Strongly Coupled Matter-Field and Non-Analytic Decay Rate of Dipole Molecules in a Waveguide

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The decay rate $\gamma$ of an excited dipole molecule inside a waveguide is evaluated for the strongly coupled matter-field case near a cutoff frequency $\omega_c$ without using perturbation analysis. Due to the singularity in the density of photon states at the cutoff frequency, we find that $\gamma$ depends non-analytically on the coupling constant $g$ as $g^{4/3}$. In contrast to the ordinary evaluation of $\gamma$ which relies on the Fermi golden rule (itself based on perturbation analysis), $\gamma$ has an upper bound and does not diverge at $\omega_c$ even if we assume perfect conductance in the waveguide walls. As a result, in contrast to the statement found in the literature, the speed of emitted light from the molecule does not vanish at $\omega_c$ and is proportional to $cg^{2/3}$ which is on the order of $10^4 \sim 10^5 \text{m/s}$ for typical dipole molecules.

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It has been well known for many years that enhanced spontaneous emission can be observed for an atom in a resonator above and below a cutoff frequency \cite{1,2}. An explanation of this alternation has been proposed by Kleppner based on the combination of the Fermi golden rule for the transition rate and a change of the density of photon states in a resonator. In his calculation, the singularity in the density of states at a cutoff frequency $\omega_c$ may lead to a vast increase of the decay rate $\gamma$ of an excited atom or molecule compared to the free-space value. This prediction has been verified by several experiments \cite{3-7}. However, Kleppner’s approach, while going in the right direction, is inconsistent. This is apparent because the Fermi golden rule is not applicable in the domain of a vast increase in the decay rate, as this rule is only valid for a weakly coupled matter-field system where the perturbation analysis may be applied. Due to this inconsistency, $\gamma$ diverges in Kleppner’s theory for the case in which the resonator is made of a perfectly conducting material and the characteristic frequency $\omega_1$ of the atom approaches $\omega_c$. The decay rate $\gamma$ then vanishes for $\omega_1 < \omega_c$.

The purpose of this Letter is to re-evaluate $\gamma$ for a strongly coupled case around $\omega_c$ without using perturbation analysis. The result shows that $\gamma$ is finite at $\omega_c$ even if we assume perfect conductance. We find that the maximum value of $\gamma$ depends non-analytically on a dimensionless coupling constant $g$ as $g^{4/3}$ (instead of $g^2$ which is assumed in Fermi’s golden rule). For small $g \ll 1$, $\gamma$ is enhanced by a factor of $g^{-2/3}$ over the free-space value of $\gamma$ that is proportional to $g^2$. Moreover, the frequency value at which the unstable solution disappears is found not at $\omega_1 = \omega_c$, but at $\omega_1 = \omega_s$, which lies slightly below $\omega_c$ with $\omega_c - \omega_s \sim g^{4/3} \omega_c$. Again, this value is much larger than the value $\sim g^2$ predicted by the perturbation analysis for the system where the density of states has no singularity at $\omega_c$.

To present the results, let us consider a dipole molecule (such as HCl, NaCl or KBr) that is on the order of a nanometer in size and which has a charge of $+Ze$ on one end and charge $-Ze$ on the other end. This charge couples the dipole to the electromagnetic field in the rectangular waveguide. The waveguide runs parallel to the $z$-axis and extends to infinity in either direction. We refer to the width of the waveguide in the $x$-direction as $a$ and to the height of the waveguide in the $y$-direction as $b$. We assume $b \geq a$. The origin of $z$ is chosen at an arbitrary point along the infinite waveguide. We choose the origin for $x$ and $y$ at the lower-left corner of the cross-section of the waveguide. We assume that the center of mass of the dipole is initially located near the center of the waveguide at coordinates $(a/2, b/2, 0)$. The characteristic frequency of vibration $\omega_1$ for a typical dipole is on the order of $10^{14}$ to $10^{13}$ Hz, corresponding to a wavelength $\lambda$ with 10 to 100$\mu$m, which is in the infrared range. Since the width of the waveguide is much larger than the size of the dipole, we can neglect the forces acting on the dipole from the walls of the waveguide.

