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LETTER TO THE EDITOR

Stark shifts due to black-body radiation

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Abstract. The free energy of the system consisting of a harmonically bound electron coupled via dipole interaction with the radiation field is calculated exactly at finite temperature. A temperature-dependent shift in the *free energy*, $\Delta F_0 = \pi e^2(kT)^2/3\hbar mc^3$ is identified. The shift in the *energy*, however, is opposite in sign, in disagreement with previous calculations. It is pointed out that, for weak binding, these results can be applied to a Rydberg electron. The Hollberg–Hall measurements of the black-body shift in high Rydberg states of rubidium are consistent with these results.

Considerable interest has been generated by the experiments of Gallagher and Cooke (1979), which indicate that black-body radiation can cause significant reductions in radiative lifetimes. These authors also calculated the dynamic (AC) Stark shifts, induced by black-body radiation, in the energy levels of high Rydberg states (Gallagher and Cooke 1979, Cooke and Gallagher 1980). The effect of black-body radiation on the Lamb shift had been considered earlier by several authors (Auluck and Kothari 1952, Walsh 1971, Barton 1972, Knight 1972) and again more recently by others (Palangues-Mestre and Tarrach 1984, Cha and Yee 1985). Farley and Wing (1981) made a more detailed calculation of the dynamic Stark shifts and obtained results which depend on the nature of the atomic species. In the high-temperature limit all these authors agree on the result for the energy shift:

$$(\pi e^2/3\hbar mc^3)(kT)^2. \tag{1}$$

Our purpose here is to point out that the previous calculations of this result are in fact incorrect, and to show that a correct calculation gives an *energy* shift which is the same as (1) but with the opposite sign. However, the *free energy* shift is given by (1) with a positive sign. This is consistent with the familiar thermodynamic relation between energy U and free energy F

$$U = F - T\frac{\partial F}{\partial T} \tag{2}$$

which makes clear that a term proportional to T^2 will have opposite signs in U and F. The point is that a Rydberg atom interacting with black-body radiation is a thermodynamic system interacting with a heat bath. At this stage, we should emphasise

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that we assume, in common with all previous investigators, thermodynamic equilibrium. The question of what the Hollberg–Hall experiment measures will be addressed later.

As an illustration of the *kind* of argument used by the previous authors consider the following simple calculation of the kinetic energy of a free electron. The energy of oscillation $W(\omega)$ of an electron moving in one dimension in an electric field $E_0\,\mathrm{e}^{-\mathrm{i}\omega t}$ is

$$W(\omega)=e^2E_0^2/4m\omega^2=(2\pi e^2/3m\omega^2)(3E_0^2/8\pi). \tag{3}$$

Identifying $3E_0^2/8\pi$ with $u(\omega, T)$, the energy density of the electromagnetic field, one substitutes the Planck distribution

$$u(\omega, T)=(\hbar\omega^3/\pi^2c^3)/[\exp(\hbar\omega/kT)-1] \tag{4}$$

and integrates over all frequencies to obtain the mean energy:

$$\bar{U}(T)=\int_0^\infty \mathrm{d}\omega\, W(\omega)=\frac{\pi e^2(kT)^2}{9\hbar mc^3}. \tag{5}$$

In three dimensions this is to be multiplied by a factor of three to give (1). Therefore this simple calculation appears to offer an explanation of the observed shifts in the high Rydberg levels. However, already here one can see that something is wrong with this argument: missing from (5) is the leading and dominant term, the equipartition energy $kT/2$. One expects this difficulty arises because the calculation has neglected the radiation damping which is a necessary ingredient in any consistent calculation of fluctuation effects such as black-body shifts (Landau and Lifshitz 1959, § 124).

