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Temperature Dependence of the Lamb Shift

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The temperature-dependent correction to the Lamb shift of a single-electron atom exposed to black-body radiation at temperature T is considered. At room temperatures, the correction for $Z>1$ is dominated by a shift, not considered before, of the $2s_{1/2}$ level, involving $2p_{3/2}$ as an intermediate state, and is given by $\pi\alpha^3 Z^2 (kT)^2/8m$. This competes with another shift $\approx x(kT)^4/Z^4(\alpha m)^3$ discussed by Walsh, where x is a purely numerical but remarkably large coefficient of order 300.

Walsh[1] has recently reconsidered the temperature dependence of the radiative self-energy of an atom exposed to black-body radiation. Here we devise what we feel is a more transparent approach; distinguish the "total" energy shift from the "adiabatic" shift which applies if the photon occupation numbers do not adjust to the presence of the atom; correct some minor errors; and exhibit a contribution not considered previously, which is formally of higher than leading order in e^2, but which in many systems can nevertheless dominate the temperature dependence.

We start from an expression suggested by Feynman[2] for that part of the electromagnetic self-energy which is due to the quantized nature of the radiation field. We have discussed elsewhere[3] its formal connection with the over-all order e^2 self-energy (though here we shall rely on it to higher order in e^2), and the nonrelativistic Bethe formula for the Lamb shift has been derived from it by Power.[4] Consider the normal modes of the radiation field in a quantization volume V; let them have wave vectors $\vec{K}$ and frequencies $\omega=|\vec{K}|$. Introduce an atom into this quantization volume; the allowed $\vec{K}$ values are unaffected, but the frequency of each mode changes[2,5] from ω to $\omega+\delta\omega$:

$$\delta\omega=-2\pi\,\mathrm{Re}f(\omega)/\omega V\ , \tag{1}$$

where $f(\omega)$ is the spin-averaged forward Compton-scattering amplitude from the atom. The consequent shift in the zero-point energy of the field, namely, $2\sum_{\vec{K}}\frac{1}{2}\delta\omega$, was recognized by Feynman as the radiative self-energy of the atom. (The factor 2 counts both polarization states.)

In a black-body cavity at temperature T, the total energy shift due to the atom is clearly

$$\Delta U_{\text{total}}=2\sum_{\vec{K}}\ \delta\omega\,\frac{d}{d\omega}\left[(n+\tfrac{1}{2})\omega\right]\ , \tag{2}$$

where, with k the Boltzmann constant,

$$n=(e^{\beta\omega}-1)^{-1},\quad \beta=1/kT\ . \tag{3}$$

Equation (2) applies if the occupation numbers n reach their new equilibrium values after the atom is introduced. In the other extreme, where the n are unchanged, (2) is replaced by

$$\Delta U_{\text{adiabatic}}=2\sum_{\vec{K}}\delta\omega\,(n+\tfrac{1}{2})\ . \tag{4}$$

We separate both (2) and (4) into their zero-point parts, and their temperature-dependent parts $\Delta(T)$, $[\Delta(0)\equiv 0]$; e.g.,

$$\Delta U_{\text{adiabatic}}=\Delta_{\text{adiabatic}}(T)+\sum_{\vec{K}}\delta\omega\ .$$

The T-dependent parts are related by

$$\Delta_{\text{total}}(T)=(1+\beta d/d\beta)\,\Delta_{\text{adiabatic}}(T)\ . \tag{5}$$

For simplicity, we shall consider only $\Delta_{\text{adiabatic}}(T)$ from now on, and denote it by Δ; thus,

$$\Delta=2\sum_{\vec{K}}\delta\omega/(e^{\beta\omega}-1)\ . \tag{6}$$

(Since, as we shall find, Δ consists of parts proportional to β^{-2} and β^{-4}, Δ_{total} and $\Delta_{\text{adiabatic}}$ have opposite signs.)

For the hydrogen atom (and for any one-electron ion if the nuclear mass is taken as infinite), the nonrelativistic dipole approximation yields

$$\mathrm{Re}f=\omega^2\Pi(\omega^2)=\frac{2\alpha}{3}\,\omega^2\sum_i E_{i0}\,|\vec{r}_{i0}|^2\,\frac{1}{E_{i0}^2-\omega^2}\ , \tag{7}$$

where Π is the real part of the electric polarizability, $\sum_i$ runs over all atomic states with the Cauchy principal value prescription for vanishing denominators, and where we have defined $E_{i0}=(E_i-E_0)$, $\vec{r}_{i0}=\langle i|\vec{r}|0\rangle$, with $|0\rangle$ the state whose shift we are calculating. From (6), (1), and (7) we obtain

$$\Delta=-\frac{4\alpha}{3\pi\beta^2}\sum_i E_{i0}\,|\vec{r}_{i0}|^2\int_0^\infty dy\,\frac{y^3}{(e^y-1)}\ \frac{1}{(\beta^2E_{i0}^2-y^2)}\ . \tag{8}$$

