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Robert Silbey

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Radiation Damping of Exciton States in Molecular Crystals

ROBERT SILBEY
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts
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Using the Heitler–Ma method, it is explicitly shown that there is no radiation damping of exciton states in molecular crystals when periodic boundary conditions are employed.

I. INTRODUCTION

RECENTLY, Hutchinson and Hameka[1] have calculated the effect on the radiative lifetime of an excited atom of the presence of an identical atom in the ground state. The interaction between these atoms is a dipole–dipole interaction if the excited state is dipole allowed (which we assume throughout). One may distinguish two regimes: one in which the atoms are far apart with respect to the wavelength of the photon ($R\gg\lambda$), and the other in which $R\ll\lambda$. In the former case, the effect on the lifetime is small, but in the latter case the effect is large, and indeed the two atoms share the excitation and two new excited states arise, one of which is dipole forbidden (and hence has infinite lifetime), the other having a lifetime one-half of the natural radiative lifetime. This arises because the correct zero-order states when $R\ll\lambda$ are the antisymmetric and symmetric linear combinations of the "free"-atom states. The question arises[2] as to the lifetime of an excited atom in a crystal of identical nonoverlapping atoms. In this case, the correct zero-order states are the exciton states, and the question must be rephrased to: what is the lifetime of an exciton state in a crystal? The following is a partial answer to this. We make the following (*perhaps severe*) approximations.

(a) Phonons are neglected, that is, we deal with a rigid lattice of atoms.
(b) Each atom has only one excited state.
(c) We neglect states in which two atoms are excited (double exciton states).

II. FORMALISM

Consider a crystal of N unit cells with one atom per unit cell. As stated above, the atoms are to have only one excited state (which is dipole allowed). The atoms do not overlap with one another, so we may write as zero-order states of the crystal

$$\Phi_G=\prod_n\varphi_n, \tag{2.1}$$

$$\psi_n{}^f=\varphi_n{}^f\prod_{m\neq n}\varphi_m, \tag{2.2}$$

in which the subscript labels the unit cell, φ_m represents a ground-state atom at site m, and $\varphi_m{}^f$ represents an excited-state atom at site m. The correct symmetry-adapted states are given by Φ_G and $\Psi(\mathbf{K})$:

$$\Psi(\mathbf{K})=N^{-1/2}\sum_n\exp(i\mathbf{K}\cdot\mathbf{R}_n)\psi_n{}^f, \tag{2.3}$$

in which $\mathbf{K}$ is a vector in reciprocal space in the first Brillouin zone, and $\mathbf{R}_n$ is a vector in real space from the origin to unit cell n.

The Hamiltonian of this problem is taken to be

$$H=H_0+\mathcal{V}+H_1, \tag{2.4}$$

with

$$H_0=\sum_n h_n+\sum_{\lambda\sigma}\hbar c\mid\mathbf{k}_\lambda\mid a_{\lambda\sigma}{}^+a_{\lambda\sigma}, \tag{2.5}$$

$$\mathcal{V}=\sum_{n>m}V_{nm}, \tag{2.6}$$

$$H_1=\sum_n\sum_j[(-e/mc)\mathbf{A}(\mathbf{r}_{nj})\cdot\mathbf{p}_j+(e^2/mc^2)\mathbf{A}^2(\mathbf{r}_{nj})], \tag{2.7}$$

where h_n is the Hamiltonian of the isolated atom, and we assume φ_n and $\varphi_n{}^f$ are eigenfunctions of h_n with eigenvalues ϵ and ϵ^f, respectively; V_{nm} is the static interaction between Atoms n and m and is given in the dipole approximation by

$$V_{nm}=(R_{nm}{}^{-3})\,\boldsymbol{\mu}_n\cdot(1-3\mathbf{R}_{nm}\mathbf{R}_{nm}/R_{nm}{}^2)\cdot\boldsymbol{\mu}_m \tag{2.8}$$

