

## Thermodynamic perturbation theory for an atom interacting with blackbody radiation

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Thermodynamic perturbation theory is used to evaluate the free energy of an atom interacting via dipole coupling with the blackbody radiation field. An expression, exact through order  $e^2$ , for the interaction free energy is obtained. In the high-temperature limit the result is  $\pi e^2(k_B T)^2/3\hbar mc^2$ , consistent with experiment and in agreement with an earlier exact calculation for the oscillator.

### I. INTRODUCTION

The system of an atom interacting with blackbody radiation has recently attracted renewed theoretical<sup>1-3</sup> and experimental<sup>4</sup> interest. In a recent publication we presented an exact calculation of the free energy of a quantum oscillator interacting with the radiation field at finite temperature.<sup>5</sup> Since our result contradicted a number of previous calculations of the blackbody Stark shift in atoms, and since our methods of quantum stochastic processes were novel, we present here an alternative perturbative calculation using familiar methods of quantum-mechanical perturbation theory. The results are in complete agreement with our previous calculation.

There are, however, a number of subtleties in the discussion. Therefore, while the system we discuss and the methods we use are standard, we describe them in some detail.

In Sec. II we specify the Hamiltonian for the system, which is that of a single-electron atom interacting with the radiation field via dipole coupling. Then in Sec. III we discuss the  $T=0$  case using the stationary perturbation theory. In Sec. IV we calculate the free energy using the thermodynamic perturbation theory. Finally, in Sec. V we discuss the results and their application to experiments on Rydberg atoms.

### II. THE HAMILTONIAN

We consider a single-electron atom interacting with the radiation field via dipole coupling. For this system the Hamiltonian can be written

$$H = \frac{1}{2m} \left[ \mathbf{p} + \frac{e}{c} \mathbf{A} \right]^2 + V(\mathbf{r}) + H_R. \quad (1)$$

Here the radiation field Hamiltonian is given by

$$H_R = \sum_{\mathbf{k}} \sum_{\alpha} \hbar \omega_{\mathbf{k},\alpha} a_{\mathbf{k},\alpha}^\dagger a_{\mathbf{k},\alpha}, \quad (2)$$

and the vector potential by

$$\mathbf{A} = \sum_{\mathbf{k}} \sum_{\alpha} \left( \frac{2\pi\hbar c^2}{\omega V} \right)^{1/2} (f_{\mathbf{k}}^* a_{\mathbf{k},\alpha} \hat{\mathbf{e}}^{(\alpha)} + f_{\mathbf{k}} a_{\mathbf{k},\alpha}^\dagger \hat{\mathbf{e}}^{(\alpha)*}), \quad (3)$$

in which  $f_{\mathbf{k}}$  is the electron form factor. For convenience we have adopted the notation for the radiation field variables used in the book of Sakurai<sup>6</sup> (see especially Secs. 2 and 3; we use Gaussian unrationalized units) and we refer to that work for the definitions and properties of the quantities appearing in (2) and (3). The vector potential (3) is independent of the electron coordinate  $\mathbf{r}$ . This corresponds to the dipole approximation in which one assumes the wavelength of the radiation is large compared with the size of the atom. Except for the use of a more modern notation, the Hamiltonian (1) is identical with that given (with the same equation number) in the classic work of van Kampen.<sup>7</sup> It is the standard Hamiltonian used in any book on atomic physics, although the general practice seems to be to begin with a more general Hamiltonian in which the dependence of  $\mathbf{A}$  upon  $\mathbf{r}$  is kept, and only at a later stage make the dipole approximation by setting a factor  $e^{i\mathbf{k}\cdot\mathbf{r}} \rightarrow 1$ .

The electron form factor is the Fourier transform of  $\rho(\mathbf{r})$ , the electron charge distribution,

$$f_{\mathbf{k}} = \int d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}. \quad (4)$$

It is frequently called a cutoff function (see, e.g., the work of Messiah,<sup>8</sup> especially Chap. XXI, Sec. 9). In general we assume  $f_{\mathbf{k}}$  is near unity up to some large cutoff wave vector, typically of order  $r_0^{-1}$  where  $r_0 = e^2/mc^2$  is the classical electron radius. For larger values of  $k$  the form factor falls rapidly to zero. It is the point of modern renormalization theory that, after renormalization, physically observable quantities are independent of the form of cutoff function.