Under these conditions, one may write the Hamiltonian of the system with the reduced mass $\mu \equiv m_am_b/(m_a + m_b)$ for the dipole and with $Z_a = -Z_b = Z$ as

\begin{equation}
H = \sum_{i=a,b} \frac{1}{2m_i} \left( p_i + Z_i e \frac{A(r_i)}{c} \right)^2 + \frac{1}{2\mu\omega_1^2} |r_b - r_a|^2 \\
+ \frac{1}{8\pi} \int d^3r \left( \frac{1}{c^2} \left| \frac{\partial A(r)}{\partial t} \right|^2 + |\nabla \times A(r)|^2 \right), \quad (1)
\end{equation}
where \( r = (x, y, z) \). The vector potential inside the waveguide consists of the TE modes (Transverse Electric field modes) and TM modes (Transverse Magnetic field modes), \( A = A_{TE} + A_{TM} \). For the case of the waveguide made of a perfectly conducting material, the solution of the sourceless Maxwell equations with the Coulomb gauge inside the rectangular waveguide leads to these modes in terms of the normal coordinates of the fields \( q_{0k} \) (with \( \sigma = E \) or \( M \) and \( k = (m, n, k) \) with \( m, n \) integers and the continuous variable \( k \)) as \( [6] \).

\[
A_{TE}(r) = \int d\mathbf{k} \sqrt{\frac{2\pi m c_{mn}^{}}{\omega_{k}}} \left[ -\frac{n\pi}{b} W_{1,k} \hat{e}_x \right. \\
+ \frac{m\pi}{a} W_{2,k} \hat{e}_y q_{0k} + h.c., \tag{2}
\]

\[
A_{TM}(r) = \int d\mathbf{k} \frac{2c}{\pi} \sqrt{\frac{\omega_{k}^{3}}{m c_{mn}^{}}} \left[ \frac{k m \pi}{a} W_{1,k} \hat{e}_x \right. \\
+ \left. i \frac{k \pi}{b} W_{2,k} \hat{e}_y + \alpha_{mn}^{2} W_{3,k} \hat{e}_z \right] Q_{M} + h.c., \tag{3}
\]

where \( W_{1,k}(r) \equiv \cos(m\pi x/a) \sin(n\pi y/b) \exp(ikz), \)
\( W_{2,k}(r) \equiv \sin(m\pi x/a) \cos(n\pi y/b) \exp(ikz), \)
\( W_{3,k}(r) \equiv \sin(m\pi x/a) \sin(n\pi y/b) \exp(ikz), \)
and \( \hat{e}_i \) are unit vectors. We put \( c_{mn} = 2c^{3}/(a\alpha_{mn}^{2}) \) with \( \alpha_{mn} = \sqrt{(m\pi/a)^{2} + (n\pi/b)^{2}}, \)
\( \omega_{k} = c \sqrt{k^{2} + \alpha_{mn}^{2}}, \)
\( \int_{\Sigma} d\mathbf{k} = \sum_{m,n} \int_{-\infty}^{\infty} dk, \)
and \( I_{mn} = 1 \) for \( m \) and \( n \neq 0, I_{mn} = 1/2 \) for \( m = n = 0 \).

We may rewrite the Hamiltonian in terms of the relative coordinate \( r_{1} \equiv r_{0} - r_{a}, \) the center-of-mass coordinate \( R, \) and their canonical conjugate momenta \( p_{1} \) and \( P. \) In this discussion we are interested in distances much larger than the size of the molecule, so that the particle interacts with the field at approximately the center-of-mass (the so-called dipole approximation). We assume that the velocity of the center-of-mass is so slow that we can neglect its kinetic energy. We also assume the field is weak enough that we can neglect terms that are proportional to \( A^{2}. \) We first consider the case in which the dipole oscillates in the \( x \) direction (thus \( r_{1} = x_{1}\hat{e}_{x} \) and \( p_{1} = p_{1}\hat{e}_{x} \)). The extension to arbitrary direction will be discussed later. We then introduce the unperturbed normal coordinate \( q_{1} \equiv \sqrt{\mu\omega_{1}}[x_{1} + i(p_{1}/\mu\omega_{1})] \) of the dipole. With these assumptions, the Hamiltonian \( [11] \) may be approximately written in a bilinear form with respect to the annihilation and creation operators (which are related to the normal coordinate through \( q_{\sigma} = \sqrt{\hbar}a_{\sigma} \)) as