where $\mathbf{R}_{nm}=\mathbf{R}_n-\mathbf{R}_m$, and $\boldsymbol{\mu}_n$ is the electric dipole operator corresponding to Atom n. H_1 is the interaction between the radiation field and the atom and A, the vector potential is given in Coulomb gauge as usual by[3]

$$\mathbf{A}(\mathbf{r}_{nj})=\sum_{\lambda\sigma}(2\bar{n}\hbar c/V\mid\mathbf{k}_\lambda\mid)^{1/2}\hat{e}_{\lambda\sigma}[a_{\lambda\sigma}\exp(i\mathbf{k}_\lambda\cdot\mathbf{r}_{nj})+a_{\lambda\sigma}{}^+\exp(-i\mathbf{k}_\lambda\cdot\mathbf{r}_{nj})], \tag{2.9}$$

[1] D. Hutchinson and H. Hameka, J. Chem. Phys. **41**, 2006 (1964).
[2] H. Hameka, *Advanced Quantum Chemistry* (Addison–Wesley Publ. Co. Inc., Reading, Mass., (1966), Chap. 11; see also H. Hameka, J. Chem. Phys. **38**, 2090 (1963).

where $a_{\lambda\sigma}$ and $a_{\lambda\sigma}^+$ are the usual photon destruction and creation operators, and $\mathbf{r}_{nj}$ is the vector from the origin to the jth electron on the nth atom and $\mathbf{p}_j$ is the momentum of the jth electron.

We wish to solve the time-dependent Schrödinger equation

$$H\psi = i\hbar(\partial\psi/\partial t). \tag{2.10}$$

We attempt a solution using the Heitler–Ma[1,3] procedure. We write ψ as a linear combination of zeroth-order functions ψ_k, which satisfy $(H_0-E_k)\psi_k=0$:

$$\psi = \sum_k a_k(t)\psi_k \exp(-iE_k t/\hbar). \tag{2.11}$$

Substituting this into the Schrödinger equation, we find

$$\dot{a}_m(t) = -(i/\hbar)\sum_k a_k H_{mk} \exp(i\omega_{mk}t), \tag{2.12}$$

where

$$H_{mk} = \langle \psi_m \mid H_1 + \mathcal{V} \mid \psi_k \rangle \tag{2.13}$$

and

$$\omega_{mk} = (E_m - E_k)/\hbar. \tag{2.14}$$

In the usual way,[3] we replace the above by

$$\dot{a}_m(t) = \delta_{m0}\delta(t) - (i/\hbar)\sum_k a_k H_{mk} \exp(i\omega_{mk}t) \tag{2.15}$$

so that at $t=0$, $a_0=1$, $a_{k\neq 0}=0$, with the subscript 0 representing the initial state of the system. Let

$$a_m(t) = \left(\frac{-1}{2\pi i}\right)\int_{-\infty}^{+\infty} G_m(E) \exp\left(\frac{i(E_m-E)t}{\hbar}\right) dE. \tag{2.16}$$

So, we may Fourier analyze Eq. (2.16) to get

$$(E-E_m)G_m(E) = \delta_{m0} + \sum_k H_{mk}G_k(E). \tag{2.17}$$

Let

$$G_m(E) = G_0(E)W_m(E) \tag{2.18}$$

then,

$$G_0(E) = [E - E_0 - H_{00} - \sum_{k\neq 0} H_{0k}W_k(E)]^{-1} \tag{2.19}$$

and

$$(E-E_m)W_m(E) = H_{m0} + \sum_{k\neq 0} H_{mk}W_k(E) \tag{2.20}$$

or

$$W_m(E) = U_m(E)\zeta(E-E_m), \tag{2.21}$$

where $\zeta(x)$ is the zeta function,[3] and

$$U_m(E) = H_{m0} + \sum_{k\neq 0} H_{mk}U_k(E)\zeta(E-E_k). \tag{2.22}$$

Let

$$\tfrac{1}{2}[i\hbar\Gamma(E)] = -[H_{00} + \sum_{k\neq 0} H_{0k}W_k(E)] \tag{2.23}$$

then,

$$a_0(t) = \left(\frac{-1}{2\pi i}\right)\int_{-\infty}^{+\infty} [E - E_0 + \tfrac{1}{2}i\hbar\Gamma(E)]^{-1} \exp[i(E_0-E)t/\hbar] dE. \tag{2.24}$$

