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Interaction energy of nonidentical atoms

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There are different results in the literature for the interaction energy of two separated nonidentical atoms in the case when one of the atoms is prepared in an excited state. Moreover, there are different ways to define this interaction energy. If the interaction energy is defined as a shift in the energy of the initial state of the combined atomic system, it is possible to carry out a time-dependent calculation that provides an unambiguous method for obtaining this shift. The time-dependent calculations lead to an interaction energy that is an oscillatory function of the interatomic separation, in contrast to the nonoscillatory behavior that is predicted using an alternative theory based on time-independent perturbation theory.

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The calculation of the interaction energy between two neutral, nonidentical atoms is considered by many to represent a fundamental problem in atomic physics. If both atoms are in their ground states, the calculation is straightforward, leading to the well-known van der Waals or Casimir-Polder interaction potentials. However, when one of the atoms (atom A) is initially in an excited state and the other atom (atom B) in its ground state, problems arise owing to the fact that this initial state undergoes decay. To talk about an interaction energy between an excited state atom and a ground state atom in a meaningful way, two conditions must be met. First the system must be in a quasistationary steady state; that is, an interaction energy can be defined only for times t satisfying

$$\gamma_A t \ll 1, \tag{1}$$

where γ_A is the decay rate of the initially excited atom. Second, there must be sufficient time to establish communication between the atoms to achieve this quasistationary state; that is, we must require

$$t > R/c, \tag{2}$$

where R is the separation of the atoms. For optical transitions, it is easy to satisfy both inequalities (1) and (2), even for atoms separated by distances much greater than a wavelength.

Exactly what constitutes the "interaction energy" is open to interpretation. For two *identical* atoms [1], there is less room for confusion. In that case, the symmetric and antisymmetric states involving one atom excited and the other in its ground state are each shifted in energy by the interaction. The shifts depend on the atoms' separation in an oscillatory fashion. However, in the case of dissimilar atoms, there are two ways to define the interaction energy for an initial condition in which atom A is excited and atom B is in its ground state.

One possibility is to define the interaction energy as the ac Stark shift experienced by atom B as a result of the field emitted by atom A. With this definition, the interaction energy, calculated in perturbation theory, is nonoscillatory since it depends on the field intensity produced by atom A at the position of atom B [2]. It seems to me that this is the definition used by Rizzuto *et al.* [3], Sherkunov [4], and Haakh *et al.* [5]. These authors all found an interaction energy that is a nonoscillatory function of the interatomic separation [6]. Experimentally, it is not easy to measure such a shift, since atom B must be probed using an external field to reveal the shift; in addition the perturbation theory calculation remains valid only for times in which the field from atom A is not modified by the back action from atom B.

On the other hand, we can define the interaction energy as the energy shift of the *initial* state obtained after adiabatically eliminating the effects of atom B. It is this definition that I adopt. With this definition, there are still contradictory results for the interaction potential. Implicit in the results of Berman and Milonni [7] and Fu and Berman [8] are interaction energies that are an oscillatory function of the interatomic separation. On the other hand, Power and Thirunamachandran [9], hereafter referred to as PT, used stationary, fourth-order nondegenerate perturbation theory to calculate the change in energy of the initial state of the combined atomic system and found no oscillatory behavior. PT argued that other authors [10], who also used time-independent perturbation theory and found an oscillatory dependence, did not properly account for δ-function contributions associated with the poles that appear in energy denominators. The PT results are in agreement with the shift calculated using the ac Stark definition of the interaction energy (see, also, another paper by Power and Thirunamachandran [11] in which the ac Stark definition of the interaction appears to be used).

In the PT calculation, there are 12 contributions to the interaction energy, corresponding to diagrams i–xii in their paper. The only energy-conserving contribution of the 12 is that associated with diagram x, described below. Other non-energy-conserving terms assure that causality is preserved with respect to physical observables and also lead to the "normal" contributions to van der Waals interaction energy. However, in the limit that the transition frequencies of the two atoms are comparable, diagram x makes the dominant contribution to the interaction energy. It is the only term considered in this paper. The use of nondegenerate, time-independent perturbation theory is problematic since some of the intermediate states are degenerate with the initial state. To deal with this problem, PT modify degenerate energy denominators by the addition of a small imaginary term, with the sign of the term chosen "depending on whether a real photon can be emitted or absorbed." In a time-dependent approach, no such approximations are needed.

It is my contention that PT calculate the energy shift of the initial state. Regardless of whether or not this is a correct interpretation of their work, I want to stress that the shift to which I refer in this work is the energy shift of the initial state of the A-B system resulting from the off-resonant interaction between atoms A and B. This shift could be measured, in principle, as a displacement of the line center of the radiation emitted by atom A.

To investigate whether or not the sign convention used by PT is correct, I first recall their stationary perturbation calculation; this helps to establish the notation and show that the PT result can be obtained using the Weisskopf-Wigner approximation. I then reevaluate the interaction energy using two time-dependent approaches, one based on coupled equations for the state amplitudes and one based on fourth-order, time-dependent perturbation theory. Both of these time-dependent calculations yield identical results—the interaction energy is an oscillatory function of interatomic separation. Thus it appears that the PT convention for choosing the signs of the imaginary terms may be unjustified.

