \omega_2) \chi_2^* | i \rangle \right], \tag{A12}$$

where E_n has been replaced by H in the last summation.

The first term of (A12) is the usual form for the two-photon decay amplitude in the transverse Coulomb gauge. We denote this term by $Q_\perp$ and perform the summations over n in the other two terms by closure to obtain

$$Q = Q_\perp + \frac{i}{c}\langle f | [t_\perp^{(2)}, \chi_1^*] + [t_\perp^{(1)}, \chi_2^*] | i \rangle$$

$$- \frac{\omega_2}{c^2}\langle f | [\chi_2^*, \chi_1^*] | i \rangle$$

$$- \frac{1}{c^2}\langle f | \chi_2^*(E_f - H)\chi_1^* - \chi_1^*(E_i - H)\chi_2^* | i \rangle. \tag{A13}$$

The commutators in (A13) vanish since χ_1^* and χ_2^* are ordinary scalar functions. The last term can be rewritten in the form

$$- \frac{1}{c^2}\langle f | (E_f - H)\chi_2^*\chi_1^* - \chi_1^*\chi_2^*(E_i - H) | i \rangle$$

$$- \frac{1}{c^2}\langle f | [[H, \chi_2^*], \chi_1^*] | i \rangle. \tag{A14}$$

This also vanishes, provided that $\langle f |$ and $| i \rangle$ are exact eigenvectors. We thus obtain

$$Q = Q_\perp \tag{A15}$$

for arbitrary gauge functions χ_1 and χ_2, provided that the eigenfunctions are exact, and the set of intermediate states is complete.

The above derivation is both simpler and more general than the usual one presented in the non-relativistic electric-dipole approximation.[23] It applies separately to each combination of partial waves if we identify

$$t_\perp^{(i)} = \vec{\alpha} \cdot \vec{a}_{L_i M_i}^{(i)*} \tag{A16}$$

and

$$t_\chi^{(i)} = G(\vec{\alpha}\cdot\vec{a}_{L_i M_i}^{(-1)*} - \Phi_{L_i M_i}^*), \quad i=1,2. \qquad (A17)$$

Since $\vec{a}_{LM}^{(-1)*} = (ic/\omega)\nabla\Phi_{LM}^*$, this corresponds to the choice of gauge function

$$\chi_i^* = \frac{icG}{\omega}\Phi_{L_i M_i}^* \qquad (A18)$$

and Eq. (A10) remains valid for the matrix elements of t_χ. The rest of the derivation follows exactly as before.

A completely analogous derivation can be written down for any other two-photon process. It can also be generalized to higher multiphoton processes involving summations over two or more sets of intermediate states.

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