We have two types of states; (1) those, $\mid \lambda\sigma\rangle$, with photons present and no excited atoms, and (2) those with no photons and one excited atom (exciton states), $\mid n\rangle = \psi(\mathbf{K}_n)$. We are neglecting all states with more than one

[3] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, London, 1954).

excited atom.[4] Then we have (we now reserve the subscripts m, n, $\cdots$, for the exciton states, and the greek subscripts for the photon states),

$$U_m(E)=H_{m0}+\sum_{n\neq 0}H_{mn}U_n(E)\zeta(E-E_n)+\sum_{\lambda\sigma}H_{m,\lambda\sigma}U_{\lambda\sigma}(E)\zeta(E-E_{\lambda\sigma}) \tag{2.25}$$

and

$$U_{\lambda\sigma}(E)=H_{\lambda\sigma,0}+\sum_{n\neq 0}H_{\lambda\sigma,n}U_n(E)\zeta(E-E_n). \tag{2.26}$$

The only matrix element connecting photon states is the diagonal element, $H_{\lambda\sigma,\lambda\sigma}$, which only contributes to the energy of the photon state $E_{\lambda\sigma}$ (and therefore has been neglected since it only leads to a redefinition of the energy of that photon state). Substituting (2.26) into (2.25), we find

$$U_m(E)=(H_{m0}+\gamma_{m0})+\sum_{n\neq 0}(H_{mn}+\gamma_{mn})U_n(E)\zeta(E-E_n), \tag{2.27}$$

where

$$\gamma_{mn}(E)=\sum_{\lambda\sigma}H_{m,\lambda\sigma}H_{\lambda\sigma,n}\zeta(E-E_{\lambda\sigma}). \tag{2.28}$$

Using (2.23) and (2.26) we find

$$-\tfrac{1}{2}[i\hbar\Gamma(E)]=(H_{00}+\gamma_{00})+\sum_{n\neq 0}(H_{0n}+\gamma_{0n})W_n(E). \tag{2.29}$$

For the states $|\,n\rangle\equiv|\,\mathbf{K}_n\rangle$, it is easy to show

$$H_{mn}=\delta_{mn}\sum_p(R_p)^{-3}\exp(i\mathbf{K}\cdot\mathbf{R}_p)\,\boldsymbol{\mu}_0\cdot(1-3\mathbf{R}_p\mathbf{R}_p/R_p^2)\cdot\boldsymbol{\mu}_p, \tag{2.30}$$

where $\boldsymbol{\mu}_p$ is the transition dipole moment of the atom at the pth site. Also

$$\begin{aligned}\gamma_{0m}&=N^{-1}\sum_{\lambda\sigma}\sum_{p,q}\exp[i(\mathbf{K}_0\cdot\mathbf{R}_p-\mathbf{K}_m\cdot\mathbf{R}_q)]\langle\varphi_p{}^f\,|\,H_1\,|\,\varphi_p\lambda\sigma\rangle\langle\varphi_q\lambda\sigma\,|\,H_1\,|\,\varphi_q{}^f\rangle\zeta(E-E_{\lambda\sigma})\\&=N^{-1}\sum_{p,q}\exp[i(\mathbf{K}_0\cdot\mathbf{R}_p-\mathbf{K}_m\cdot\mathbf{R}_q)]\gamma(\mathbf{R}_p-\mathbf{R}_q),\end{aligned} \tag{2.31}$$

where

$$\gamma(\mathbf{R}_p-\mathbf{R}_q)=\sum_{\lambda\sigma}\langle\varphi_p{}^f\,|\,H_1\,|\,\varphi_p\lambda\sigma\rangle\langle\varphi_q\lambda\sigma\,|\,H_1\,|\,\varphi_q{}^f\rangle\zeta(E-E_{\lambda\sigma}). \tag{2.32}$$