\[
H = \hbar\omega_{1}a_{1}^{\dagger}a_{1} + \sum_{\sigma}^{E,M} \int_{\Sigma} d\mathbf{k} \hat{h}_{W_{k\sigma}} a_{1}^{\dagger}a_{\sigma k} \\
+ g \sum_{\sigma}^{E,M} \int_{\Sigma} d\mathbf{k} (V_{\sigma k} a_{\sigma k} - V_{\sigma k}^{*} a_{\sigma k}^{\dagger})(a_{1}^{\dagger} - a_{1}), \tag{4}
\]

with the dimensionless coupling constant \( g \equiv \sqrt{(Ze^{2})\omega_{1}/(\mu_{1}c^{3})}. \) We have \( g \sim 10^{-6} \) to \( 10^{-7} \) for the typical dipole molecules. The interactions are given by \( V_{E,k} = -i(n/b)\sqrt{m c_{mn}}F_{1,k}(R), \)
\( V_{M,k} = -(mck/\omega_{k})F_{1,k}(R), \) with \( F_{1,k}(R) = \hbar\pi^{2} c_{mn} W_{1,k}(R)/\sqrt{\omega_{k}}. \) The operators \( a_{\sigma} \) satisfy the usual commutation relations. For each \( (m, n) \) mode, the continuous spectrum \( \omega_{k} > \omega_{mn} \) is bounded from below at \( c\omega_{mn}. \) These lower bounds form a set of cutoff frequencies in the sense that only electromagnetic modes with frequency \( \omega_{k} > \omega_{mn} \) may propagate inside the waveguide. Among these branches of continuum, the TE mode with \( m = 0 \) and \( n = 1 \) has the smallest value for its cutoff frequency \( \omega_{c} = c\omega_{01} = \pi c/b. \)

The Hamiltonian \( [11] \) has exactly the same structure as the Hamiltonian for the well-known Friedrichs model with virtual processes \([10, 11]. \) This model has been investigated extensively in order to analyze the spontaneous decay of an excited atom \([10-15]. \) Since the Hamiltonian is bilinear, one can find its exact diagonal form as \( H = h\omega_{1}b_{1}^{\dagger}b_{1} + \sum_{\sigma} \int_{\Sigma} d\mathbf{k} \hat{h}_{W_{k\sigma}} b_{1}^{\dagger}b_{k}. \) where \( \omega_{1} \) is the shifted real frequency for the stable dressed harmonic oscillator. The new dressed annihilation operators \( b_{\sigma} \) are obtained by the Bogoliubov transformation and satisfy the usual commutation relations. The explicit form of the Bogoliubov transformation is presented in \([8, 10]. \)

In this short letter we limit our studies to the shifted frequency and the decay rate of the harmonic oscillator. These are found by solving the dispersion equation \( \xi(z) = 0 \) for the dressed harmonic oscillator, where

\[
\xi(z) \equiv z^{2} - \omega_{1}^{2} - g^{2} \sum_{\sigma}^{E,M} \int_{\Sigma} d\mathbf{k} \frac{\omega_{1} \omega_{k} |V_{\sigma k}|^{2}}{z^{2} - \omega_{k}^{2}}. \tag{5}
\]

The solution of \( \xi(z) = 0 \) gives a real solution \( z = z_{0} \equiv \omega_{1} \) with a shifted frequency for the stable mode of the harmonic oscillator and a complex solution \( z = z_{1} \equiv \omega_{1} - i\gamma \) with shifted frequency \( \omega_{1} \) and decay rate \( \gamma \) for the unstable mode.