In order to show how the inclusion of dissipative effects modifies the above argument, we consider an exactly solvable model of an atomic system: a harmonically bound electron (oscillator) interacting with the radiation field via electric dipole coupling. We base our treatment on the quantum Langevin equation (Ford *et al* 1965) which for motion in one dimension takes the general form

$$m\ddot{x}+\int_{-\infty}^{t}\mathrm{d}t'\,\mu(t-t')\dot{x}(t')+Kx=F(t). \tag{6}$$

This is an equation for the time-dependent Heisenberg operator $x(t)$. The coupling with the radiation field is described by two terms: the radiation reaction term, characterised by the memory function $\mu(t)$, and the fluctuating term characterised by the operator-valued random force $F(t)$. For our purposes we need this equation only to extract the generalised susceptibility, which is done by forming the Fourier transform of (6) and writing the result in the form

$$\tilde{x}(\omega)=\alpha(\omega)\tilde{F}(\omega) \tag{7}$$

where we use the superposed tilde to denote the Fourier transform, e.g. $\tilde{x}(\omega)$ is the Fourier transform of the operator $x(t)$. Here $\alpha(\omega)$ is the generalised susceptibility (a c number) given by

$$\alpha(\omega)=(-m\omega^2+K-\mathrm{i}\omega\tilde{\mu}(\omega))^{-1} \tag{8}$$

where

$$\tilde{\mu}(\omega)=\int_0^\infty \mathrm{d}t\,\mu(t)\,\mathrm{e}^{\mathrm{i}\omega t}\qquad \operatorname{Im}\omega>0 \tag{9}$$

is the Fourier transform of the memory function.

Clearly $\tilde{\mu}(\omega)$ is analytic in the upper half of the ω plane. In addition, energy considerations require that the real part of $\tilde{\mu}(\omega)$ be positive on the real axis. Functions satisfying these two requirements are termed positive functions (Meixner 1965, Guillemin 1957). This condition of positivity is of fundamental physical importance; its violation is tantamount to a violation of the second law of thermodynamics. It is also very restrictive: positive functions have neither zeros nor poles in the upper half plane; on the real axis they can have only simple zeros with negative imaginary coefficient and simple poles with positive imaginary residues; the reciprocal of a positive function is a positive function, etc.

The system of the oscillator coupled to the radiation field in thermal equilibrium at temperature T has a well defined free energy. The free energy ascribed to the oscillator, $F_0(T)$, is the free energy of this system minus the free energy of the radiation field in the absence of the oscillator. For this free energy we have the remarkable formula:

$$F_0(T)=\frac{1}{\pi}\int_0^\infty \mathrm{d}\omega\, f(\omega, T)\, \mathrm{Im}\left(\frac{\mathrm{d}\ln \alpha(\omega)}{\mathrm{d}\omega}\right) \tag{10}$$

where $f(\omega, T)$ is the free energy of a single oscillator of frequency ω, given by the familiar formula (Landau and Lifshitz 1959, § 49)

$$f(\omega, T)=kT\ln[1-\exp(-\hbar\omega/kT)]. \tag{11}$$

Note that we discard the $T=0$ contributions since our interest is in the temperature-dependent effects.

Formula (10) is striking because it expresses the free energy of the *interacting* oscillator in terms of the susceptibility (8) alone. It can be derived explicitly for general microscopic heat bath models which lead to a quantum Langevin equation, but the following simple argument contains the essence of the proof. From (8) it is not difficult to see that $-\mathrm{i}\omega\alpha(\omega)$ is a positive function provided that $\tilde{\mu}(\omega)$ is a positive function and that m and K are positive. If the normal modes are discrete, $\alpha(\omega)$ will have poles on the real axis at the normal mode frequencies of the interacting system and zeros at the normal mode frequencies of the radiation field in the absence of the oscillator. This should be apparent from (7): if $\alpha(\omega)=0$ there can be a fluctuating force with no $\tilde{x}$, while if $\alpha(\omega)^{-1}=0$ there can be a motion of $\tilde{x}$ with no force. Therefore, one can write

$$\alpha(\omega)\propto\prod_i(\omega^2-\omega_i^2)\left(\prod_j(\omega^2-\bar{\omega}_j^2)\right)^{-1} \qquad \mathrm{Im}\,\omega>0 \tag{12}$$