I. FOURTH-ORDER STATIONARY-STATE PERTURBATION THEORY

The physical system consists of two atoms and the radiation field, which is initially in its vacuum state. Each atom is modeled as having a $J=0$ ground state and a $J=1$ excited state. The atoms are assumed to be stationary, with the nucleus of atom A at the origin and that of atom B at position $\mathbf{R}$. Atom A has a transition frequency ω_A and is excited initially to the $m=0$ sublevel of its excited state. Atom B has a transition frequency ω_B and is initially in its ground state. The initial state for the atoms and the field is denoted by $|A\rangle$. The atoms interact via the transverse radiation field, whose electric field vector is given by

$$\mathbf{E}(\mathbf{r}) = i\sum_{\mathbf{k},\lambda}\sqrt{\frac{2\pi\hbar\omega_k}{\mathcal{V}}}\epsilon_{\mathbf{k}}^{(\lambda)}\left(a_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}} - a_{\mathbf{k}\lambda}^{\dagger}e^{-i\mathbf{k}\cdot\mathbf{r}}\right), \tag{3}$$

where $\mathcal{V}$ is the quantization volume and $a_{\mathbf{k}\lambda}$ ($a_{\mathbf{k}\lambda}^{\dagger}$) is an annihilation (creation) operator for a photon having propagation vector $\mathbf{k}$, frequency ω_k, and polarization $\epsilon_{\mathbf{k}}^{(\lambda)}$. The unit polarization vectors are defined by

$$\epsilon_{\mathbf{k}}^{(1)} = \cos\theta_{\mathbf{k}}\cos\phi_{\mathbf{k}}\hat{\mathbf{x}} + \cos\theta_{\mathbf{k}}\sin\phi_{\mathbf{k}}\hat{\mathbf{y}} - \sin\theta_{\mathbf{k}}\hat{\mathbf{z}}, \tag{4}$$

$$\epsilon_{\mathbf{k}}^{(2)} = -\sin\phi_{\mathbf{k}}\hat{\mathbf{x}} + \cos\phi_{\mathbf{k}}\hat{\mathbf{y}}. \tag{5}$$

In dipole approximation, the interaction Hamiltonian is

$$V = -\left[\mu_A\cdot\mathbf{E}(\mathbf{0}) + \mu_B\cdot\mathbf{E}(\mathbf{R})\right], \tag{6}$$

where μ_A and μ_B are the dipole operators of atoms A and B, respectively. The lowest-order contribution to the energy shift of the initial state that is $\mathbf{R}$-dependent occurs to fourth order in V. In the limit that

$$|\omega_{BA}| = |\omega_B - \omega_A| \ll \omega_A, \tag{7}$$

the dominant contribution to this energy shift, corresponding to diagram x in PT, involves a chain of three intermediate states denoted by $|\mathbf{k}\lambda\rangle$ (corresponding to both atoms in their ground states and a photon of type $\mathbf{k}\lambda$ in the field), $|Bm\rangle$ (corresponding to atom B in the m sublevel of its excited state, atom A in its ground state, and no photons in the field), and $|\mathbf{k}'\lambda'\rangle$ (corresponding to both atoms in their ground states and a photon of type $\mathbf{k}'\lambda'$ in the field).

Using stationary perturbation theory with these intermediate states, I find that the fourth-order contribution to the energy shift of the initial state is given by

$$\delta E = -\frac{1}{\hbar^3}\sum_{m=-1}^{1}\sum_{\mathbf{k}\lambda,\mathbf{k}'\lambda'} \times\frac{\langle A|V|\mathbf{k}'\lambda'\rangle\langle\mathbf{k}'\lambda'|V|Bm\rangle\langle Bm|V|\mathbf{k}\lambda\rangle\langle\mathbf{k}\lambda|V|A\rangle}{(\omega_{k'}-\omega_A)\,\omega_{BA}\,(\omega_k-\omega_A)}. \tag{8}$$

Immediately, we run into a problem since the frequency denominators $(\omega_{k'}-\omega_A)$ and $(\omega_k-\omega_A)$ lead to divergent results. To avoid these divergences, one often adds small imaginary terms to these terms. A critical question then relates to the choice of sign for these imaginary terms. It is my contention that the appropriate signs must be chosen on the basis of a *time-dependent* calculation (which I provide in Secs. III and IV). However, in an attempt to reproduce the results of PT, I replace Eq. (8) by

$$\delta E = -\frac{1}{\hbar^3}\lim_{\epsilon\to0^+}\sum_{m=-1}^{1}\sum_{\mathbf{k}\lambda,\mathbf{k}'\lambda'} \times\frac{\langle A|V|\mathbf{k}'\lambda'\rangle\langle\mathbf{k}'\lambda'|V|Bm\rangle\langle Bm|V|\mathbf{k}\lambda\rangle\langle\mathbf{k}\lambda|V|A\rangle}{(\omega_{k'}-\omega_A-i\epsilon)\,\omega_{BA}\,(\omega_k-\omega_A+i\epsilon)}, \tag{9}$$

using the sign choice made by PT. As we shall see, the use of such a prescription does not appear to be justified.

Despite the fact that I believe Eq. (9) to be incorrect, I evaluate it to establish some notation and to check that it reproduces the PT result. Going to continuum field states and carrying out the angular integrations in Eq. (9), I arrive at

$$\delta E = \hbar\frac{\gamma_A\gamma_B}{\omega_{AB}(2\pi i)^2}\lim_{\epsilon\to0^+}\sum_{m=-1}^{1}\int_0^\infty d\omega_k\int_0^\infty d\omega_{k'}\frac{\omega_k^3}{\omega_A^3}\frac{\omega_{k'}^3}{\omega_B^3} \times\frac{f_m(k',\mathbf{R})f_m^*(k,\mathbf{R})}{(\omega_{k'}-\omega_A-i\epsilon)(\omega_k-\omega_A+i\epsilon)}, \tag{10}$$

where

$$\gamma_A = \frac{4}{3}\frac{|\mu_A|^2\omega_A^3}{\hbar c^3} \quad\text{and}\quad \gamma_B = \frac{4}{3}\frac{|\mu_B|^2\omega_B^3}{\hbar c^3} \tag{11}$$

are the excited state decay rates of atoms A and B, μ_A (μ_B) are matrix elements of the dipole moment operator between the ground state and the $m=0$ excited state of atom A (B),

$$f_0(k,\mathbf{R}) = \sqrt{4\pi}\left[j_0(kR)Y_{00}(\theta,\phi) + \frac{1}{\sqrt{5}}j_2(kR)Y_{20}(\theta,\phi)\right], \tag{12a}$$

$$f_{\pm1}(k,\mathbf{R}) = -\sqrt{4\pi}\sqrt{3/20}\,j_2(kR)Y_{2,\pm1}(\theta,\phi), \tag{12b}$$

j_n is a spherical Bessel function, and $Y_{\ell m}$ is a spherical harmonic.