Here we come to a crucial point. If one works strictly to order e^2, then there are no contributions to (8) from intermediate states $|i\rangle$ that have the same principal quantum number as $|0\rangle$, i.e., which, nonrelativistically, are degenerate with $|0\rangle$, since for them, and to this order, $E_{i0}=0$. On the other hand, the temperature-dependent shifts Δ, due to the contributions "n" to (4), are minute compared to the zero-temperature shifts, due to the "$\frac{1}{2}$" in

(4). Therefore, when evaluating Δ, we include the true zero-temperature splitting of the nonrelativistically degenerate states into the "unperturbed" problem, so that both the Lamb shift $\lambda = E(2s_{1/2}) - E(2p_{1/2})$, and the fine-structure splitting $\nu = E(2p_{3/2}) - E(2p_{1/2})$ are taken as finite. Here it is essential to have expressed f in terms of the matrix elements of $\vec{r}$ rather than[6] of $\vec{p}$, because $\langle 2s|\vec{p}|2p\rangle = 0$, while

$$\begin{aligned} |\langle 2s_{1/2}|\vec{r}\,|2p_{1/2}\rangle|^2 &= 9a^2 \,, \\ |\langle 2s_{1/2}|\vec{r}\,|2p_{3/2}\rangle|^2 &= 18a^2 \,, \end{aligned} \tag{9}$$

where a is the Bohr radius, so that, with m = electron mass,

$$a = 1/\alpha Z m \;. \tag{10}$$

Accordingly, we subdivide the shift Δ of the $2p_{1/2}$ $(2s_{1/2})$ state into a "degenerate" part Δ_d due to the intermediate states $i = 2s_{1/2}$ ($2p_{1/2}$ and $2p_{3/2}$), and a "nondegenerate" part Δ_{nd} due to all other intermediate states.

The shift Δ_{nd} is the one considered by Walsh. Here the excitations E_{i0} all correspond to orbital excitation energies, $|E_{i0}| \sim (Z\alpha)^2 m$, so that at practicable temperatures $|\beta E_{i0}| \gg 1$, and we can simplify (8) accordingly:

$$\begin{aligned} \Delta_{nd} &= -\frac{4\alpha}{3\pi\beta^4} {\sum_i}' \frac{1}{E_{i0}} |\vec{r}_{i0}|^2 \int_0^\infty dy\, \frac{y^3}{e^y - 1} + O(\beta^{-6}) \,, \\ \Delta_{nd} &\approx -\frac{4\pi^3\alpha}{45} (kT)^4 {\sum_i}' \frac{|\vec{r}_{0i}|^2}{E_{i0}} \;. \end{aligned} \tag{11}$$

The prime on ${\sum_i}'$ excludes states with $n = 2$.

Note the following points. (i) Equations (11) agree with Walsh's state-dependent expression [his Eqs. (6) and (7)] in magnitude but not in sign. (ii) The sign of (11) is easily checked by comparing the *total* energy density of black-body radiation *in vacuo* with that of radiation in a dilute medium consisting of the atoms in question, expressing the refractive index in terms of $\Pi(0)$, and attributing the difference to the self-energy of the atom.[2] (iii) Δ_{nd} has no state-independent part proportional to T^2 at low temperatures, i.e., for $|\beta E_{i0}| \gg 1$. The expression of this type found by Walsh [his Eq. (5), which should actually have its sign reversed] should have been canceled, in his approach, by a shift due to the quadratic interaction Hamiltonian $e^2\vec{A}^2/2m$. Such a T^2-proportional part exists only for a free electron (cf. also the last paragraph of the present paper); it is absent for a bound electron, basically because binding to an atom suppresses the scattering amplitude for low-frequency photons, which, by the Bose-Einstein factor, are precisely those responsible for the leading term when Δ_{nd} is expanded in powers of T. (iv) Dimensionally, the sum in (11) is estimated as $a^2(Z\alpha/a)^{-1} = a^3/Z\alpha$, whence we write, with x_0 a purely numerical coefficient,

$$\Delta_{nd} = x_0 (kT)^4 / Z^4 (\alpha m)^3 . \tag{12}$$

Remarkably, detailed calculation shows that $|x_{2s1/2} - x_{2p_{1/2}}| \sim 300$, a result already implicit in the numbers given by Walsh.

Finally, we turn to the degenerate contribution, which has not been considered before. Here, E_{i0} is either the Lamb shift λ or the fine-structure splitting ν. But in hydrogen for instance we have $\lambda \approx 0.05$ °K and $\nu \approx 0.5$ °K, so that at room temperature, and for all low Z, $|\beta E_{i0}| \ll 1$, and we approximate the integrand of Δ_d by dropping $(\beta E_{i0})^2$ from the denominators altogether. This is a high-temperature approximation, contrasting with the low-temperature approximation which was appropriate to Δ_{nd}. The individual contributions to (8) then become proportional to E_{i0}; since $\nu \gg \lambda$, the dominant effect on the Lamb shift is evidently the displacement of the $2s_{1/2}$ state due to the $i = 2p_{3/2}$ intermediate state, when $E_{i0} \approx \nu = (\alpha Z)^4 m/32$. Accordingly, from (8) and (9) we obtain

$$\begin{aligned} \Delta_d(2s_{1/2}) &= \frac{4\alpha}{3\pi\beta^2}\, \nu\, |\langle 2s_{1/2}|\vec{r}\,|2p_{3/2}\rangle|^2 \int_0^\infty dy\, \frac{y}{e^y - 1} \\ &= \frac{\pi\alpha^3 Z^2}{8}\, \frac{(kT)^2}{m} \approx 5.4 \times 10^{-7}\, T^2 Z^2 \text{ Hz} \;. \end{aligned} \tag{13}$$