where the first term is the product over the normal modes of the free radiation field and the second term is the product over those of the interacting system. In (10) it is understood that $\alpha(\omega)$ is the boundary value as ω approaches the real axis from above. If, therefore, one recalls the well known formula, $1/(x+\mathrm{i}0^+)=P(1/x)-\mathrm{i}\pi\delta(x)$, one sees that

$$\frac{1}{\pi}\,\mathrm{Im}\left(\frac{\mathrm{d}}{\mathrm{d}\omega}\ln\alpha(\omega)\right)=\sum_j[\delta(\omega-\bar{\omega}_j)+\delta(\omega+\bar{\omega}_j)]-\sum_i[\delta(\omega-\omega_i)+\delta(\omega+\omega_i)]. \tag{13}$$

When this is put into (10) the result can be written

$$F_0(T)=\sum_j f(\bar{\omega}_j, T)-\sum_i f(\omega_i, T) \tag{14}$$

where the first sum is clearly the free energy of the interacting field, the second that of the free field. This demonstrates our assertion.

To apply the formula (10) we must have an expression for the generalised susceptibility or, equivalently, the function $\tilde{\mu}(\omega)$. For a non-relativistic electron interacting via dipole coupling with the radiation field, the memory function is given by (Ford *et al* 1985)

$$\mu(t)=\frac{e^2}{3\pi^2}\int \mathrm{d}\boldsymbol{k}\,|f_k|^2\cos ckt \tag{15}$$

where f_k is the electron form factor. Our results are insensitive to the detailed shape of f_k and for convenience of calculation we choose $|f_k|^2=\Omega^2/(\Omega^2+c^2k^2)$, where Ω is a large cut-off frequency. Then (9) gives

$$\tilde{\mu}(\omega)=2e^2\Omega^2\omega/3c^3(\omega+\mathrm{i}\Omega). \tag{16}$$

Note that $\tilde{\mu}(\omega)$ is a positive function. It does not show the pole structure on the real axis evoked in the argument of the previous paragraph because, in the infinite volume limit, the normal mode frequencies of the radiation field are continuously distributed. In this case the real axis becomes a branch cut and the pole of (16) in the lower half plane is on the 'unphysical sheet' reached by analytically continuing through the cut.

When (16) is put into (8) one gets

$$\alpha(\omega)=\frac{\omega+\mathrm{i}\Omega}{-m\omega^3-\mathrm{i}M\Omega\omega^2+K(\omega+\mathrm{i}\Omega)} \tag{17}$$

where M is the renormalised (observed) electron mass

$$M=m+2e^2\Omega/3c^3. \tag{18}$$

The denominator in (17) can be factored to write

$$\alpha(\omega)=\frac{(\omega+\mathrm{i}\Omega)}{m(\omega+\mathrm{i}\Omega')(\omega_0^2-\omega^2-\mathrm{i}\gamma\omega)}. \tag{19}$$

The point here is that $\alpha(\omega)$ has three poles, all in the lower half plane in accord with the positivity condition. Equating coefficients in the denominators of (17) and (19) we find the relations

$$\frac{1}{\Omega}=\frac{1}{\Omega'}+\frac{\gamma}{\omega_0^2}\qquad \frac{K}{M}=\frac{\omega_0^2\Omega'}{\Omega'+\gamma}\qquad \frac{M}{m}=\frac{(\omega_0^2+\gamma\Omega')(\Omega'+\gamma)}{\omega_0^2\Omega'}. \tag{20}$$

Alternatively, one can view these as expressions for the parameters Ω, K, M in terms of the parameters Ω', ω_0, γ which when substituted in (17) give (19).

