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Resonance interaction between one excited and one ground state atom

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Abstract. The nature of the resonance interaction between two isotropic atoms in an excited configuration is reinvestigated. The currently accepted oscillatory form for the long-range retarded resonance interaction is shown to be a subtle artefact that arises due to too drastic approximations. Formulation of the resonance interaction energy problem in terms of the *interacting* system leads to a form that it is $\propto r^{-4}$ in the retarded limit. We also demonstrate that the resonance interaction energy at any finite temperature goes over to purely classical long-range asymptote. This manifestation of the correspondence principle is due to thermal excitation of the electromagnetic field. We finally discuss why the textbook result for the Förster energy transfer between two atoms is incorrect for the same reasons.

PACS. 34.20.Cf Interatomic potentials and forces – 34.30.+h Intramolecular energy transfer; intramolecular dynamics; dynamics of van der Waals molecules

1 Introduction

A detailed knowledge of the nature of interaction energies and transition rates for diatomic systems in excited configurations is important to understand cold collision processes, laser cooling of atomic samples, and coherent control of cold molecule formation. It is also relevant to possible future developments like mooted molecular quantum computation. Efficient formation of long-lived cold molecules *via* photoassociation has been achieved experimentally [1]. The theoretical explanation involves the resonance interaction between excited and ground state atoms [2]. Atomic radiative life times are sensitive tests of atomic-structure calculations, and experiments have been performed on molecules created from two atoms, one in its ground state and one in an excited electronic state [3–5]. Binding energies and life times were determined using photoassociation spectroscopy of laser-cooled atoms and the results compared to the theoretical results of McLone and Power [6]. However, as we will show here the standard oscillating long-range retarded interaction is erroneous. We derive the correct form of the interaction.

In a series of publications Mitchell, Ninham, Richmond and Mahanty [7–9] developed a semi-classical method for the van der Waals energy of interaction between two atoms in their ground states. The atoms were represented as polarizable dipoles. In the appropriate limits both the London [10] ($\propto r^{-6}$) and Casimir-Polder [11] ($\propto r^{-7}$) potentials were obtained. In the present work we will use this formalism to study the interaction between two identical atoms (or two identical molecules) when one is in its ground state and the other in an excited state. The semiclassical technique that we use is precisely equivalent to the full QED interaction problem as given by Dzyaloshinskii, Lifshitz and Pitaevskii for ground state interactions [9,12,13]. It can also be used to derive an estimate of the Lamb shift [9]. The quantum mechanical perturbation treatment of the problem is well-known [14]. Here, in the non-retarded case the interaction is $\propto r^{-3}$, where r is the distance between the atoms. In the retarded limit McLone and Power [6] found that it was $\propto (\omega_0 r/c)^{-1}\cos(\omega_0 r/c)$ where ω_0 is the oscillator absorption frequency and c is the velocity of light. Potentials of this form have been used to study exciton transfer in molecular crystals [15]. This leads to a shape dependence of the physical properties of these crystals in so far as conditionally convergent series arise from use of the long-range potential. The retarded resonance interaction problem then presents something of a puzzle, particularly since the basic theory from which it is derived has appeared to be correct. The puzzle is here resolved. The self-consistent method that we use yields the usual non-retarded resonance interaction potential $\propto r^{-3}$. But the retarded resonance potential between identical isotropic atoms in an excited configuration turns out to be $\propto r^{-4}$, which is physically very sensible.

The paper is organized as follows. We derive in Section 2 the correct resonance interaction energy between two atoms in an excited configuration. The currently

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accepted oscillating form for the retarded interaction is demonstrated to be a subtle artefact of approximations that do not take the coupling *via* the field properly into account. We discuss in Section 3 how the interaction changes at any finite temperature. As we will discuss in Section 4 the resonance interaction is closely related to the Förster energy transfer. The Förster energy transfer [16] underpins many problems in biology. It underlies photosynthesis, artificial light harvesting, and fluorescent light-emitting devices [17–19]. Förster energy transfer was discovered experimentally by Cario and Franck in 1923 [20]. They exposed a mixture of mercury and thallium to a frequency which could only be absorbed by the mercury atoms. The fluorescence spectrum contained frequencies that could only be emitted by the thallium demonstrating a transfer of energy between mercury and thallium atoms. However, while resonant energy transfer certainly exists, we will demonstrate that the existent underlying theory derived from perturbative quantum electrodynamics (QED) is incorrect. This interaction furthermore underlies the interpretation of many problems in circular and optical dichroism and related techniques standard in biophysical chemistry. Subtraction of an erroneous (theoretical) result from experiment to infer electron transfer in macromolecules causes serious difficulties in interpretation.