The Hamiltonian (1) can be written

$$H = H_A + H_R + H_I, \quad (5)$$

where  $H_A$  is the Hamiltonian for the uncoupled atom

$$H_A = \frac{p^2}{2m} + V(\mathbf{r}), \quad (6)$$

while the interaction Hamiltonian is

$$H_I = \frac{e}{mc} \mathbf{p} \cdot \mathbf{A} + \frac{e^2}{2mc^2} A^2. \quad (7)$$

Here we should remark that, although for many physically interesting processes (e.g., the radiative lifetime of an excited atomic state) the second term does not contribute, to have a physically consistent theory we must keep that term.<sup>9</sup>

### III. STATIONARY PERTURBATION THEORY

The eigenstates of the free-atom Hamiltonian (6) are labeled by an index  $a, b, c$ , etc.,

$$H_A \phi_a = \epsilon_a \phi_a. \quad (8)$$

In general, there is a discrete ground state and an infinite number of discrete excited states, with a continuum of scattering states above an ionization threshold. The eigenstates of the free radiation field Hamiltonian are Fock states, corresponding to a given number of photons in each normal mode (see, e.g., Ref. 6, p. 26),

$$H_R \Phi_{\{n_{k,\alpha}\}} = \left[ \sum_k \sum_\alpha \hbar\omega \right] \Phi_{\{n_{k,\alpha}\}}. \quad (9)$$

It will be convenient to introduce a special notation for the vacuum state,  $\Phi_0$ , and the one-photon state  $\Phi_{k,\alpha}$ . The spectrum of the Hamiltonian  $H_A$  and  $H_R$  for the noninteracting system of atoms and radiation field is therefore as indicated in Fig. 1(a). There is a lowest-energy eigenvalue, corresponding to the field being in the vacuum state

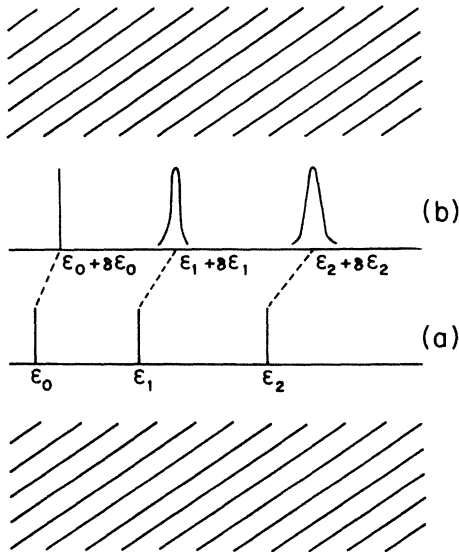


FIG. 1. Energy spectrum for a system of atoms and radiation field where (a) and (b) refer to the noninteracting and interacting cases, respectively. The  $\epsilon_a$  ( $a=0,1,2,\dots$ ) refer to the atomic energies and a background continuum due to the radiation field is indicated by the sloping lines (which have not been continued through the center of the figure for reasons of clarity).

and the atom in its ground state. Above this there is a sequence of discrete energy eigenvalues, corresponding to the field in the vacuum state and the atom in one of its excited states, i.e., states of the form  $\phi_a \Phi_0$ . Also above this, starting from the ground-state energy, is a continuum of energies, corresponding to the atom in one of its states and one or more photons in the radiation field. One speaks of the discrete eigenvalues embedded in a continuum.

When the interaction between the atom and field is included, so that the system is described by the full Hamiltonian (5), the spectrum (aside from the ground state) becomes purely continuous, no matter how weak the interaction. One says that the discrete eigenvalues at the excited atomic energy levels have been "absorbed" by the continuum. In their place [see Fig. 1(b)] are only local peaks in the density of continuum states. (For a mathematical description of this phenomenon see the book of Kato, or Reid and Simon.<sup>10</sup>) One can, however, introduce "pseudoeigenvalues" which are defined in terms of the resolvent operator as follows. The resolvent operator is