We show later that $\gamma(\mathbf{R}_p-\mathbf{R}_q)$ is only dependent on $\boldsymbol{\tau}=\mathbf{R}_p-\mathbf{R}_q$. Thus, it is easy to see

$$\gamma_{0m}=\delta_{0,m}\sum_{\boldsymbol{\tau}}\exp(i\mathbf{K}_m\cdot\boldsymbol{\tau})\gamma(\boldsymbol{\tau}). \tag{2.33}$$

Thus,

$$-\tfrac{1}{2}i\hbar\Gamma(E)=H_{00}+\gamma_{00}. \tag{2.34}$$

III. CALCULATION OF γ_{00}

The matrix elements necessary for calculating $\gamma(\boldsymbol{\tau})$ are well known:

$$\langle\varphi_p{}^f\,|\,H_1\,|\,\varphi_p\lambda\sigma\rangle=i\exp(i\mathbf{k}_\lambda\cdot\mathbf{R}_p)k'(2\pi\hbar c/V\,|\,\mathbf{k}_\lambda\,|)^{1/2}\hat{e}_{\lambda\sigma}\cdot\boldsymbol{\mu}_p, \tag{3.1}$$

where $k'=(\epsilon'-\epsilon)/\hbar c$. Since all the $\boldsymbol{\mu}$ are parallel, we have

$$\gamma(\boldsymbol{\tau})=\sum_\lambda\zeta(E-E_{\lambda\sigma})(2\pi\hbar c/V\,|\,\mathbf{k}_\lambda\,|)(k')^2\exp(i\mathbf{k}_\lambda\cdot\boldsymbol{\tau})\{\boldsymbol{\mu}\cdot[1-(\mathbf{k}_\lambda\mathbf{k}_\lambda/k_\lambda^2)]\cdot\boldsymbol{\mu}\}, \tag{3.2}$$

which shows that $\gamma(\boldsymbol{\tau})$ is only dependent on $\boldsymbol{\tau}$.

Since

$$\sum_{\boldsymbol{\tau}}\exp[i(\mathbf{K}_0-\mathbf{k}_\lambda)\cdot\boldsymbol{\tau}]=N\sum_{\mathbf{b}}\delta(\mathbf{k}_\lambda-\mathbf{K}_0-\mathbf{b}), \tag{3.3}$$

[4] The states which consist of one exciton and one photon will not contribute to the problem since the Hamiltonian has no matrix elements between them and the states we are considering.

where $\mathbf{b}$ is a lattice vector of the reciprocal lattice, then

$$\gamma_{00}=\sum_{\lambda}\sum_{b}(N2\pi\hbar c/V\mid \mathbf{k}_\lambda\mid)(k')^2\delta(\mathbf{k}_\lambda-\mathbf{K}_0-\mathbf{b})\zeta(E-E_{\lambda\sigma})\{\boldsymbol{\mu}\cdot[1-(\mathbf{k}_\lambda\mathbf{k}_\lambda/k_\lambda^2)]\cdot\boldsymbol{\mu}\}. \tag{3.4}$$

Notice that for longitudinal excitons ($\boldsymbol{\mu}\parallel\mathbf{K}_0$), the first (and most important) term ($\mathbf{b}=0$) is zero, as it should be.

IV. CALCULATION OF $a_m(t)$

We are now in a position to calculate $a_m(t)$. Using (2.27), (2.30), and (2.33), we have

$$U_m(E)=[H_{mm}+\gamma_{mm}(E)]U_m(E)\zeta(E-E_m). \tag{4.1}$$

Multiplying both sides by $(E-E_m)$, we have

$$\{(E-E_m)-[H_{mm}+\gamma_{mm}(E)]\}U_m(E)=0. \tag{4.2}$$

Thus

$$U_m(E)=0 \tag{4.3}$$

and

$$a_m(t)=0,\qquad m\neq 0. \tag{4.4}$$

From (2.26), we have

$$U_{\lambda\sigma}(E)=H_{\lambda\sigma,0} \tag{4.5}$$

and

$$a_{\lambda\sigma}(t)=\left(\frac{-1}{2\pi i}\right)\int_{-\infty}^{+\infty}dEG_0(E)H_{\lambda\sigma,0}\zeta(E-E_{\lambda\sigma})\exp\left(\frac{i(E_{\lambda\sigma}-E)t}{\hbar}\right), \tag{4.6}$$