2 Resonance interaction at zero temperature

We first outline the present accepted status of the problem before coming to difficulties with this approach. We will write down the equations of motion and obtain a characteristic Green function for the system [21]. We also show that results obtained by McLachlan [21] which pertains to the time dependent case of energy transfer can be deduced from this Green function. We then use this Green function to determine the interaction energy. The reasons for the breakdown of the conventional quantum field theoretic perturbation treatment are explored and discussed below.

Following the earlier treatment for two atoms in their ground states [7–9] we consider two identical polarizable dipoles and choose a coordinate system with origin at dipole 1. The positive z-axis is directed toward dipole 2. The oscillating moment of dipole 1, $\mathbf{P}(1,t) = \mathbf{P}(1)\mathrm{e}^{-\mathrm{i}\omega t}$, gives rise to an oscillating field $\mathbf{E}(t) = \mathbf{E}(\mathbf{r}|1)\mathrm{e}^{-\mathrm{i}\omega t}$ where

$$\mathbf{E}(\mathbf{r}|1) = \mathbf{T}(\mathbf{r}|\omega)\mathbf{P}(1), \tag{1}$$

and

$$\mathbf{T}(\mathbf{r}|\omega)_{ij} = \left(\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} - \delta_{ij}\nabla^2\right) G(\mathbf{r}|\omega). \tag{2}$$

The Green function is defined as

$$G(\mathbf{r}|z) = \frac{1}{(2\pi)^3}\int \mathrm{d}^3k \frac{\mathrm{e}^{\mathrm{i}\mathbf{kr}}}{z^2/c^2 - k^2}\,\cdot \tag{3}$$

This function is analytic everywhere in the complex z-plane except on the real frequency axis where it has a branch cut. When evaluating the free space susceptibility matrix $\mathbf{T}$ in equation (2) we must prescribe how to approach this cut. The retarded form which approaches the cut from above yields the following non-zero matrix elements [21],

$$T_{xx} = T_{yy} = \left(\frac{\omega^2}{c^2} + \frac{\mathrm{i}\omega}{rc} - \frac{1}{r^2}\right)\frac{\mathrm{e}^{\mathrm{i}\omega r/c}}{r},$$
$$T_{zz} = 2\left(\frac{1}{r^2} - \frac{\mathrm{i}\omega}{rc}\right)\frac{\mathrm{e}^{\mathrm{i}\omega r/c}}{r}\cdot \tag{4}$$

Substituting this into equation (1) yields the usual retarded field [7–9]. Now the matrix can be separated into real and imaginary parts. Thus

$$\mathbf{T}(\mathbf{r}|\omega) = \mathbf{T}'(\mathbf{r}|\omega) + \mathrm{i}\mathbf{T}''(\mathbf{r}|\omega). \tag{5}$$

These give rise to in phase and out of phase components of the electric field. In the limit $|\mathbf{r}| \to 0$ the real part of G is a principal value integral which is identically zero for real ω. This can be proved using the fact that

$$P\int_0^\infty \frac{\cos(\alpha x)}{x^2 - a^2} = \frac{\pi \sin(a\alpha)}{2a} \tag{6}$$

differentiating twice with respect to α and going to the limit $\alpha \to 0$. Hence the real part of $\mathbf{T}(0,\omega)$ is zero. The imaginary part yields an out of phase contribution to $\mathbf{T}$ which is the well known radiation damping.

$$\mathbf{T}''(0|\omega)_{ij} = \delta_{ij}\frac{2}{3}\frac{\omega^3}{c^3} \equiv \delta_{ij}\frac{\omega}{\alpha_0}\gamma(\omega). \tag{7}$$