The integrals over frequency can be carried out easily if a Weisskopf-Wigner type approximation is made. That is, all k

and k's appearing in Eq. (10) are evaluated at $k_A = \omega_A/c$ and all ω_k and $\omega_{k's}$ are evaluated at ω_A, except when they appear in phases. Moreover the frequency integrals are extended to $-\infty$. Since the ω_k pole is in the lower half plane and the $\omega_{k'}$ pole is in the upper half plane, only terms varying as $\exp(-ikR)\exp(ik'R)$ contribute to the integral. In other words,

$$\begin{aligned}\delta E &\sim \hbar\frac{\gamma_A\gamma_B}{\omega_{AB}}\sum_{m=-1}^{1}|g_m(k_A\mathbf{R})|^2\frac{\omega_A^3}{\omega_B^3}\\ &\quad\times\lim_{\epsilon\to0^+}\sum_{m=-1}^{1}\frac{1}{(2\pi i)^2}\int_{-\infty}^{\infty}d\omega_k\\ &\quad\times\int_{-\infty}^{\infty}d\omega_{k'}\frac{e^{ik'R}e^{-ikR}}{(\omega_{k'}-\omega_A-i\epsilon)(\omega_k-\omega_A+i\epsilon)}\\ &=\hbar\frac{\gamma_A\gamma_B}{\omega_{AB}}\frac{\omega_A^3}{\omega_B^3}\sum_{m=-1}^{1}|g_m(k_A\mathbf{R})|^2,\end{aligned}\tag{13}$$

where

$$\begin{aligned}g_0(\mathbf{x}) &= \sqrt{4\pi}\left\{-\frac{i}{2x}Y_{00}(\theta,\phi)\right.\\ &\quad\left.+\frac{1}{\sqrt{5}}\left[-\frac{i}{2}\left(\frac{3}{x^3}-\frac{1}{x}\right)-\frac{3}{2x^2}\right]Y_{20}(\theta,\phi)\right\},\end{aligned}\tag{14a}$$

$$g_{\pm1}(\mathbf{x}) = -\sqrt{4\pi}\sqrt{3/20}\,Y_{2,\pm1}(\theta,\phi)\left[-\frac{i}{2}\left(\frac{3}{x^3}-\frac{1}{x}\right)-\frac{3}{2x^2}\right].\tag{14b}$$

For example, if we take atom B to lie on the positive x axis, then

$$\delta E = \hbar\frac{\gamma_A\gamma_B}{\omega_{AB}}\frac{\omega_A^3}{\omega_B^3}\frac{9}{16}\left[\frac{1-(k_AR)^2+(k_AR)^4}{(k_AR)^6}\right].\tag{15}$$

On the other hand, if we average over all orientations of atom B, as do PT, we find

$$\delta E = \hbar\frac{\gamma_A\gamma_B}{\omega_{AB}}\frac{\omega_A^3}{\omega_B^3}\frac{3}{8}\left[\frac{3+(k_AR)^2+(k_AR)^4}{(k_AR)^6}\right].\tag{16}$$

The term in brackets is identical to that in the second term of Eq. (2.17) in PT. To compare the coefficients, I use Eq. (11) to write the coefficient appearing in Eq. (16) as

$$C = \frac{3}{8}\hbar\frac{\gamma_A\gamma_B}{\omega_{AB}}\frac{\omega_A^3}{\omega_B^3} = \frac{2}{3}\frac{|\mu_A|^2\,|\mu_B|^2\,k_A^6}{\hbar\omega_{AB}},\tag{17}$$

whereas, in the limit (7), PT obtain

$$C_{\mathrm{PT}} = \frac{2}{9}\frac{|\mu(A)|^2\,|\mu(B)|^2\,k_A^6}{\hbar\omega_{AB}}.\tag{18}$$

In PT, $|\mu(A)|^2$ represents the average dipole moment of the initial state; that is, $|\mu(A)|^2 = |\mu_A|^2$ for our initial conditions. On the other hand $|\mu(B)|^2$ is a sum over all components; that is, $|\mu(B)|^2 = 3\,|\mu_B|^2$ for our $J = 0$ to $J = 1$ transition. Thus the two results, Eqs. (17) and (18), are identical.

I should stress that the Weisskopf-Wigner approximation introduces negligibly small errors (of order ϵ/ω_A or $\gamma_A,\gamma_B/\omega_A$) in this and subsequent calculations in this paper. The result given by Eq. (16) agrees with PT's calculation of the contribution of diagram x to the interaction energy. This provides the dominant contribution to the interaction energy when inequality (7) is satisfied.

II. COUPLED EQUATIONS

As I have indicated, there are four probability amplitudes, b_A, b_{Bm}, $b_{\mathbf{k}\lambda}$, and $b_{\mathbf{k}'\lambda'}$ which enter the calculation. By eliminating the intermediate-state amplitudes $b_{\mathbf{k}\lambda}$ and $b_{\mathbf{k}'\lambda'}$, one can obtain the following coupled equations for the state amplitudes b_A and b_{Bm} [7,8]:

$$\begin{aligned}\dot{b}_A &= -\frac{\gamma_A}{2}b_A - \frac{\gamma_A}{2}\frac{\mu_B}{\mu_A}e^{i\omega_{AB}t}\\ &\quad\times\sum_{m=-1}^{1}\int_0^t G_m(\mathbf{R},\tau,\omega_B)b_{Bm}(t-\tau)d\tau,\end{aligned}\tag{19a}$$

$$\begin{aligned}\dot{b}_{Bm} &= -\frac{\gamma_B}{2}b_{Bm} - \frac{\gamma_A}{2}\frac{\mu_B}{\mu_A}e^{-i\omega_{AB}t}\\ &\quad\times\int_0^t H_m(\mathbf{R},\tau,\omega_A)b_A(t-\tau)d\tau,\end{aligned}\tag{19b}$$

where

$$G_m(\mathbf{R},\tau,\omega_B) = \pi^{-1}\omega_B^{-3}\int_0^{\infty}d\omega_k\,\omega_k^3e^{-i(\omega_k-\omega_B)\tau}f_m(k,\mathbf{R}),\tag{20a}$$