where $G_0(E)$ is given above (2.19). We have then,

$$a_0(t)=\left(\frac{-1}{2\pi i}\right)\int_{-\infty}^{+\infty}G_0(E)\exp\left(\frac{i(E_0-E)t}{\hbar}\right)dE. \tag{4.7}$$

If we neglect Umklapp processes, i.e., restrict $\mathbf{b}$ to be $\mathbf{0}$ in (3.4), we have

$$a_0(t)=\left(\frac{-1}{2\pi i}\right)\int_{-\infty}^{+\infty}\frac{\exp[i(E_0-E)t/\hbar]}{E-E_0-H_{00}-\alpha\zeta(E-\hbar c\mid\mathbf{K}_0\mid)}\,dE, \tag{4.8}$$

where

$$\alpha=[2\pi\hbar c(k')^2/\mid\mathbf{K}_0\mid V_0][\boldsymbol{\mu}\cdot(1-\mathbf{K}_0\mathbf{K}_0/K_0^2)\cdot\boldsymbol{\mu}], \tag{4.9}$$

$$V_0=V/N. \tag{4.10}$$

Using the representation of the zeta function[3],

$$\zeta(x)=(x+i\epsilon)^{-1},\qquad \epsilon=0_+, \tag{4.11}$$

we find

$$a_0(t)=\left(\frac{-1}{2\pi i}\right)\int_{-\infty}^{+\infty}\frac{dE\exp[i(E_0-E)t/\hbar](E-\hbar c\mid\mathbf{K}_0\mid+i\epsilon)}{(E-E_+)(E-E_-)}, \tag{4.12}$$

where

$$E_\pm=[\tfrac{1}{2}(E_0+H_{00}+\hbar c\mid\mathbf{K}_0\mid-i\epsilon)]\pm\{[\tfrac{1}{2}(E_0+H_{00}-\hbar c\mid\mathbf{K}_0\mid+i\epsilon)]^2+\alpha\}^{1/2}. \tag{4.13}$$

Thus

$$a_0(t)=\left(\frac{(E_+-\hbar c\mid\mathbf{K}_0\mid)\exp[i(E_0-E_+)t/\hbar]-(E_--\hbar c\mid\mathbf{K}_0\mid)\exp[i(E_0-E_-)t/\hbar]}{(E_+-E_-)}\right). \tag{4.14}$$

Since ϵ is taken to by $0+$, we have no exponential decay for $a_0(t)$. Similarly we find

$$a_{\lambda\sigma}(t)=\frac{H_{\lambda\sigma,0}}{(E_+-E_-)}\left(\frac{E_+-\hbar c\mid\mathbf{K}_0\mid}{E_+-E_{\lambda\sigma}}\right)\left[\exp\left(\frac{i(E_{\lambda\sigma}-E_+)t}{\hbar}\right)-1\right]-\left(\frac{E_--\hbar c\mid\mathbf{K}_0\mid}{E_--E_{\lambda\sigma}}\right)\left[\exp\left(\frac{i(E_{\lambda\sigma}-E_-)t}{\hbar}\right)-1\right], \tag{4.15}$$

where

$$H_{\lambda\sigma,0}=-i\sum_{\mathbf{b}}\delta(\mathbf{k}_\lambda-\mathbf{K}_0-\mathbf{b})\,(2\pi\hbar c/V_0\mid\mathbf{k}_\lambda\mid)^{1/2}k'\boldsymbol{\mu}\cdot\hat{e}_{\lambda\sigma}. \tag{4.16}$$