$$R(z) = (H - z)^{-1}, \quad (10)$$

where  $z$  is a complex variable. Clearly  $R(z)$  is an analytic function of  $z$  except at points on the real axis in the spectrum of  $H$ . At discrete eigenvalues  $R(z)$  has a simple pole, but at points in the continuous spectrum there is only a "branch cut" and one may analytically continue across the real axis onto the "unphysical sheet." In general, essentially because one assumes the interaction has been switched on in the distant past, one begins with  $z$  in the upper half plane. In this case when one analytically continues  $R(z)$  across the real axis one finds poles in the lower half plane in the neighborhood of each of the discrete eigenvalues of  $H_A$ . For the position of the pole in the neighborhood of the eigenvalue  $\epsilon_a$  we have the perturbation expansion

$$E_a - \frac{1}{2}i\Gamma_a = \epsilon_a + \langle \phi_a \Phi_0, H_I \phi_a \Phi_0 \rangle + \langle \phi_a \Phi_0, H_I R_0(\epsilon_a + i0^+) H_I \phi_a \Phi_0 \rangle + \dots, \quad (11)$$

where  $R_0(z)$  is the resolvent operator for the noninteracting Hamiltonian,

$$R_0(z) = (H_A + H_R - z)^{-1}, \quad (12)$$

and where

$$H_I' = H_I - \langle \phi_a \Phi_0, H_I \phi_a \Phi_0 \rangle P_a, \quad (13)$$

in which  $P_a$  is the projection operator corresponding to the eigenstate  $\phi_a \Phi_0$  of the noninteracting system. The quantity  $E_a - \frac{1}{2}i\Gamma_a$  is the pseudoeigenvalue associated with the peak in the density of states in the neighborhood of the eigenvalues  $\epsilon_a$  of  $H_A$ . The expansion (11) is identical with that in the old Heitler damping theory.<sup>11</sup> For a more mathematical discussion see the book of Messiah,<sup>8</sup> especially Chap. XXI, p. 13. For a still more mathematical discussion see Ref. 10.

We now use the form (7) of  $H_I$  to evaluate the terms in the expansion (11). First, we have

$$\begin{aligned} \langle \phi_a \Phi_0, H_I \phi_a \Phi_0 \rangle &= \frac{e^2}{2mc^2} \langle \Phi_0, A^2 \Phi_0 \rangle & \langle \phi_a \Phi_0, H_I \phi_a \Phi_0 \rangle &= \frac{e^2 \hbar}{4\pi^2 m} \int d\mathbf{k} \frac{|f_{\mathbf{k}}|^2}{\omega} . \end{aligned} \quad (16)$$

$$= \frac{\pi e^2 \hbar}{mV} \sum_{\mathbf{k}} \sum_{\alpha} \frac{|f_{\mathbf{k}}|^2}{\omega} . \quad (14)$$

The sum over polarizations  $\alpha$  gives a factor of 2, and in the infinite volume limit

$$\sum_{\mathbf{k}} \rightarrow [V/(2\pi)^3] \int d\mathbf{k} . \quad (15)$$

Hence we get

Next consider the second-order term in (11). Since we will keep only contributions of order  $e^2$ , there we can drop the  $A^2$  terms in (7) and, as well, ignore the difference between  $H_I$  and  $H'_I$ . Then

$$\begin{aligned} H_I \phi_a \Phi_0 &= \frac{e}{mc} (\mathbf{p} \phi_a) \cdot (\mathbf{A} \Phi_0) \\ &= \frac{e}{m} \sum_{\mathbf{k}} \sum_{\alpha} \left[ \frac{2\pi \hbar}{\omega V} \right]^{1/2} f_{\mathbf{k}} (\hat{\epsilon}^{(\alpha)*} \cdot \mathbf{p} \phi_a) \Phi_{\mathbf{k}, \alpha} . \end{aligned} \quad (17)$$

With this we find

$$\langle \phi_a \Phi_0, H'_I R_0(\epsilon_a + i0^+) H'_I \phi_a \Phi_0 \rangle = \frac{2\pi e^2 \hbar}{m^2 V} \sum_{\mathbf{k}} \sum_{\alpha} \frac{|f_{\mathbf{k}}|^2}{\omega} \langle \phi_a, \hat{\epsilon}^{(\alpha)} \cdot \mathbf{p}(\epsilon_a - \hbar\omega - H_A + i0^+)^{-1} \hat{\epsilon}^{(\alpha)*} \cdot \mathbf{p} \phi_a \rangle . \quad (18)$$