The equation of motion for two coupled dipoles separated by a distance r are now [21]

$$(\omega_0^2 - \omega^2)\mathbf{P}(1) = \alpha_0[\mathrm{i}\mathbf{T}''(0|\omega)\mathbf{P}(1) + \mathbf{T}(\mathbf{r}|\omega)\mathbf{P}(2)], \tag{8}$$
$$(\omega_0^2 - \omega^2)\mathbf{P}(2) = \alpha_0[\mathrm{i}\mathbf{T}''(0|\omega)\mathbf{P}(2) + \mathbf{T}(\mathbf{r}|\omega)\mathbf{P}(1)], \tag{9}$$

where $\alpha_0 = fe^2/m$, f the oscillator strength, e and m charge and mass of the oscillator, and ω_0 its frequency. If we introduce the isotropic polarizability,

$$\alpha(\omega)_{ij} = \frac{\alpha_0\delta_{ij}}{\omega_0^2 - \omega^2 - \mathrm{i}\omega\gamma(\omega)} = \alpha(\omega)\delta_{ij}, \tag{10}$$

Equations (8, 9) can be rearranged to give

$$\mathbf{P}(1) = \alpha(\omega)\mathbf{T}(\mathbf{r}|\omega)\mathbf{P}(2), \tag{11}$$
$$\mathbf{P}(2) = \alpha(\omega)\mathbf{T}(\mathbf{r}|\omega)\mathbf{P}(1). \tag{12}$$

These equations are identical to those derived in references [7–9], except that the polarizability is modified by explicit inclusion of the radiation damping term. The interaction between two identical oscillators where one initially is in its ground state and the other is in an excited state can be represented by a superposition of states: one symmetric and one antisymmetric with respect to interchange of the atoms. The two atoms are coupled by the exchange of the single excitation and one cannot say which atom is excited. While the symmetric state is likely to decay into two ground-state atoms, the antisymmetric state is long-lived. The system can thus be trapped in the antisymmetric state. The excitation migrates back and forth between the two atoms until a photon is emitted away from the system. First order dispersion interactions are caused by this coupling of the system, *i.e.* the energy difference between the two states is separation dependent.

Now for identical dipoles the normal modes of the interacting system are the symmetric ($P_i(1) = P_i(2)$) state P_i^+ and the antisymmetric ($P_i(1) = -P_i(2)$) state P_i^-. It can be seen by inspection of equations (8, 9) that these satisfy

$$[\mathbf{I} \mp \alpha(\omega)\mathbf{T}(\mathbf{r}|\omega)]\mathbf{P}^{\pm} = 0, \tag{13}$$

where $\mathbf{I}$ is the unit matrix. For the simple case of isotropic oscillators considered here $\mathbf{T}$ and $\boldsymbol{\alpha}$ are diagonal matrices. To calculate resonant energy transfer times and interaction energies it is more convenient to use the retarded Green function which for $\mathrm{Im}(z) > 0$ satisfies

$$\{[\omega_0^2 - z^2 - \mathrm{i}z\gamma(z)]\mathbf{I} \mp \alpha_0 \mathbf{T}(\mathbf{r}|z)\}\mathbf{G}^{\pm}(\mathbf{r}|z) = \omega_0^2 \mathbf{I}. \tag{14}$$

The factor ω_0^2 on the right hand side is a normalization factor. If we introduce the notation

$$\mathbf{G}_0(z) = \frac{\omega_0^2}{\omega_0^2 - z^2}\mathbf{I}, \tag{15}$$

$$\boldsymbol{\Sigma}(\mathbf{r}|z) = \alpha_0 \mathbf{T}(\mathbf{r}|z)/\omega_0^2, \tag{16}$$

then from equations (14–16) we can write the Green function in the form

$$\mathbf{G}^{\pm}(\mathbf{r}|z) = \frac{\mathbf{I}}{\mathbf{G}_0(z)^{-1} - [\boldsymbol{\Sigma}(0|z) \pm \boldsymbol{\Sigma}(\mathbf{r}|z)]} \cdot \tag{17}$$

This form is familiar from many particle physics [22] as a solution of Dyson's equation. The frequencies and lifetimes for energy transfer between two oscillators are determined by the singularities of this Green function (17).