To find the explicit form of these solutions, let us consider the case in which \( \omega_{c} \) is located below the next smallest cutoff frequency \( \omega_{c,2}. \) The geometry of the waveguide can be chosen in such a way that the cutoff frequency \( \omega_{c} \) is well separated from \( \omega_{c,2}, \) and as such, we may have \( \omega_{1} < \omega_{c}, \) or \( \omega_{c} < \omega_{1} < \omega_{c,2} \) where \( \omega_{1} \) is much closer to \( \omega_{c} \) than \( \omega_{c,2}. \) For this case the predominant contribution to the integration in Eq. \([5] \) comes from the component with \( \sigma = E, m = 0 \) and \( n = 1. \) Approximating the integration by leaving out all other components and explicitly performing the integration, we obtain the dispersion equation \([10] \)

\[
\zeta = w_{1}^{2} \equiv \frac{g^{2}G^{2}\omega_{1}}{\sqrt{1 - \zeta}}. \tag{6}
\]

where we have introduced the dimensionless variables, \( w_{1} \equiv \omega_{1}/\omega_{c}, \) \( \zeta \equiv (z/\omega_{1})^{2}, \) and a dimensionless constant \( G^{2} \equiv (4c/\omega_{c}) \sin^{2}(\pi \xi_{y}/b). \) The minus branch of Eq. \([6] \) gives the real solution \( z = z_{0} \) for the stable mode,
while the plus branch gives the complex solution $z = z_1$ for the unstable mode. In the following discussion we shall consider the case where the dipole remains near the center of the waveguide, without loss of generality, and put $G_0 \equiv G|_{R_x=b/2}$. Squaring Eq. (3), we obtain a cubic equation for $\zeta$. Using the standard method to solve the cubic equation, one can explicitly find the shifted frequency and the decay rate. However, since the equation was squared, we must take care to exclude non-physical solutions. The discriminant of the cubic equation is given by $D(w_1) = 4p_w^3 + q_w^2$, where

$$p_w \equiv -\frac{1}{3}s(w^2 - 1)^2, \quad q_w \equiv \frac{2}{3}(w^2 - 1)^3 + g^4G_0^4w^2.$$ \hspace{1cm}(7)

The stability of the dipole is determined by the critical frequency at $w_1 = w_s$, which is given by $D(w_s) = 0$. This gives

$$w_s^2 = 1 - \frac{3g^8/3G_0^8/3}{2(\sqrt[3]{1 + g^4G_0^4} - 1)^{1/3}} + \frac{3}{2}g^4G_0^4/3(\sqrt[3]{1 + g^4G_0^4} - 1)^{1/3}.$$ \hspace{1cm}(8)

For $g \ll 1$ we have $\omega_s \approx \omega_c[1 - 2^{1/3}(3/4)(gG_0)^{4/3}]$ where $\omega_s \equiv w_s\omega_c$. For a given value of $\omega_c$ only the stable mode exists with real $z = z_0$ for $\omega_1 < \omega_s$, while both the stable mode and the unstable mode with a complex $z = z_1$ exist for $\omega_1 > \omega_s$.

Then, we define $\alpha_{\omega \pm} \equiv (-q_{\omega} \pm \sqrt{q_{\omega}^2 + 4p_\omega^2})/2$ in order to write the solutions of Eq. (6) as

$$z_n = \omega_c\sqrt{e^{2ni\pi/3}c_{w_1s}^{1/3} + e^{-2ni\pi/3}c_{w_1-}^{1/3} + \frac{1}{3}(2w_1^2 + 1)}.$$ \hspace{1cm}(9)

where $n = 0$ for the stable solution and $n = 1$ for the unstable solution.

In Fig. 1 we plot the value of $\bar{w}_1 = \omega_1/\omega_c$ and $\bar{w}_1 = \omega_1/\omega_c = \text{Re}(z_1/\omega_c)$ as functions of $w_1 = \omega_1/\omega_c$ with a fixed value of $\omega_c$. In this and the next figures we set $G_0 = 2$ and use a large coupling constant $g = 0.005$ to exaggerate the effect of the interaction. We indicate the location of the critical value $w_s$. The thin line is $y = w_s$. The thick curve below the thin line is $\bar{w}_1$ for the stable mode. The thick curve above the thin line is $\bar{w}_1$ for the unstable mode. The two dashed curves in the domain $w_1 < w_s$ are unphysical real solutions obtained from $z_n$ by putting $n = 1$ and 2.