We sum over polarizations and average over photon directions, using the result

$$\left\langle \sum_{\alpha} \hat{\epsilon}_j^{(\alpha)} \hat{\epsilon}_m^{(\alpha)*} \right\rangle_{av} = \langle \delta_{jm} - \hat{k}_j \hat{k}_m \rangle_{av} = \frac{2}{3} \delta_{jm} , \quad (19)$$

and again take the infinite volume limit to obtain

$$\begin{aligned} \langle \phi_a \Phi_0, H'_I R_0(\epsilon_a + i0^+) H'_I \phi_a \Phi_0 \rangle &= \frac{e^2 \hbar}{6\pi^2 m^2} \int d\mathbf{k} \frac{|f_{\mathbf{k}}|^2}{\omega} \langle \phi_a, p_j(\epsilon_a - \hbar\omega - H_A + i0^+)^{-1} p_j \phi_a \rangle \\ &= \frac{e^2 \hbar}{6\pi^2 m^2} \int d\mathbf{k} \frac{|f_{\mathbf{k}}|^2}{\omega} \sum_b \frac{|\langle \phi_a, \mathbf{p} \phi_b \rangle|^2}{\epsilon_a - \epsilon_b - \hbar\omega + i0^+} . \end{aligned} \quad (20)$$

Collecting these results, we find

$$\delta\epsilon_a - \frac{1}{2} i\Gamma_a = \frac{e^2 \hbar}{6\pi^2 m^2} \int d\mathbf{k} \frac{|f_{\mathbf{k}}|^2}{\omega} \left[ \frac{3m}{2} + \sum_b \frac{|\langle \phi_a, \mathbf{p} \phi_b \rangle|^2}{\epsilon_a - \epsilon_b - \hbar\omega + i0^+} \right] , \quad (21)$$

where we have introduced the shift  $\delta\epsilon_a = E_a - \epsilon_a$ . If we introduce the  $f$ -sum rule,<sup>12</sup>

$$\sum_b \frac{|\langle \phi_a, \mathbf{p} \phi_b \rangle|^2}{\epsilon_a - \epsilon_b} = -\frac{3m}{2} , \quad (22)$$

we can write

$$\delta\epsilon_a - \frac{1}{2} i\Gamma_a = \frac{e^2 \hbar^2}{6\pi^2 m^2} \int d\mathbf{k} |f_{\mathbf{k}}|^2 \frac{|\langle \phi_a, \mathbf{p} \phi_a \rangle|^2}{(\epsilon_a - \epsilon_b)(\epsilon_a - \epsilon_b - \hbar\omega + i0^+)} . \quad (23)$$

#### IV. THERMODYNAMIC PERTURBATION THEORY

Thermodynamic perturbation theory is an expansion of the free energy of an interacting system in powers of the interaction. For a system with Hamiltonian  $H$  and at temperature  $T$ , the free energy is

$$F(T) = -\frac{1}{\beta} \ln(\text{tr}\{e^{-\beta H}\}) , \quad (24)$$

where  $\beta = (k_B T)^{-1}$ . If  $H$  is of the form

$$H = H_0 + H_I , \quad (25)$$

then thermodynamic perturbation theory gives the following expression:<sup>13,14</sup>

$$F = F_0 + \langle H_I \rangle - \frac{1}{\beta} \int_0^\beta d\beta' \int_0^\beta d\beta'' (\langle e^{(\beta' - \beta'')H_0} H_I e^{-(\beta' - \beta'')H_0} H_I \rangle - \langle H_I \rangle^2) + \dots , \quad (26)$$

where  $F_0$  is the free energy of the noninteracting system, given by (24) with  $H$  replaced by  $H_0$ , and where the angular brackets indicate the thermal average,

$$\langle O \rangle \equiv \text{tr}(e^{-\beta H_0} O) / \text{tr}(e^{-\beta H_0}). \quad (27)$$

We want to evaluate this expansion for the system of atoms coupled to the radiation field, for which  $H_0 = H_A + H_R$ . Then

$$F_0(T) = -\frac{1}{\beta} \ln Z_A + F_R(T), \quad (28)$$

where

$$Z_A \equiv \sum_a e^{-\beta \epsilon_a} \quad (29)$$

is the free-atom partition function, and where (Ref. 6, p. 63)

$$F_R(T) = -V \frac{\pi^2 k_B^4}{45 \hbar^3 c^3} T^4 \quad (30)$$

is the free energy of the free radiation field. Next consider the first order terms, with  $H_I$  given by (7),

$$\begin{aligned} \langle H_I \rangle &= \frac{e^2}{2mc^2} \langle A^2 \rangle \\ &= \frac{\pi e^2 \hbar}{mV} \sum_{\mathbf{k}} \sum_{\alpha} \frac{|f_{\mathbf{k}}|^2}{\omega} \langle a_{\mathbf{k},\alpha} a_{\mathbf{k},\alpha}^\dagger + a_{\mathbf{k},\alpha}^\dagger a_{\mathbf{k},\alpha} \rangle. \end{aligned} \quad (31)$$