From (12) and (13), we estimate the order of magnitude of the ratio

$$\left|\frac{\Delta_d}{\Delta_{nd}}\right| \sim \frac{\pi}{8x_0} (\alpha Z)^6 \left(\frac{m}{kT}\right)^2 \sim \frac{2.2 \times 10^6 Z^6}{x_0 T^2} \;. \tag{14}$$

At 300 °K, (14) takes the value $\sim 25Z^6/x_0$. Because of the large numerical value of x_0, Δ_d dominates Δ_{nd} only for $Z > 1$. But the effect is still very small: For $Z = 2$ at 300°, (13) yields only 0.2 Hz.

For completeness it may be amusing to record the high temperature limit appropriate when $|\beta E_{i0}| \ll 1$ even for orbital excitation, but where retardation may still be neglected, i.e., $\beta \gtrsim a$. In this regime Δ_d and Δ_{nd} combine, up to relativistic corrections of relative order $(\alpha Z)^2$, to reproduce the free-electron shift $\alpha\pi(kT)^2/3m$. This is obtainable directly from (6) and (1) by putting $f = -\alpha/m$, which by virtue of the dipole sum rule is just the high-frequency limit of (7). Of course, at such temperatures the atoms are almost fully ionized, and the problem becomes yet more academic.

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Effect of Core Polarizability on Photoionization Cross-Section Calculations

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The inclusion of dipole polarizability of the core for argon is shown to substantially improve the agreement between the theoretical and experimental photoionization cross sections for the ground-state configuration.

Core polarization has previously been included in the calculation of photoionization cross sections by Klein and Brueckner.[1] Bates[2] found that for potassium, where the cancellation within the matrix element is excessive near the series limit, the inclusion of core polarizability improved the agreement between the calculated and experimental cross sections. The purpose of this paper is to point out the importance of core polarizability in a case where cancellation is only moderate and to suggest an improvement to the scaled Thomas-Fermi (STF) wave functions of Stewart and Rotenberg.[3]

Stewart and Rotenberg introduced the use of a scaling factor to provide a means of empirically improving the wave functions provided by a Thomas-Fermi potential. The resulting wave functions may be computed rapidly making them most practical for the calculation of some atomic parameters such as photoionization cross sections and recombination coefficients, which require large numbers of wave functions. For the ground state the positions of the nodes and maxima compare well with the wave functions of Clementi,[4] but one major defect of the STF wave functions is apparently caused by the neglect of the polarizability of the core.

To include the effect of dipole polarizability of the core in the calculations presented here, the STF potential was modified by adding an effective polarization potential:

$$V_p = \alpha_d/(r^2 + r_c^2)^2 ,$$

where α_d is the dipole polarizability of the core and r_c is the effective radius of the core.[5] The polarizability was derived from the energies of the ng levels by applying the polarization theory of Edlen,[6] while $\langle r\rangle$ for the ground-state wave function for the next-higher ion was used for r_c. The phase of the continuum wave function, and subsequently the amplitude of the cross section, is related to the scale factor used to obtain it. This scale factor is obtained by linear extrapolation in energy from the bound-state values in much the same manner as the quantum-defect extrapolations for the quantum-defect method.[7] For argon, the inclusion of V_p in the calculations reduces the energy dependence of the scale factors for the bound-state wave functions from -0.078 to -0.055 Ry^{-1} for the s series, and from -0.183 to -0.160 Ry^{-1} for the d series. Linear extrapolation seems quite adequate for energies up to a few times the threshold energy. For high values of l, the wave functions are less sensitive of the scale factor, since the amplitudes of these wave functions are small in the non-Coulombic region of the STF potential.

The results for argon with and without polarizability are presented in Table I, where it is apparent that the effect of dipole polarizability of the core is large. For the dipole polarizability of the

TABLE I. Argon I $3p^6$ photoionization cross section.

λ	$\sigma(\alpha_d = 7.4a_0^3)$ $(10^{-18}\,\mathrm{cm}^2)$	$\sigma(\alpha_d = 0)$ $(10^{-18}\,\mathrm{cm}^2)$
787	35.74	107.18
774	37.23	106.66
754	39.14	94.57
671	43.97	65.69
625	44.53	53.48
549	42.21	38.42
490	38.04	29.80
422	31.64	22.37
343	23.45	15.97
289	17.94	12.54