$$H_m(\mathbf{R},\tau,\omega_A) = \pi^{-1}\omega_A^{-3}\int_0^{\infty}d\omega_k\,\omega_k^3e^{-i(\omega_k-\omega_A)\tau}f_m^*(k,\mathbf{R}),\tag{20b}$$

and a standard interaction representation is used with the f's given by Eqs. (12) [12]. Retardation is readily apparent in these equations. If we set

$$b_{Bm}(t) = e^{-i\omega_{AB}t}d_{Bm}(t),\tag{21}$$

then

$$\begin{aligned}\dot{b}_A &= -\frac{\gamma_A}{2}b_A - \frac{\gamma_A}{2}\frac{\mu_B}{\mu_A}\frac{\omega_A^3}{\omega_B^3}\\ &\quad\times\sum_{m=-1}^{1}\int_0^t G_m(\mathbf{R},\tau,\omega_A)d_{Bm}(t-\tau)d\tau,\end{aligned}\tag{22a}$$

$$\begin{aligned}\dot{d}_{Bm} &= -\left(\frac{\gamma_B}{2}-i\omega_{AB}\right)d_{Bm}\\ &\quad-\frac{\gamma_A}{2}\frac{\mu_B}{\mu_A}\int_0^t H_m(\mathbf{R},\tau,\omega_A)b_A(t-\tau)d\tau.\end{aligned}\tag{22b}$$

Note that both G_m and H_m are now evaluated at ω_A.

The integrals over ω_k in Eq. (20) can be carried out using a Weisskopf-Wigner type approximation, as in the previous section. In this manner, we find [7,8]

$$\begin{aligned}G_m(\mathbf{R},\tau,\omega_B) &= [e^{ik_AR}\delta(\tau-R/c)\,M_m(k_A,\mathbf{R})\\ &\quad+e^{-ik_AR}\delta(\tau+R/c)\,M_m^*(k_A,\mathbf{R})],\end{aligned}\tag{23a}$$

$$\begin{aligned}H_m(\mathbf{R},\tau,\omega_A) &= [e^{ik_AR}\delta(\tau-R/c)\,P_m(k_A,\mathbf{R})\\ &\quad+e^{-ik_AR}\delta(\tau+R/c)\,P_m^*(k_A,\mathbf{R})],\end{aligned}\tag{23b}$$

where

$$M_0(k,\mathbf{R}) = P_0(k,\mathbf{R}) = -\sqrt{4\pi}\left\{\frac{i}{\rho}Y_{00}(\theta,\phi) + \frac{1}{\sqrt{5}}\left[i\left(\frac{3}{\rho^3}-\frac{1}{\rho}\right)+\frac{3}{\rho^2}\right]Y_{20}(\theta,\phi)\right\}, \tag{24a}$$

$$M_{\pm 1}(k,\mathbf{R}) = \sqrt{4\pi}\sqrt{3/20}\left[i\left(\frac{3}{\rho^3}-\frac{1}{\rho}\right)+\frac{3}{\rho^2}\right]Y_{2,\pm 1}(\theta,\phi), \tag{24b}$$

$$P_{\pm 1}(k,\mathbf{R}) = \sqrt{4\pi}\sqrt{3/20}\left[i\left(\frac{3}{\rho^3}-\frac{1}{\rho}\right)+\frac{3}{\rho^2}\right]Y^{*}_{2,\pm 1}(\theta,\phi), \tag{24c}$$

and $\rho = kR$. For fixed R, the δ functions $\delta(\tau + R/c)$ do not contribute to the time integrals in Eq. (22). As a consequence, we obtain

$$\dot{b}_A = -\frac{\gamma_A}{2}b_A - \frac{\gamma_A}{2}\frac{\mu_B}{\mu_A}\frac{\omega_A^3}{\omega_B^3}e^{ik_AR} \times \sum_{m=-1}^{1} M_m(k_A,\mathbf{R})d_{Bm}(t-R/c), \tag{25a}$$

$$\dot{d}_{Bm} = -\left(\frac{\gamma_B}{2} - i\omega_{AB}\right)d_{Bm} - \frac{\gamma_A}{2}\frac{\mu_B}{\mu_A}e^{ik_AR}P_m(k_A,\mathbf{R})b_A(t-R/c). \tag{25b}$$

The atoms are dissimilar; in other words the frequency difference $|\omega_{BA}|$ is assumed to be much greater than $\gamma_A + \gamma_B$ so there cannot be resonant exchange of excitation between the two atoms. In the limit $|\omega_{AB}| \gg \gamma_A, \gamma_B$, the solution of Eq. (25b) is approximately

$$d_{Bm} \approx -i\frac{\gamma_A}{2\omega_{AB}}\frac{\mu_B}{\mu_A}e^{ik_AR}P_m(k_A,\mathbf{R})b_A(t-R/c), \tag{26}$$

which implies that

$$\dot{b}_A = -\frac{\gamma_A}{2}b_A + i\frac{\gamma_A\gamma_B}{4\omega_{AB}} \times e^{2ik_AR}M_m(k_A,\mathbf{R})P_m(k_A,\mathbf{R})b_A(t-2R/c). \tag{27}$$

When inequality (1) holds, we can set $b_A(t-2R/c) \approx b_A(t)$. It then follows that the energy shift is simply

$$\delta E = -\hbar\frac{\gamma_A\gamma_B}{4\omega_{AB}}\frac{\omega_A^3}{\omega_B^3}\,\mathrm{Re}\left[e^{2ik_AR}\sum_{m=-1}^{1}M_m(k_A,\mathbf{R})P_m(k_A,\mathbf{R})\right], \tag{28}$$

an oscillatory function of k_AR. For atom B on the x axis ($\theta = \pi/2, \phi = 0$),

$$\delta E = -\hbar\frac{\gamma_A\gamma_B}{4\omega_{AB}}\frac{\omega_A^3}{\omega_B^3} \times \mathrm{Re}\left(e^{2i\rho_A}\left\{-\frac{3}{2}\left[i\left(\frac{1}{\rho_A^3}-\frac{1}{\rho_A}\right)+\frac{1}{\rho_A^2}\right]\right\}^2\right), \tag{29}$$

where

$$\rho_A = k_AR.$$

If we average over all orientations of atom B, we find

$$\delta E = -\hbar\frac{\gamma_A\gamma_B}{4\omega_{BA}}\frac{\omega_A^3}{\omega_B^3}\,\mathrm{Re}\left(e^{2i\rho_A}\left\{\left(\frac{1}{\rho_A}\right)^2 \times + \left(\frac{1}{2}\right)\left[\left(\frac{3}{\rho_A^3}-\frac{1}{\rho_A}\right)-\frac{3i}{\rho_A^2}\right]^2\right\}\right). \tag{30}$$