Using the result (Ref. 6, p. 63)

$$\langle a_{\mathbf{k},\alpha}^\dagger a_{\mathbf{k},\alpha} \rangle = \langle a_{\mathbf{k},\alpha} a_{\mathbf{k},\alpha}^\dagger \rangle - 1 = 1/(e^{\beta \hbar \omega} - 1), \quad (32)$$

and using (15), we get

$$\langle H_I \rangle = \frac{e^2 \hbar}{4\pi^2 m} \int d\mathbf{k} \frac{|f_{\mathbf{k}}|^2}{\omega} \coth(\beta \hbar \omega / 2). \quad (33)$$

Consider now the second-order terms of the expansion (26). The result (33) being of order  $e^2$ , we can neglect  $\langle H_I \rangle^2$  in the second-order term, and otherwise keep only the contributions of the first term in (7). Using the fact that atom variables and field variables commute, we can then write

$$\begin{aligned} &\langle e^{(\beta - \beta') H_0} H_I e^{-(\beta - \beta') H_0} H_I \rangle \\ &= \frac{e^2}{m^2 c^2} \langle e^{(\beta - \beta') H_A} p_j e^{-(\beta - \beta') H_A} p_l \rangle \\ &\quad \times \langle e^{(\beta - \beta') H_R} A_j e^{-(\beta - \beta') H_R} A_l \rangle. \end{aligned} \quad (34)$$

Using the expressions (2) and (3) for  $H_R$  and  $\mathbf{A}$ , and the commutation rules for the field variables,<sup>6</sup> we see that

$$e^{(\beta - \beta') H_R} A_j e^{-(\beta - \beta') H_R} = \sum_{\mathbf{k}} \sum_{\alpha} \left[ \frac{2\pi \hbar c^2}{\omega V} \right]^{1/2} (f_{\mathbf{k}}^* a_{\mathbf{k},\alpha} e^{-(\beta - \beta') \hbar \omega} \hat{\epsilon}_j^{(\alpha)} + f_{\mathbf{k}} a_{\mathbf{k},\alpha}^\dagger e^{(\beta - \beta') \hbar \omega} \hat{\epsilon}_j^{(\alpha)*}). \quad (35)$$

With this, the steps in evaluating the first-order terms can be repeated to get

$$\langle e^{(\beta - \beta') H_R} A_j e^{-(\beta - \beta') H_A} A_l \rangle = \delta_{jl} \frac{\hbar c^2}{6\pi^2} \int d\mathbf{k} \frac{|f_{\mathbf{k}}|^2}{\omega} \frac{e^{(\beta - \beta') \hbar \omega} + e^{(\beta - \beta') \hbar \omega}}{e^{\beta \hbar \omega} - 1}. \quad (36)$$

For the first factor in (34) a sum over intermediate atomic states can be introduced to give

$$\langle e^{(\beta - \beta') H_A} p_j e^{-(\beta - \beta') H_A} p_l \rangle = \frac{1}{Z_A} \sum_a \sum_b e^{-\beta \epsilon_a + (\beta - \beta')(\epsilon_a - \epsilon_b)} \langle \phi_a, p_j \phi_b \rangle \langle \phi_b, p_l \phi_a \rangle, \quad (37)$$

with  $Z_A$  given by (29). Putting these results in (34), then after a little manipulation involving interchanges of the summation labels  $a$  and  $b$ ,

$$\begin{aligned} &\frac{1}{\beta} \int_0^\beta d\beta' \int_0^\beta d\beta'' \langle e^{(\beta - \beta') H_0} H_I e^{-(\beta - \beta') H_0} H_I \rangle \\ &= -\frac{e^2 \hbar}{6\pi^2 m^2} \int d\mathbf{k} \frac{|f_{\mathbf{k}}|^2}{\omega} \frac{1}{e^{\beta \hbar \omega} - 1} \sum_a \frac{e^{-\beta \epsilon_a}}{Z_A} \sum_b |\langle \phi_a, \mathbf{p} \phi_b \rangle|^2 \left[ \frac{e^{\beta \hbar \omega}}{\epsilon_a - \epsilon_b - \hbar \omega} + \frac{1}{\epsilon_a - \epsilon_b - \hbar \omega} \right]. \end{aligned} \quad (38)$$