The treatment so far is unexceptionable in that there is no conflict with alternative formulations *via* quantum field theory. We now show however that the further standard development becomes flawed. A standard procedure in quantum-field theoretic treatments of atom-field interactions is to replace the strength of the atom-field coupling for a given mode $g(\omega)$ with the value for a resonant mode $g(\omega_0)$. For most situations this seems reasonable as $g(\omega)$ varies slowly with ω and the optical resonances are sharp. However, we demonstrate below that it is due to this approximation that previous treatments of the problem have failed to give correct results. To see this recall that the approximate Green function is,

$$\mathbf{G}^{\pm}(\mathbf{r}|\omega) \simeq \frac{\omega_0^2}{\omega_0^2 - \omega^2 - \omega_0^2[\boldsymbol{\Sigma}(0|\omega_0) \pm \boldsymbol{\Sigma}(\mathbf{r}|\omega_0)]} \cdot \tag{18}$$

For most distances $\boldsymbol{\Sigma}(\mathbf{r}|\omega_0)$ is small. To leading order the singularities are simple poles just off the real axis. The real part of the singularities yields the perturbed frequencies:

$$\omega_{i\pm} \simeq \omega_0 \mp \frac{\alpha_0 T'_{ii}(\mathbf{r}|\omega_0)}{2\omega_0} \cdot \tag{19}$$

The corresponding lifetimes are given by the imaginary part. Thus

$$\begin{aligned}\frac{2\pi}{\tau_i} &= \omega_0 \mathrm{Im}[\Sigma_{ii}(0|\omega_0) \pm \Sigma_{ii}(\mathbf{r}|\omega_0)] \\ &= \gamma(\omega_0) \pm \frac{\alpha_0 T''_{ii}(\mathbf{r}|\omega_0)}{\omega_0} \cdot\end{aligned} \tag{20}$$

This approximate picture reveals many of the qualitative features of the system. Notice that when the oscillators are very close together ($r \to 0$) the damping factor for the antisymmetric mode goes to zero, while the factor for the symmetric mode goes to twice that for a single oscillator. Thus an antisymmetric mode can act as a "trap" for resonant radiation if the oscillators are very close. This is in accordance with the dipole selection rules. To see how close the oscillators must be for the trap to be effective we proceed as follows. Construct a time dependent state such that at $t = 0$ $P(1) = P$ and $P(2) = 0$. This is a simple linear combination of the normal modes P^+ and P^-:

$$\begin{aligned}P(1) &= \frac{P^+(t) + P^-(t)}{2}; \\ P(2) &= \frac{P^+(t) - P^-(t)}{2} \cdot\end{aligned} \tag{21}$$

The energy now moves between the two oscillators with a frequency $\alpha_0 T'(\mathbf{r}|\omega_0)/(2\omega_0)$ and mean decay frequency $\gamma(\omega_0)$. Efficient transfer can only occur when the corresponding transfer time is much less than the natural decay time. From equations (4, 19, 20) we see that this criterion implies that $r < 2\pi c/\omega_0$. The atoms must be in the near fields of each other. These results were first derived by McLachlan [21] using a simple perturbation procedure which for the time dependent resonant transfer problem does give physically meaningful results.

However, as stated earlier, our equations can also be be used to deduce interaction energies. Stephen [23] interprets what is essentially $\hbar\alpha_0 T'_{ii}(\mathbf{r}|\omega_0)/(2\omega_0)$ in our notation as the interaction energy of two atoms in an excited configuration. A similar result follows from quantum mechanical perturbation theory. As mentioned earlier the expression for the potential so obtained behaves in the retarded limit as $r^{-1}\cos(\omega_0 r/c)$. We now turn our attention to this problem and show how the approximations made to arrive at such a result are too drastic.

The resonance interaction energy $V(r)$ is given in terms of the energies corresponding to those of the normal modes of the complete interacting system. Besides this interaction energy there will also be ground-state contributions from the modes that have not been excited. These energy contributions vanish asymptotically and decay as r^{-7} which is much faster than the resonance interaction. We will henceforth ignore these ground-state contributions. When the system is in an excited configuration the interaction energy becomes

$$V(r)_{i,\sigma} = \hbar[\omega_i^{\sigma}(r) - \omega_i^{\sigma}(\infty)], \tag{22}$$

where $\omega_i^{\sigma}(r)$ are the poles of (17). As the first two terms dominate the denominator of (17), $\mathbf{G}^{\pm}(\mathbf{r}|\omega)$ only has one pole in each (σ, i) branch. States corresponding to these poles are eigenstates of the coupled atoms-field system, with the restriction made that such a state must be a linear combination of basis states where one atom is excited. These are not quite eigenstates of the total atoms-field system and thus have a finite lifetime in the same way as does a single excited atom interacting with a field.

We can in a standard way [9,12,24] deform a contour of integration around this pole to obtain a simple expression for the resonance interaction energy. The position of the pole represents the energy of a quasi-eigenstate of the system.