III. FOURTH-ORDER TIME-DEPENDENT PERTURBATION THEORY

To make a closer connection with the PT result, I use time-dependent perturbation theory, holding off evaluating the integrals over frequency until the end of the calculation. The appropriate equations for the field amplitudes (in an interaction representation) are

$$\dot{b}_A(t) = -\frac{\gamma_A}{2}b_A(t) + \frac{1}{i\hbar}\sum_{\mathbf{k}\lambda}\langle A|\,V\,|\mathbf{k}\lambda\rangle\, e^{i\omega_{Ak}t}b_{\mathbf{k}\lambda}(t), \tag{31a}$$

$$\dot{b}_{\mathbf{k}\lambda}(t) = \frac{1}{i\hbar}\sum_{\mathbf{k}\lambda}\langle\mathbf{k}\lambda|\,V\,|A\rangle\, e^{-i\omega_{Ak}t}b_A(t) + \frac{1}{i\hbar}\sum_{m=-1}^{1}\sum_{\mathbf{k}\lambda}\langle\mathbf{k}\lambda|\,V\,|Bm\rangle\, e^{-i\omega_{Bk}t}b_{Bm}(t), \tag{31b}$$

$$\dot{b}_{Bm}(t) = -\frac{\gamma_B}{2}b_{Bm}(t) + \frac{1}{i\hbar}\sum_{\mathbf{k}\lambda}\langle Bm|\,V\,|\mathbf{k}\lambda\rangle\, e^{i\omega_{Bk}t}b_{\mathbf{k}\lambda}(t), \tag{31c}$$

where

$$\omega_{\alpha k} = \omega_\alpha - \omega_k, \quad \alpha = A,B. \tag{32}$$

At this point it is appropriate to say something about the initial conditions. Up to this point and in this section, it is assumed implicitly that atom A is excited *suddenly* at time $t = 0$. By "suddenly," I mean that the excitation time is short compared with R/c and $|\omega_{BA}|^{-1}$. There are some who might argue that this sudden excitation introduces spurious terms into the calculation. To alleviate such fears, I show in the Appendix that the results are unchanged even if we excite atom A adiabatically, that is, in a time interval T satisfying the inequalities $\gamma_A^{-1} \gg T > |\omega_{BA}|^{-1}$.

To fourth order in perturbation theory, assuming that, to zeroth order in V, $b_A(t) \approx e^{-\gamma_At/2}$,

$$i\hbar\dot{b}_A(t) = i\hbar\left(\frac{1}{i\hbar}\right)^4\sum_{m=-1}^{1}\sum_{\mathbf{k}\lambda,\mathbf{k}'\lambda'}\langle A|\,V\,|\mathbf{k}'\lambda'\rangle \times \langle\mathbf{k}'\lambda'|\,V\,|Bm\rangle\langle Bm|\,V\,|\mathbf{k}\lambda\rangle\langle\mathbf{k}\lambda|\,V\,|A\rangle\, e^{i\omega_{Ak'}t} \times \int_0^t dt' e^{i\omega_{k'B}t'}\int_0^{t'} dt'' e^{i\omega_{Bk}t''}e^{-\gamma_B(t'-t'')/2} \times \int_0^{t''} dt''' e^{i\omega_{kA}t'''}e^{-\gamma_At'''/2}. \tag{33}$$

The real part of the term on the right-hand side can be identified as δE for $\gamma_A t \ll 1$. After carrying out the angular averages, I obtain

$$\delta E = \text{Re}\left\{ i\hbar \frac{\gamma_A\gamma_B}{4(2\pi i)^2}\int_0^\infty d\omega_k \int_0^\infty d\omega_{k'} \frac{\omega_k^3}{\omega_A^3}\frac{\omega_{k'}^3}{\omega_B^3} I(k,k') \times \sum_{m=-1}^{1}\left[M_m(k,\mathbf{R})e^{ikR}+M_m^*(k,\mathbf{R})e^{-ikR}\right] \times \left[P_m(k',\mathbf{R})e^{ik'R}+P_m^*(k',\mathbf{R})e^{-ik'R}\right]\right\}, \tag{34}$$

where

$$\begin{aligned} I(k,k') ={}& \frac{e^{-\gamma_A t/2}}{(\omega_{kA}+i\gamma_A/2)(\omega_{k'A}+i\gamma_A/2)(i\omega_{AB}+\gamma_A/2-\gamma_B/2)} \\ &- \frac{e^{-\gamma_B t + i\omega_{AB}t}}{(\omega_{kB}+i\gamma_B/2)(\omega_{k'B}+i\gamma_B/2)(i\omega_{AB}+\gamma_A/2-\gamma_B/2)} \\ &- \frac{i e^{-i\omega_{kA}t}}{\omega_{kk'}(\omega_{kA}+i\gamma_A/2)(\omega_{kB}+i\gamma_B/2)} \\ &+ \frac{i e^{-i\omega_{k'A}t}}{\omega_{kk'}(\omega_{k'A}+i\gamma_A/2)(\omega_{k'B}+i\gamma_B/2)}. \end{aligned} \tag{35}$$