At first glance this integral appears to be improper, with a pole in the first term in the final factor at  $\omega = (\epsilon_a - \epsilon_b) / \hbar$ . But upon interchanging the labels  $a$  and  $b$  in the summation, the second term in this factor is seen to have the same pole which cancels the first. Thus the integral is in fact proper (and real). For convenience in the later discussions we can take the integral for the individual terms to be a principal value integral.

Collecting the results (28), (33), and (38), the expansion (26) for the free energy gives

$$F = F_R - \frac{1}{\beta} \ln Z_A + \delta F, \quad (39)$$

where  $\delta F$ , the interaction free energy of the system of the atom interacting with the radiation field, is given by

$$\delta F = \frac{e^2 \hbar}{6\pi^2 m^2} \int d\mathbf{k} \frac{|f_{\mathbf{k}}|^2}{\omega} \left[ \frac{3m}{2} \coth(\frac{1}{2}\beta \hbar \omega) + \sum_a \frac{e^{-\beta \epsilon_a}}{Z_a} \sum_b |\langle \phi_a, \mathbf{p} \phi_b \rangle|^2 \left[ \frac{e^{\beta \hbar \omega}}{e^{\beta \hbar \omega} - 1} \frac{1}{\epsilon_a - \epsilon_b - \hbar \omega} + \frac{1}{e^{\beta \hbar \omega} - 1} \frac{1}{\epsilon_a - \epsilon_b + \hbar \omega} \right] \right]. \quad (40)$$

Using in the first term in square brackets the  $f$ -sum rule (22), this expression can be rearranged to write

$$\delta F(T) = \sum_a \frac{e^{-\beta \epsilon_a}}{Z_A} [\delta \epsilon_a + \delta f_a(T)], \quad (41)$$

where  $\delta \epsilon_a$  is the (temperature-independent) energy shift given by (23), and where

$$\delta f_a(T) = \frac{e^2 \hbar^2}{6\pi^2 m^2} \int d\mathbf{k} \frac{|f_{\mathbf{k}}|^2}{e^{\beta \hbar \omega} - 1} \sum_b \frac{|\langle \phi_a, \mathbf{p} \phi_b \rangle|^2}{\epsilon_a - \epsilon_b} \left[ \frac{1}{\epsilon_a - \epsilon_b - \hbar \omega} - \frac{1}{\epsilon_a - \epsilon_b + \hbar \omega} \right] \quad (42)$$

is an additional term which vanishes at  $T=0$ . Note that, as remarked above, in this expression the integrals over vanishing denominators are to be interpreted as the principal value. It is for this reason that only the real part  $\delta \epsilon_a$  of the complex shift of the pseudoeigenvalue (23) occurs. The result (41) is our desired expression for the first-order interaction free energy. In the next section we discuss the interpretation of this result.

## V. DISCUSSION

The first part of the expression (41) for the free energy of interaction has a simple interpretation. If the atomic energy levels were to remain discrete but were shifted so that  $\epsilon_a \rightarrow \epsilon_a + \delta \epsilon_a$ , then the partition function (29) would become

$$Z_A \rightarrow \sum_a e^{-\beta(\epsilon_a + \delta \epsilon_a)} \simeq Z_A \left[ 1 - \beta \sum_a \frac{e^{-\beta \epsilon_a}}{Z_a} \delta \epsilon_a \right]. \quad (43)$$

The corresponding change in the free energy would therefore be

$$\delta \left[ -\frac{1}{\beta} \ln Z_A \right] = \sum_a \frac{e^{-\beta \epsilon_a}}{Z_A} \delta \epsilon_a. \quad (44)$$

This is just the first part of (41), which therefore has the interpretation of the change in free energy due to the atomic energy level shifts.