Subtracting off the energy at infinity we obtain,

$$\begin{aligned}\hbar\omega_i^\sigma(r) - \hbar\omega_i^\sigma(\infty) &= \frac{\hbar}{\pi}\int_0^\infty \mathrm{d}\xi \ln\left[1 \mp \frac{\Sigma_{ii}(\mathbf{r}|\mathrm{i}\xi)G_0}{1-\Sigma_{ii}(0|\mathrm{i}\xi)G_0}\right] \\ &= \frac{\hbar}{\pi}\int_0^\infty \mathrm{d}\xi \ln[1 \mp \alpha(\mathrm{i}\xi)T_{ii}(\mathbf{r}|\mathrm{i}\xi)]. \quad (23)\end{aligned}$$

This is similar in structure to the expressions used in references [7–9] to derive the ground state energy for the system. If the modes in the $(\pm, x)$ branch are excited, the resonance interaction energy is,

$$V(r) = \frac{\hbar}{\pi}\int_0^\infty \mathrm{d}\xi \ln[1 \mp \alpha(\mathrm{i}\xi)T_{xx}(\mathbf{r}|\mathrm{i}\xi)]. \quad (24)$$

If we substitute T_{xx} from equation (4) into this expression for the interaction energy it can be seen that in the limit of large separations we can expand the logarithm and retain only the leading term. This first term is

$$V(r) \simeq \frac{\mp\hbar}{\pi}\int_0^\infty \mathrm{d}\xi\alpha(\mathrm{i}\xi)\frac{\mathrm{e}^{-\xi r/c}}{r^3}[1+\xi r/c+(\xi r/c)^2]. \quad (25)$$

In the large r limit we can replace $\alpha(\mathrm{i}\xi)$ by its static value $\alpha(0)$ and evaluate the integral to obtain,

$$V(r) \simeq \mp 4\hbar c\alpha(0)/\left(\pi r^4\right). \quad (26)$$

This represents the dominating term in the interaction energy for oscillators in an excited configuration at zero temperature. When the system is trapped in an antisymmetric state the attraction is many orders of magnitude larger than the ground-state interaction energy. In the limit $c \to \infty$, the well known non-retarded form for the resonance interaction ($\propto r^{-3}$) follows immediately from equation (25).

We now ask why the standard treatment of the problem gives rise to a long-range oscillating form for the retarded interaction energy instead of the simpler result equation (25). As we remarked earlier Stephen identified the real part of the perturbed normal mode frequencies with the interaction energies. Such a result follows from equation (24) if we use the approximate Green function equation (18) after dropping the lifetime. To leading order we then obtain

$$V(r) \simeq \pm\frac{\hbar\alpha_0 T'_{xx}(\mathbf{r}|\omega_0)}{\pi}\int_0^\infty \mathrm{d}\xi\frac{1}{\omega_0^2+\xi^2}\,. \quad (27)$$

Substituting for $T'_{xx}(\mathbf{r}|\omega_0)$ from equation (4) we see that as $r \to \infty$, the oscillating form of $V(r) \propto r^{-1}\cos(\omega_0 r/c)$ is obtained. This repulsive potential is usually referred to as the Π potential. If the z-branch (T_{zz}) is excited the incorrect treatment gives $V(r) \propto r^{-2}\sin(\omega_0 r/c)$. This attractive potential is commonly referred to as the Σ potential. Thus, the standard use of perturbation theory is equivalent to using the simplified Green function (18) after dropping the lifetime. Such an approximation is commonly used in the treatment of atom-field interactions. In this case however it clearly represents too drastic a simplification. The correct answer is obtained in a non-perturbative approach of the sort given above.