I neglect the second term in $I(k,k')$ since it is rapidly varying in time. Moreover, I set $e^{-\gamma_A t/2} \approx 1$ and replace $(\omega_{kB}+i\gamma_B)$ [and $(\omega_{k'B}+i\gamma_B)$] by ω_{AB} and $(i\omega_{AB}+\gamma_A-\gamma_B)$ by $i\omega_{AB}$, since this leads to corrections of order $\gamma_{A,B}/\omega_{AB}$ [13]. As a consequence,

$$\begin{aligned} I(k,k') \approx{}& \frac{1}{i\omega_{AB}(\omega_{kA}+i\gamma_A/2)(\omega_{k'A}+i\gamma_A/2)} \\ &- \frac{i e^{-i\omega_{kA}t}}{\omega_{kk'}\omega_{AB}(\omega_{kA}+i\gamma_A/2)} \\ &+ \frac{i e^{-i\omega_{k'A}t}}{\omega_{kk'}\omega_{AB}(\omega_{k'A}+i\gamma_A/2)}. \end{aligned} \tag{36}$$

The sum of the second and third terms in Eq. (36) does not diverge at $\omega_{kk'}=0$. As a consequence, we can set

$$\begin{aligned} \frac{1}{\omega_{kk'}} &= \frac{1}{2}\lim_{\epsilon\to 0^+}\left(\frac{1}{\omega_{kk'}+i\epsilon}+\frac{1}{\omega_{kk'}-i\epsilon}\right) \\ &= \lim_{\epsilon\to 0^+}\frac{\omega_{kk'}}{(\omega_{kk'})^2+\epsilon^2} = P\left(\frac{1}{\omega_{kk'}}\right), \end{aligned} \tag{37}$$

since excluding the nondivergent *point* $\omega_{kk'}=0$ does not change the value of the integral expression (34). Once this substitution is made, we can neglect any terms varying as $\gamma_A t$ or $\gamma_A R/c$ in what follows based on inequalities (1), (2), and (7). By substituting Eqs. (36) and (37) into Eq. (34) and interchanging k and k' in the last term [that is, the term multiplied by the last line in Eq. (36)], I find

$$\begin{aligned} \delta E ={}& \hbar\frac{\gamma_A\gamma_B}{4\omega_{AB}}\frac{1}{(2\pi i)^2}\sum_{m=-1}^{1}\text{Re}\int_0^\infty d\omega_k\int_0^\infty d\omega_{k'}\frac{\omega_k^3}{\omega_A^3}\frac{\omega_{k'}^3}{\omega_B^3} \\ &\times\left[\frac{A_m(k,k')}{(\omega_{kA}+i\gamma_A)(\omega_{k'A}+i\gamma_A)} + \frac{B_m(k,k')+C_m(k,k')+D_m(k,k')+E_m(k,k')}{(\omega_{kA}+i\gamma_A)} \times e^{-i\omega_{kA}t}P\left(\frac{1}{\omega_{kk'}}\right)\right], \end{aligned} \tag{38}$$

where

$$A_m(k,k') = [M_m(k,\mathbf{R})e^{ikR}+M_m^*(k,\mathbf{R})e^{-ikR}] \times [P_m(k',\mathbf{R})e^{ik'R}+P_m^*(k',\mathbf{R})e^{-ik'R}], \tag{39a}$$

$$B_m(k,k') = [M_m(k,\mathbf{R})P_m(k',\mathbf{R}) + M_m(k',\mathbf{R})P_m(k,\mathbf{R})]e^{i(k+k')R}, \tag{39b}$$

$$C_m(k,k') = [M_m(k,\mathbf{R})P_m(k',\mathbf{R}) + M_m(k',\mathbf{R})P_m(k,\mathbf{R})]^* e^{-i(k+k')R}, \tag{39c}$$

$$D_m(k,k') = [M_m(k,\mathbf{R})P_m^*(k',\mathbf{R}) + M_m^*(k',\mathbf{R})P_m(k,\mathbf{R})]e^{i(k-k')R}, \tag{39d}$$

$$E_m(k,k') = [M_m(k,\mathbf{R})P_m^*(k',\mathbf{R}) + M_m^*(k',\mathbf{R})P_m(k,\mathbf{R})]^* e^{-i(k-k')R}. \tag{39e}$$

I have carried out the integrations in the radiation zone without making the Weisskopf-Wigner approximation and verified that they reproduce the same results that I obtain using the Weisskopf-Wigner approximation. In the Weisskopf-Wigner approximation, it is a simple matter to carry out the contour integrations. The first term in Eq. (38), arising from Eq. (39a), yields

$$\delta E_1 = \hbar\frac{\gamma_A\gamma_B}{4\omega_{AB}}\frac{\omega_A^3}{\omega_B^3}\,\text{Re}\sum_{m=-1}^{1}M_m^*(k_A,\mathbf{R})P_m^*(k_A,\mathbf{R})e^{-2ik_AR}. \tag{40}$$

The fourth and fifth terms, arising from Eqs. (39d) and (39e) cancel one another, while the second and third terms, arising from Eqs. (39b) and (39c), contribute

$$\begin{aligned} \delta E_2 ={}& -\hbar\frac{\gamma_A\gamma_B}{4\omega_{AB}}\frac{\omega_A^3}{\omega_B^3} \\ &\times\text{Re}\sum_{m=-1}^{1}[M_m^*(k_A,\mathbf{R})P_m^*(k_A,\mathbf{R})e^{-2ik_AR} \\ &+ M_m(k_A,\mathbf{R})P_m(k_A,\mathbf{R})e^{2ik_AR}\Theta(t-2R/c)], \end{aligned} \tag{41}$$

where Θ is a Heaviside function. The first term Eq. (41) cancels the δE_1 contribution to δE given in Eq. (40), while the remaining term in Eq. (41) provides the correct retardation. For $t > 2R/c$, we find

$$\delta E = -\hbar\frac{\gamma_A\gamma_B}{4\omega_{AB}}\frac{\omega_A^3}{\omega_B^3}\,\text{Re}\sum_{m=-1}^{1}M_m(k_A,\mathbf{R})P_m(k_A,\mathbf{R})e^{2ik_AR}, \tag{42}$$

in agreement with Eq. (28).