Neglecting Umklapp processes we have $\mathbf{k}_\lambda=\mathbf{K}_0$, and $E_{\lambda\sigma}=\hbar c\mid\mathbf{K}_0\mid$, thus,

$$a_{\lambda\sigma}(t)=[\delta(\mathbf{k}_\lambda-\mathbf{K}_0)\,(-ik')\,(2\pi\hbar c/V_0\mid\mathbf{k}_\lambda\mid)^{1/2}\boldsymbol{\mu}\cdot\hat{e}_{\lambda\sigma}]$$
$$\times(E_+-E_-)^{-1}\{\exp[i(E_{\lambda\sigma}-E_+)t/\hbar]-\exp[i(E_{\lambda\sigma}-E_-)t/\hbar]\}, \tag{4.17}$$

which again points out the absence of interaction of light with longitudinal excitons. Thus, each exciton state is coupled to only one photon state (in which $\mathbf{k}_\lambda=\mathbf{K}_0$) and the energy is trapped between these two states. We notice that for the state in which $hc\mid\mathbf{K}_0\mid=E_0+H_{00}$ (that is, where the photon energy is equal to the exciton energy) we have

$$E_\pm=\hbar c\mid\mathbf{K}_0\mid\pm\alpha^{1/2} \tag{4.18}$$

and

$$a_0(t)=\exp(-iH_{00}t/\hbar)\,\cos(\alpha^{1/2}t/\hbar), \tag{4.19}$$

$$a_{\lambda\sigma}(t)=-ik'(2\pi\hbar c/V_0\mid\mathbf{k}_\lambda\mid)^{1/2}\boldsymbol{\mu}\cdot\hat{e}_{\lambda\sigma}\sin(\alpha^{1/2}t/\hbar)\delta(\mathbf{k}_\lambda-\mathbf{K}_0), \tag{4.20}$$

$$\mid a_0(t)\mid^2+\sum_\sigma\mid a_{\lambda\sigma}(t)\mid^2=1. \tag{4.21}$$

V. DISCUSSION

The present calculation explicitly shows that when periodic boundary conditions are used, there can be no meaning attached to the lifetime of an exciton state. That is, the exciton field and the photon field exchange energy between one another, and there is no radiation damping, hence no natural radiative lifetime. The reason for this is clearly that the periodic boundary conditions require that only one photon tate interacts with each exciton state and so the density of states for the transition probability becomes a delta function. Since the periodic boundary conditions also ensure that an exciton state does not interact with any other exciton state, this result will be unchanged if the initial state were a linear combination of exciton states. Of course, this result has been known for some time,[5] and the resultant states (mixtures of exciton and photon) are called polaritons. The use of nonperiodic boundary conditions may lead to a natural lifetime for crystals of finite size. The fact that the crystal is finite and the box (in which the radiation field is quantized) infinite will lead to the interaction of many photon states with one exciton state, and therefore damping will result. A calculation of this effect is underway at the present time. It should be pointed out that the result [Eq. (3.4)] can be obtained by summation of the retarded dipole–dipole interaction over the infinite crystal.[6] [One must be careful in this case not to make the approximation equivalent to assuming $\gamma_{00}(E)$ small compared to $E-E_0-H_{00}$ in Eq. (2.24).]

This result, as stated above, has been known for some time; however, because the question of natural radiative lifetimes of exciton states still appears in the literature,[2] we have felt that it is worthwhile to perform this calculation using the same techniques used for previous calculations[1] to demonstrate the result explicitly.

The absence of phonons in the above calculation amounts to the neglect of the main mechanism for absorption of energy. Phonons will act to couple many photon states to one exciton state (and vice versa) and thus lead to a large density of states in the transition probability. Hopfield[5] has a clear presentation of these ideas.

The use of one atom per unit cell and one excited state per atom are not essential to the above arguments and may be easily removed.

[5] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).

[6] See for example, S. A. Rice and J. Jortner, "Comments on the Theory of the Exciton States of Molecular Crystals" in *The Physics and Chemistry of the Organic Solid State* (Academic Press Inc., New York), Vol. 3.