3 Resonance interaction at finite temperatures

We next demonstrate that finite temperature effects can be easily dealt with as for the corresponding ground state problem [13,25]. In fact as for the interaction between two ground state atoms the correct long-range interaction can only be found when finite temperature is accounted for [13]. To account for the temperature (T) dependence we simply replace the integration over imaginary frequencies by a summation over discrete frequencies [24,26],

$$\frac{\hbar}{2\pi}\int_0^\infty \mathrm{d}\xi \to k_\mathrm{B}T\sum_{n=0}^{\infty\,\prime}, \quad (28)$$

where $\xi_n = 2\pi k_\mathrm{B}Tn/\hbar$, k_B is the Boltzmann constant and the prime indicates that the $n = 0$ term should be divided by 2. Combining this with equation (25) we find that the correct leading term at large separation is

$$V(r,T) \simeq \mp\frac{2k_\mathrm{B}T\alpha(0)}{r^3}\sum_{n=0}^{\infty\,\prime}\frac{\mathrm{e}^{-xn}}{(1+An^2)(1+xn+x^2n^2)}, \quad (29)$$

where $x = 2\pi k_\mathrm{B}Tr/(\hbar c)$ and $A = [(2\pi k_\mathrm{B}T)/(\hbar\omega_0)]^2$. We can again replace the polarizability with $\alpha(0)$ at large enough separations (or strictly speaking when x is much larger than unity and A is sufficiently small). Within this approximation the resonance free energy is,

$$\begin{aligned}V(r,T) &\simeq \mp 2k_\mathrm{B}T\alpha(0) \\ &\times\frac{[1+\mathrm{e}^{3x}-\mathrm{e}^{x}(1+2x-2x^2)+\mathrm{e}^{2x}(-1+2x+2x^2)]}{2r^3(\mathrm{e}^x-1)^3}\,. \quad (30)\end{aligned}$$

For small values of x this free energy of interaction does indeed have equation (26) as its leading term. Clearly, for any finite temperature the long-range interaction is dominated by the $n = 0$ term. This term is here

$$V(r,T)_{n=0} = \mp k_\mathrm{B}T\alpha(0)/r^3. \quad (31)$$

This is the correct asymptotic long-range resonance interaction at any finite temperature. Expressed in terms of the classical Bohr radius (a_0) and the first excited state of a real hydrogen atom the long-ranged purely classical result is $k_{\mathrm{B}}Ta_0^3/r^3$. This manifestation of the correspondence principle is very similar in nature to the result obtained for the retarded van der Waals interaction between two ground-state atoms [13]. It is not only the correct result at high enough temperatures, but also at any finite temperature for large enough separations. In the limit when A is large and x is sufficiently small the resonance interaction energy equation (29) takes on the following approximate form,

$$V(r,T) \approx \mp \frac{k_{\mathrm{B}}T\alpha(0)}{r^3}[1+\pi^2/(3A)]. \tag{32}$$

The change in power-law at large separations has usually been interpreted as being simply due to the finite velocity of light. However, the long-range interaction at finite temperatures between two atoms is independent of the velocity of light. This demonstrates that there is more to it than a simple loss of inter-correlation due to the finite velocity of light. As pointed out by Wennerström, Daicic, and Ninham [13] the quantum nature of light must be important to the softening of the interaction potential.

4 The Förster energy transfer revisited

What the previous sections have demonstrated is that it is essential to reconsider the complete reliance on perturbation techniques when it comes to intermolecular interactions. We will as an important example discuss energy transfer between two molecules (that in general may be different). The derivation of the Förster energy transfer [16,27–30] follows closely the derivation for the resonance interaction. The idea has been that the first atom emits a photon by spontaneous emission (unaffected by the second atom), which is subsequently adsorbed by the second atom. The overall rate should then decay away as the area of a spherical shell. However, we argue that this is an unphysical assumption. When the electromagnetic coupling of the two atoms is taken into account a totally different result follows.

We first define what we mean by transfer rate. Following Förster [16] we can discuss two different regions: the strong-coupling limit and the weakly-coupled limit. In the strong-coupling limit one can define the rate of "fast" transfer between two identical molecules, one in the ground state and the other in an excited state, as [16]:

$$n \approx 2|U|/(\pi\hbar), \tag{33}$$

where U is the resonance energy and $\hbar$ is Planck's constant. This is the region discussed in the previous sections. Förster demonstrated how the transfer rate of both strongly and weakly coupled molecules can be treated within the same formalism [16]. Between two weakly interacting molecules (that in general may be different) there is enough that there is an overlap of the energy-bands to have energy transfer. Application of time-dependent perturbation theory gives the following approximation (Fermi golden rule rate) for this "slow" transfer rate [15,16]:

$$n \approx 2\pi|U|^2\delta/\hbar, \tag{34}$$

where δ is the "density of final states" (related to the spread in the energy of the optical band associated with slow energy transfer [16]).