With the form (19) we see that

$$\mathrm{Im}\left(\frac{\mathrm{d}\ln\alpha(\omega)}{\mathrm{d}\omega}\right)=\frac{\gamma(\omega_0^2+\omega^2)}{(\omega^2-\omega_0^2)^2+\gamma^2\omega^2}+\frac{\Omega'}{\omega^2+\Omega'^2}-\frac{\Omega}{\omega^2+\Omega^2}. \tag{21}$$

When this is put in (5) we can then pass to the limit of large cut-off, assuming $kT/\hbar\Omega\ll 1$. Then using the first of the relations (20) we obtain the following exact expression for the oscillator free energy

$$F_0(T)=\frac{1}{\pi}\int_0^\infty \mathrm{d}\omega\, f(\omega,T)\left(\frac{\gamma(\omega_0^2+\omega^2)}{(\omega_0^2-\omega^2)^2+\omega^2\gamma^2}-\frac{\gamma}{\omega_0^2}\right). \tag{22}$$

In this result the parameters ω_0 and γ are to be taken in the large cut-off limit ($\Omega'\gg\gamma$), which from (18) and (20) can be shown to give

$$\omega_0 = (K/M)^{1/2} \qquad \gamma = 2e^2\omega_0^2/3Mc^3. \tag{23}$$

The result (22) can be written

$$F_0(T) = F_0'(T) + \Delta F_0(T) \tag{24}$$

where the first term

$$F_0'(T) = \frac{1}{\pi}\int_0^\infty \mathrm{d}\omega\, f(\omega, T)\frac{\gamma(\omega_0^2+\omega^2)}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} \tag{25}$$

should be recognised as the free energy of an oscillator with natural frequency ω_0 and width γ, and the second term,

$$\Delta F_0(T) = -\frac{\gamma}{\omega_0^2\pi}\int_0^\infty \mathrm{d}\omega\, f(\omega, T) = \frac{\pi e^2(kT)^2}{9\hbar Mc^3} \tag{26}$$

is a quantum electrodynamic correction.

The expression (25) is exactly what one would obtain if in (10) one were to use (8) with $\tilde{\mu} = m\gamma$ a constant (the friction constant) and with $K = m\omega_0^2$. In this connection it is instructive to form the corresponding energy, using (2), and to consider the weak-coupling limit ($\gamma \to 0$) to get

$$U_0'(T) \to \hbar\omega_0[\exp(\hbar\omega_0/kT) - 1]^{-1}. \tag{27}$$

This is just the Planck energy of the quantum oscillator. Thus, $F_0'(T)$ corresponds to the Planck energy, including the effect of finite width of the oscillator levels. Therefore, the additional term $\Delta F_0(T)$ is to be interpreted as a temperature-dependent *shift* in the free energy of each level. The corresponding energy level shift,

$$\Delta U_0(T) = -\pi e^2(kT)^2/9\hbar Mc^3 \tag{28}$$

is negative.

We emphasise that for the oscillator this is an *exact* result. Since this free energy shift is independent of the oscillator force constant, it is the same as the expression that one would obtain for a nearly free electron and, therefore, is to be interpreted as the observed shift in Rydberg atoms. Perhaps we should stress that we are not invoking an analogy between the oscillator and a Rydberg electron, but rather—and here we agree with some previous investigators—we are recognising that the effect of black-body radiation interacting with a Rydberg electron is well approximated by that for a nearly free electron.

Our result (26) is in accord with the experiment of Hollberg and Hall (1984). Perhaps we should stress once more that we are working within the same framework as that of all previous investigators in that we have assumed thermal equilibrium. Whether or not the Hollberg–Hall experiment actually corresponds to this situation is certainly a matter for debate but, since the experiment is carried out by *repeated sampling* of atoms which go through an active volume, in our opinion this corresponds to the *ensemble average* which is implied by thermodynamic equilibrium. They observe an increase with temperature of the work supplied (i.e. the energy supplied by laser photons) in an isothermal change of state of this system (i.e. the transition from the ground state to the Rydberg state). It is a fundamental principle of thermodyanics that this work equals the change in free energy (Landau and Lifshitz 1959, § 20).

We turn now to a brief discussion of what went wrong with previous calculations. The common omission of all previous investigators was to neglect the dynamical character of the radiation field. In our illustrative example this is seen in (5), which is in fact the correct expression for the energy of an electron driven by a *c* number field whose spectrum is the Planck distribution. But the electromagnetic field is a dynamical system which can give and receive energy (heat) from the atom. We have shown that the formalism of quantum stochastic processes and the quantum Langevin equation are useful for computing this effect.

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