IV. DISCUSSION

I have shown that the interaction energy between an initially excited atom and a ground state atom is an oscillatory function of their separation if only energy-conserving terms are included, that is, terms that dominant the interaction energy when $|\omega_{BA}| \ll \omega_A$. My results do not agree with those of PT, who found a nonoscillatory dependence. I have argued that the choice of the signs of the ϵ's used in such a calculation must be justified on the basis of a time-dependent calculation, which I have carried out. Had PT used the prescription

$$\frac{1}{(\omega_{k'A} - i\epsilon)\,\omega_{BA}\,(\omega_{kA} - i\epsilon)} \tag{43}$$

instead of

$$\frac{1}{(\omega_{k'A} - i\epsilon)\,\omega_{BA}\,(\omega_{kA} + i\epsilon)}, \tag{44}$$

they would have obtained our result, Eq. (42), in the limit that $t > 2R/c$ (note that prescription (43) is the one used by Philpott [10]). On a physical basis, the oscillatory dependence is to be expected. Atom A emits radiation whose frequency is centered at ω_A and this radiation is scattered back to atom A by atom B; in other words there is not an integral over a large range of frequencies as there is for non-energy-conserving transitions. As a consequence, we would expect that the spatial phase factor e^{2ik_AR} associated with this scattering process should enter into the expression for the interaction energy. As a reminder, I am defining the interaction energy as the shift in energy of the initial state resulting from the interatomic interaction.

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APPENDIX: ADIABATIC EXCITATION OF ATOM *A*

It may be argued that the sudden excitation of atom A leads to spurious terms in the interaction energy. In this appendix, I show that the only spurious term of this nature that could be attributed to a sudden excitation of atom A actually corresponds to the second term of Eq. (35), a term that was neglected in any event since it was rapidly varying on a time scale of order $1/|\omega_{AB}|$.

In trying to ascertain the effect of a sudden turn-on of an excitation field, it is good practice to begin with all atoms in their ground states. That is the procedure I follow. I denote by $|g\rangle$ the state in which both atoms are in their ground states. The atoms are subjected to a field pulse whose carrier frequency is resonant with ω_A; this field acts only on atom A. As such, in the absence of any *interatomic* interactions [that is, to zeroth order in the interaction potential V appearing in Eqs. (31)], the amplitude equations are

$$\dot{b}_g(t) = -\chi(t)b_A(t), \tag{A1a}$$

$$\dot{b}_A(t) = -\frac{\gamma_A}{2}b_A(t) + \chi(t)b_g(t), \tag{A1b}$$

where $\chi(t)$ is one-half the Rabi frequency associated with the pulsed field excitation of atom A. It is assumed that the field is turned on adiabatically (with respect to $1/|\omega_{AB}|$) in a time interval $T > 1/|\omega_{AB}|$ centered at $t = 0$ and I consider only times t satisfying

$$\frac{1}{|\omega_{AB}|} < T \ll t \ll \frac{1}{\gamma_A} \tag{A2}$$

(the only time range that makes sense for an adiabatic field turn-on and one for which we can define an interaction energy). In the limit that inequality (A2) holds, the approximate solution of Eqs. (A1) is

$$b_A^{(0)}(t) \approx A(t)e^{-\gamma_A t/2}, \tag{A3}$$

where

$$A(t) = \sin \int_{-\infty}^{t} \chi(t')dt'. \tag{A4}$$

Under these conditions, $A(t) \approx 0$ for $t < -T/2$ and $A(t) \approx 1$ for $t > T/2$ (assuming a π pulse).

Thus the expression

$$e^{i\omega_{Ak'}t}\int_0^t dt' e^{i\omega_{k'B}t'}\int_0^{t'} dt'' e^{i\omega_{Bk}t''}e^{-\gamma_B(t'-t'')/2} \times \int_0^{t''} dt''' e^{i\omega_{kA}t'''}e^{-\gamma_A t'''/2} \tag{A5}$$

appearing in Eq. (33) should be replaced by

$$\begin{aligned} G &= e^{i\omega_{Ak'}t}\int_0^t dt' e^{i\omega_{k'B}t'}\int_0^{t'} dt'' e^{i\omega_{Bk}t''} \\ &\quad\times \int_0^{t''} dt''' e^{i\omega_{kA}t'''}e^{-\gamma_A t'''/2}A(t''') \\ &= e^{i\omega_{Ak'}t}\int_{-\infty}^t dt_1 e^{i\omega_{k'B}t_1}\int_{-\infty}^{t_1} dt_2 e^{i\omega_{BA}t_2} \\ &\quad\times \int_{-\infty}^{t_2} dt_3 e^{i\omega_{kA}(t_3-t_2)}e^{-\gamma_A t_3/2}A(t_3), \end{aligned} \tag{A6}$$

where I set $\gamma_B = 0$ as it is unimportant in this calculation. Since the function

$$f(t_2) = \int_{-\infty}^{t_2} dt_3 e^{i\omega_{kA}(t_3-t_2)}e^{-\gamma_A t_3/2}A(t_3) \tag{A7}$$

is slowly varying with respect to $e^{i\omega_{BA}t_2}$, we can do the integral over t_2 in Eq. (A6) by parts to arrive at

$$\begin{aligned} G &\approx -\frac{1}{i\omega_{AB}}e^{-i\omega_{k'A}t}\int_{-\infty}^t dt_1 e^{i\omega_{k'B}t_1}e^{i\omega_{BA}t_1}f(t_1) \\ &= -\frac{1}{i\omega_{AB}}e^{-i\omega_{k'A}t}\int_{-\infty}^t dt_1 e^{i\omega_{k'A}t_1} \\ &\quad\times \int_{-\infty}^{t_1} dt_2 e^{i\omega_{kA}(t_2-t_1)}e^{-\gamma_A t_2/2}A(t_2) \\ &= -\frac{1}{i\omega_{AB}}e^{-i\omega_{k'A}t}\int_{-\infty}^t dt_1 e^{i\omega_{k'k}t_1} \\ &\quad\times \int_{-\infty}^{t_1} dt_2 e^{i\omega_{kA}t_2}e^{-\gamma_A t_2/2}A(t_2). \end{aligned} \tag{A8}$$