In the nonretarded limit the Förster energy transfer rate vanishes asymptotically as r^{-6}. In the "standard approach" (using only the real part of the interaction energy obtained from perturbation theory) the averaged decay rate in the retarded limit becomes proportional to $\cos^2(\omega r/c)/r^2$ [28]. This oscillating form was correctly assumed to be incorrect (after comparison with the "expected" r^{-2}). When the complex interaction energy obtained from perturbation theory is used the transfer rate averaged over possible orientations was found to decay as r^{-2} [27,28].

There are however no obvious physical reason why the system should be considered as uncoupled. We argue that it is much more realistic to consider the system of two atoms to be coupled by the field. At large separations the transfer rate then vanishes as r^{-8} (or as r^{-6} if thermal effects are important).

The problem of Förster energy transfer is one of obvious importance and one that deserves close and careful examination in the near future. In the same way as the DLVO theory of colloid interactions separates the dispersion (quantum mechanical) interactions from the electrostatic double layer forces and is very badly flawed and erroneous [31,32] so too the separation of photon transfer from electron transfer is equally flawed and misleading. We will come back to how the problem of photon transfer in the presence of a plasma is non analytic in the presence of an electron density. The slightest perturbation which introduces an infinitesimal electron density changes the analytic form of the photon transfer completely.

5 Conclusions

In conclusion we have studied the problem of the interaction of two atoms in an excited configuration. The semiclassical approach, when applied to the time dependent problem of energy transfer, confirms the earlier work by McLachlan and Stephen. However, we conclude that the generally accepted form for the retarded interaction energy between excited atoms is not correct. Brennen *et al.* [33] have proposed a mechanism for creating entangled states for quantum computing exploiting resonantly induced dipole-dipole interaction. While the proposed mechanism offers a very interesting avenue to quantum logic, the underlying theory presented for the dipole-dipole interaction is as incorrect as all previous perturbative treatments. We have formulated the energy of interaction in terms of a steady state situation where the normal modes of the *interacting* system are excited. This yields in the limit $r \to \infty$ an interaction energy $\propto r^{-4}$. For any finite temperature the long-range asymptote is $k_B T\alpha(0)/r^3$. We have also highlighted the need for a revised theory for the Förster energy transfer.

It is instructive to compare numerically how our correctly evaluated resonance interaction energy differs from previous incorrect treatments. Experiments are usually compared with a sum of different energy contributions. The resonance interaction is there modelled with a potential that goes as C_3/r^3. Retardation effects is then taken into account by multiplying this expression with a separation dependent prefactor [6]. This approach is flawed for two reasons. First, as we have described above it uses an incorrect Green function. It also assumes that a small argument series expansion can be applied to the logarithmic term. This is also invalid at the shortest distances considered in experiments. We have performed numerical model calculations for a system consisting of two sodium atoms with $\omega_0 = 3.2 \times 10^{15}$ rad/s and $C_3 = 4.018\ z\text{Jnm}^3$. At atomic separations relevant for experiments (20–170 Bohr radii) we found that the deviations between correctly and incorrectly evaluated resonance interaction energies where less than 1% (5%) for the Π potential (Σ potential). However, at larger atomic separations (and for higher values of ω_0) retardation effects become much more important. The point of the paper is to correct a fundamental error that effects the real nature of retardation.

We finally mention that it is straightforward to extend the formalism to obtain the correct result for the resonance interaction in narrow channels following reference [34]. We recently exploited the zero-temperature formalism developed in the present paper to consider the resonance interaction in narrow channels [35]. We demonstrated that the long-range resonance interaction can be enhanced in narrow channels. The interaction can also change from long-range attraction to short-range repulsion giving rise to bound states where molecules can be trapped.