We note that the stable solution $\bar{w}_1$ exists for all values of $w_1$ inside the waveguide. This is the result of the singularity in the density of states at the cutoff frequency $\omega_1 = \omega_c$ in Eq. (3) appearing as $cdk = \omega_kd\omega_k/(\omega_k^2 - \omega_c^2)^{1/2}$. Because of this singularity, there may be a large deviation in the value of $\omega_1$ from $w_1$ for $w_1 \gg 1$ no matter how small the coupling constant $g$ might be. This is a striking difference from the ordinary Friederichs model which is used to analyze the spontaneous emission of the photon from the atom located in the vacuum without boundary [17]. In contrast to $\omega_1$, the deviation of $\bar{w}_1$ from $w_1$ for the unstable mode is always small for $g \ll 1$.

In Fig. 2 we plot the decay rate $\gamma/\omega_c = \text{Im}(z_1/\omega_c)$ of the unstable mode for a fixed value of $\omega_c$ as a function of $w_1$. The maximum value of $\gamma$ in our system is obtained at $w_1 = 1$ (i.e., $\omega_1 = \omega_c$). At this point we have $p_{w_1} = \alpha_{w_1^+} = 0$, $q_{w_1} = \alpha_{w_1^-} = (gG_0)^4$, and we obtain for $g \ll 1$,

$$\gamma_{\text{max}} = \frac{\sqrt{3}}{4}g^{4/3}(\frac{4b}{\pi a})^{2/3}\omega_c + O(g^{8/3}).$$ \hspace{1cm}(10)

The maximum value is a nonanalytic function at $g = 0$, and hence one cannot obtain this result from perturbation analysis. For $g \ll 1$ this is much larger than the decay rate $\gamma_2 \equiv 2g^2(c/a)(\omega_c/\omega_1)$ which is found in the perturbation region where $|w_1 - 1|/|w_1 - 1| \gg 1$. Indeed, the enhanced factor for the decay rate $\gamma_{\text{max}}/\gamma_2 \propto g^{-2/3}$ is extremely large for the case $w_1 > 1$ with $w_1 \sim 1$ and $g \ll 1$.

Notice that the critical value $w_s$ of the unstable mode is located below the cutoff frequency, i.e., $w_s < 1$. This is another striking difference from the ordinary Friederichs model, in which the critical value is located inside the continuous spectrum of the field [17].

We note that $\gamma$ does not depend on the size of the molecule in the dipole approximation. One can show that the vibrating motion of the dipole is stable when it oscillates in the $y$ direction, or in the $z$ direction for our illustrated case with $\omega_1 < \omega_c/2$. As a result, we have the same value of $\gamma$ for molecules oriented in any direction of space.
We also note that the $g^{4/3}$ law obtained in our system is rather universal around the cutoff frequency, as it can be shown to be independent of the particular model we choose. Indeed, one can find the $g^{4/3}$ law by estimating the lower bound of $\omega_1$ at which the Fermi golden rule is applicable in the vicinity of the singularity in the density of states at $\omega_c$. Due to lack of space in this Letter, we will present this estimation elsewhere. Finally, we remark on the velocity $v_f$ of the light emitted from the dipole. Through the exact form of the Bogoliubov transformation, we find

$$v_f = \frac{c\gamma}{\sqrt{\frac{1}{2}(\tilde{\omega}_1^2 - \gamma^2 - \omega_0^2)^2 + \tilde{\omega}_1^2\gamma^2 - \frac{1}{2}(\tilde{\omega}_1^2 - \gamma^2 - \omega_0^2)}}.$$  \hspace{1cm} (11)

In the perturbation region $|w_1 - 1|/|w_n - 1| \gg 1$ in which $|\tilde{\omega}_1 - \omega_1| \sim g^2 \omega_1$ and $\gamma \sim g^2 \omega_1$, this expression reduces to the well-known formula for the ordinary group velocity $v_g \equiv c[1 - (\omega_0/\omega_1)^2]^{1/2}$ inside the waveguide. However, since the perturbation analysis fails at $\omega_1 = \omega_c$, one should not conclude from the form of $v_g$ that the group velocity vanishes at the cutoff frequency as stated, for example, in [4]. Indeed, Eq. (11) leads to $v_f \approx 2cg^{-2/3}\gamma_{\text{max}} \approx (\sqrt{3}/2)g^{2/3}c$ at $\omega_1 = \omega_c$ for the group velocity. For typical dipole molecules, $v_f$ at $\omega_1 = \omega_c$ is on the order of $10^3 \sim 10^4$ m/s, which is comparable with the speed of phonons propagating on the walls of the waveguide.

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