I now switch the order of integration and find

$$\begin{aligned} G &= -\frac{1}{i\omega_{AB}} e^{-i\omega_{k'A}t} \int_{-\infty}^{t} dt_2 e^{i\omega_{kA}t_2} e^{-\gamma_A t_2/2} A(t_2) \\ &\quad \times \int_{t_2}^{t} dt_1 e^{i\omega_{k'k}t_1} dt_1 \\ &= \frac{-1}{\omega_{AB}\omega_{kk'}} e^{-i\omega_{k'A}t} \int_{-\infty}^{t} dt_2 e^{i\omega_{kA}t_2} e^{-\gamma_A t_2/2} A(t_2) \\ &\quad \times \left(e^{i\omega_{k'k}t} - e^{i\omega_{k'k}t_2}\right) \\ &= \frac{1}{\omega_{AB}\omega_{kk'}} \int_{-\infty}^{t} dt_2 e^{-\gamma_A t_2/2} A(t_2) \left(e^{i\omega_{k'A}(t_2-t)} - e^{i\omega_{kA}(t_2-t)}\right). \end{aligned} \tag{A9}$$

Note that this expression is well defined in the limit that $\omega_{kk'} \sim 0$.

What is important to note is that $A(t_2)$ varies from 0 to 1 in a time interval T centered about $t = 0$. Thus we have

$$\begin{aligned} G &\approx \frac{1}{\omega_{AB}\omega_{kk'}} \int_{-T/2}^{T/2} dt_2 A(t_2) \left(e^{i\omega_{k'A}(t_2-t)} - e^{i\omega_{kA}(t_2-t)}\right) \\ &\quad + \frac{1}{\omega_{AB}\omega_{kk'}} \int_{T/2}^{t} dt_2 e^{-\gamma_A t_2/2} \left(e^{i\omega_{k'A}(t_2-t)} - e^{i\omega_{kA}(t_2-t)}\right). \end{aligned} \tag{A10}$$

The first term is of order $T/t \ll 1$ times the second so we can replace the entire expression by

$$\begin{aligned} G &\approx \frac{1}{\omega_{AB}\omega_{kk'}} \int_{T/2}^{t} dt_2 e^{-\gamma_A t_2/2} \left(e^{i\omega_{k'A}(t_2-t)} - e^{i\omega_{kA}(t_2-t)}\right) \\ &\approx \frac{1}{\omega_{AB}\omega_{kk'}} \int_{0}^{t} dt_2 e^{-\gamma_A t_2/2} \left(e^{i\omega_{k'A}(t_2-t)} - e^{i\omega_{kA}(t_2-t)}\right), \end{aligned} \tag{A11}$$

where I used the fact that $|\omega_{k'A}|T$, $|\omega_{kA}|T$, and $\gamma_A T$ are much less than unity.

Carrying out the integration, I find

$$\begin{aligned} G &\approx \frac{1}{i\omega_{AB}(\omega_{k'A} + i\gamma_A/2)(\omega_{kA} + i\gamma_A/2)} \\ &\quad - \frac{i e^{-i\omega_{kA}t}}{\omega_{AB}\omega_{kk'}(\omega_{kA} + i\gamma_A/2)} + \frac{i e^{-i\omega_{k'A}t}}{\omega_{AB}\omega_{kk'}(\omega_{k'A} + i\gamma_A/2)}, \end{aligned} \tag{A12}$$

which reproduces Eq. (36). Thus, whether we excite atom A suddenly or adiabatically (with respect to $1/|\omega_{BA}|$) from an initial condition in which both atoms are in their ground states, we get an oscillatory interaction energy. The "spurious" term introduced by a sudden turn-on of the field, represented by the second term in Eq. (35), does not appear in the adiabatic calculation; however, this term contributed negligibly to the final result given by Eq. (36), under the assumption that it is rapidly oscillating and averages to zero on a time scale greater than $1/|\omega_{AB}|$.

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[1] See, for example, M. J. Stephen, J. Chem. Phys. **40**, 669 (1964).

[2] If a Heisenberg approach to the problem is used to derive an equation for the time evolution of the lowering operator of atom B, the level shift appearing in that equation would be (twice) the ac Stark shift produced by the field from atom A on atom B. In such an approach there is an implicit trace over the states of atom A so the quantity calculated is different from the level shift of the initial state calculated in this paper.

[3] L. Rizzuto, R. Passante, and F. Persico, Phys. Rev. A **70**, 012107 (2004).

[4] Y. Sherkunov, Phys. Rev. A **79**, 032101 (2009).

[5] H. R. Haakh, J. Schiefele, and C. Henkel, Int. J. Mod. Phys.: Conf. Ser. **14**, 347 (2012).

[6] Both Rizzuto *et al.* [3] and Haakh *et al.* [5] also calculate a transient contribution to the interaction potential that contributes only for times $t \lesssim 1/\omega_A$. To simultaneously satisfy $t > R/c$, this term can contribute only if the atoms are separated by less than a wavelength. Moreover, the time-dependent term calculated by these authors would not be present if atom A is excited adiabatically on a time scale greater than $1/\omega_A$. This term is not included in my calculation.

[7] P. R. Berman and P. W. Milonni, Phys. Rev. Lett. **92**, 053601 (2004).

[8] H. Fu and P. R. Berman, Phys. Rev. A **72**, 022104 (2005).

[9] E. A. Power and T. Thirunamachandran, Phys. Rev. A **51**, 3660 (1995).

[10] R. R. McLone and E. A. Power, Proc. R. Soc. London, Ser. A **286**, 573 (1965); M. R. Philpott, Proc. Phys. Soc. **87**, 619 (1966).

[11] E. A. Power and T. Thirunamachandran, Chem. Phys. **198**, 5 (1995).

[12] Any R-independent level shifts are assumed to be incorporated into the definition of frequencies ω_A and ω_B.

[13] The contributions to $I(k,k')$ for the poles near $\omega_{kB} = 0$ and $\omega_{k'B} = 0$ are neglected since they give rise to terms that vary rapidly in time with frequency $|\omega_{AB}|$. Such terms will not appear, in any event, if the field is turned on slowly compared with $1/|\omega_{AB}|$.