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References

1. A. Fioretti, D. Comparat, A. Crubellier, O. Dulieu, F. Masnou-Seeuws, P. Pillet, Phys. Rev. Lett. **80**, 4402 (1998); C. Gabbanini, A. Fioretti, A. Lucchesini, S. Gozzini, M. Mazzoni, Phys. Rev. Lett. **84**, 2814 (2000)
2. C.M. Dion, C. Drag, O. Dulieu, B. Laburthe Tolra, F. Masnou-Seeuws, P. Pillet, Phys. Rev. Lett. **86**, 2253 (2001); J. Vala, O. Dulieu, F. Masnou-Seeuws, P. Pillet, R. Kosloff, Phys. Rev. A **63**, 013412 (2000)
3. K.M. Jones, P.S. Julienne, P.D. Lett, W.D. Phillips, E. Tiesinga, C.J. Williams, Eur. Phys. Lett. **35**, 85 (1996)
4. W.I. McAlexander, E.R.I. Abraham, R.G. Hulet, Phys. Rev. A **54**, R5 (1996)
5. H. Wang, J. Li, X.T. Wang, C.J. Williams, P.L. Gould, W.C. Stwalley, Phys. Rev. A **55**, R1569 (1997)
6. R.R. McLone, E.A. Power, Mathematika **11**, 91 (1964); W.J. Meath, J. Chem. Phys. **48**, 227 (1968)
7. D.J. Mitchell, B.W. Ninham, P. Richmond, J. Phys. A: At. Mol. Phys. **4**, L81 (1971)
8. D.J. Mitchell, B.W. Ninham, P. Richmond, Aust. J. Phys. **25**, 33 (1972)
9. J. Mahanty, B.W. Ninham, J. Phys. A: Gen. Phys. **5**, 1447 (1972); *Dispersion Forces* (Academic, London, 1976)
10. F. London, J. Phys. Chem. **46**, 305 (1942)
11. H.G.B. Casimir, D. Polder, Phys. Rev. **73**, 360 (1948)
12. B.W. Ninham, V.A. Parsegian, G.H. Weiss, J. Stat. Phys. **2**, 323 (1970)
13. B.W. Ninham, J. Daicic, Phys. Rev. A **57**, 1870 (1998); H. Wennerström, J. Daicic, B.W. Ninham, Phys. Rev. A **60**, 2581 (1999)
14. H. Margenau, N.R. Kestner, *Theory of Intermolecular Forces* (Pergamon, New York, 1969)
15. D.P. Craig, E.A. Power, T. Thirunamachandran, Chem. Phys. Lett. **6**, 211 (1970)
16. Th. Förster, *Modern Quantum Chemistry*, edited by O. Sinanoglu (Academic, New York, 1965), Pt. 3 and references therein
17. R. van Groendelle, J.P. Dekker, T. Gillbro, V. Sundström, Biochim. Biophys. Acta **1187**, 1 (1994)
18. H. Bergström, W.H.J. Westerhuis, V. Sundström, R. van Groendelle, R.A. Niederman, T. Gillbro, FEBS Lett. **233**, 12 (1988)
19. P.A. Lane *et al.*, Phys. Rev. B **63**, 235206 (2001)
20. G. Cario, J. Franck, Z. Phys. **17**, 202 (1923)
21. A.D. McLachlan, Molec. Phys. **8**, 409 (1964)
22. G.D. Mahan, *Many-Particle Physics*, 2nd edn. (Plenum, New York, 1993)
23. M.J. Stephen, J. Chem. Phys. **40**, 669 (1964)
24. Bo.E. Sernelius, *Surface Modes in Physics* (Wiley, Berlin, 2001)
25. M. Boström, J.J. Longdell, B.W. Ninham, Phys. Rev. A **64**, 62702 (2001)
26. E.M. Lifshitz, Zh. Eksp. Teor. Fiz. **29**, 94 (1955) [Sov. Phys. JETP **2**, 73 (1956)]
27. J.S. Avery, Proc. Phys. Soc. **88**, 1 (1966)
28. D.L. Andrews, B.S. Sherbone, J. Chem. Phys. **86**, 4011 (1987)
29. E.A. Power, T. Thirunamachandran, Phys. Rev. A **28**, 2671 (1983)
30. H.T. Dung, L. Knöll, D.-G. Welsch, Phys. Rev. A **65**, 43813 (2002)
31. B.W. Ninham, V. Yaminsky, Langmuir **13**, 2097 (1997)
32. M. Boström, D.R.M. Williams, B.W. Ninham, Phys. Rev. Lett. **87**, 168103 (2001); Langmuir **17**, 4475 (2001)
33. G.K. Brennen, I.H. Deutsch, P.S. Jessen, Phys. Rev. A **61**, 062309 (2000)
34. J. Mahanty, B.W. Ninham, J. Phys. A: Math. Nucl. Gen. **6**, 1140 (1973); Phys. Lett. A **43**, 495 (1973)
35. M. Boström, J.J. Longdell, B.W. Ninham, Europhys. Lett. **59**, 21 (2002)