One might be tempted by the above interpretation to interpret the quantity  $\delta f_a(T)$  in the second part of (41) as a temperature-dependent energy shift. But this is a trap laid for the unwary; that interpretation is valid only for temperature-independent shifts. For one thing, as remarked in Sec. III, the spectrum of the interacting system has no discrete levels but rather peaks in the density of states, and  $\delta f_a(T)$  must contain a contribution due to the finite width of the peak. Another way of seeing the difficulty is to recall the familiar relation between free energy  $F$ , energy  $U$ , and entropy  $S$ ,

$$F = U - TS. \quad (45)$$

At zero temperature, free energy and energy are the same, but at finite temperature they are different. In particular,

for our system there should be a contribution to the entropy arising from the population distribution over the *continuum* of energy levels. We must therefore look more carefully at the interpretation of  $\delta f_a(T)$ .

Before we do so, however, it will be convenient to introduce a special notation for the second part of (40):

$$\delta \tilde{F}(T) = \sum_a \frac{e^{-\beta \epsilon_a}}{Z_A} \delta f_a(T). \quad (46)$$

This is the interaction free energy which would have resulted if we had used the shifted levels,  $\epsilon_a + \delta \epsilon_a$ , in place of the unperturbed levels  $\epsilon_a$  in the free-atom free energy. It vanishes at  $T=0$ .

Consider now the high-temperature limit of  $\delta f_a(T)$ . If we assume

$$k_B T \gg |\epsilon_a - \epsilon_b|,$$

we can replace the factor in large parentheses in (42) by its high-frequency approximation ( $-2/\hbar \omega$ ). We can then use the sum rule (22). Finally, we assume

$$k_B T \ll \hbar c / r_0 = \hbar m c^2 / e^2,$$

i.e., photons with energy  $k_B T$  have wavelength long compared with the classical electron radius. The electron form factor may then be replaced with unity and the integral in (42) performed in closed form. The result is

$$\delta f_a(T) \sim \pi e^2 (k_B T)^2 / 3 \hbar m c^3. \quad (47)$$

This is independent of the atomic state, so when it is put in (46) we get

$$\delta \tilde{F}(T) \sim \pi e^2 (k_B T)^2 / 3 \hbar m c^3. \quad (48)$$

This is exactly the result obtained in Ref. 5. Note that if we use the relation (45), which can be written

$$U = F - T \frac{\partial F}{\partial T}, \quad (49)$$

then (48) will correspond to a shift in the energy,  $\delta \tilde{U}(T)$ , which is the same as (48) but opposite in sign.

We conclude with some remarks concerning the application of our results to experiments on Rydberg atoms.

In these experiments a beam of ground-state atoms passes through a small blackbody cavity. While an atom is in the cavity the energy of the pair of photons required to make the transition to an excited Rydberg state is measured. (This of course is a grossly simplified description of the experiments of Hollberg and Hall.<sup>4</sup>) Now, the first thing to note is that the lifetime of the Rydberg state is long compared with the duration of a measurement, i.e., the transit time through the cavity. This means there is not enough time for thermodynamic equilibrium between the atomic states to be established and the free energy calculated in Sec. IV does not apply. On the other hand, this means that the *Rydberg state of the atom* is a metastable thermodynamic state of the system to which equilibrium thermodynamics can be applied. In particular, in the sum in the expression (41) for the interaction free energy, the quantity  $\delta\epsilon_a + \delta f_a(T)$  corresponds to the sum (or, rather, integral) over the peak in the density of states corresponding to the atom in state  $a$ . Thus, *in the high-temperature limit*,  $\delta f_a(T)$  may be interpreted as the shift in the free energy of any of the metastable states of the thermodynamic system. In this connection it is interesting to compare our

result (41) with that obtained in Ref. 3. If we use the identity<sup>12</sup>

$$\langle \phi_a, \mathbf{p} \phi_b \rangle = (im/\hbar)(\epsilon_a - \epsilon_b) \langle \phi_a, \mathbf{r} \phi_b \rangle, \quad (50)$$

and set  $f_k = 1$ , our expression (42) becomes identical with the expression (7) in the paper of Farley and Wing,<sup>3</sup> which they claim is an expression for the energy shift. We have seen, however, that in the high-temperature limit, this is in fact an expression for the interaction *free energy* of the state. Since the free energy of a metastable state is a measure of the work which must be supplied (in the experiment the energy of the pair of photons) to prepare the system in that state, it is the free energy which is measured in the experiment.

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