Optical absorption and emission spectra of molecular crystals - Theory

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Abstract

These notes describe the theory used in the Molecular-crystals-spectra software. The basic theory comes from Davydov's book on molecular excitons [1]. The phonon cloud basis set has been adapted from Hoffmann and Soos [2]. The implementation has been described in [4] and references therein. Ewald sums are discussed in [3] and transition charges in [5]. Some text has been cut and pasted from these sources.

1 Introduction

Organic molecular semiconductors are formed by molecules interacting via relatively weak van der Waals forces. Parallel molecular stacking, herringbone, and face-to-face arrangements are often found in the solid state. Absorption and emission spectra of molecular crystals are dominated by Frenkel excitons, which are very different from the Wannier-Mott excitons of conventional inorganic semiconductors. Molecular crystals are characterized by electronic energy bands separated by energy gaps. However, the band gap is strongly influenced by the molecular electronic transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and it can be easily tuned to cover the whole UV-visible range by selecting the appropriate organic molecule. Molecular crystals are also characterized by narrow bands as a function of momentum k (typical bandwidths of tenths of an electronvolt), relatively large effective masses, and small dielectric constants. Due to these structural properties, they support Frenkel excitons, which consist of electron-hole pairs residing on the same molecule and have large binding energies (of the order of 1 eV). In addition, excitonic transitions in these materials typically show strong optical anisotropy, often associated with strong directional dispersion depending on the direction of the incoming light. By contrast, inorganic semiconductors, which are made of covalently bonded atoms, have relatively wide bands, small effective masses, and large dielectric constants. They therefore support Wannier-Mott excitons, characterized by a large electron-hole separation (much larger than the lattice constant) and by a small binding energy (of the order of 1 meV). Another striking difference between the two classes of semiconductors is that an optical excitation can easily create Frenkel excitons in molecular crystals, while it usually creates free carriers in inorganic semiconductors, Wannier-Mott exciton absorption lines appearing only at low temperatures just below the band edge.[4] It is important to recognize that the properties of excitons in molecular crystals are strongly influenced by their coupling to intramolecular phonons, which give rise to the vibronic progressions typically observed in optical spectra. This is because in organic semiconductors electronic excitation is accompanied by significant nuclear rearrangements, which do not occur in inorganic semiconductors instead. The conventional treatment of exciton-phonon coupling identifies different regimes by comparing the nuclear relaxation energy to a measure of the intermolecular (excitonic) interactions, usually taken to be the free-exciton bandwidth or, in the case of more than one molecule per unit cell, the free-exciton Davydov splitting W. For a single harmonic intramolecular vibrational mode of energy $\hbar\Omega$, the nuclear relaxation energy is given by $\lambda^2\hbar\Omega$, where λ^2 is the Huang-Rhys factor. Strong, intermediate and weak excitonic coupling corresponds to the three situations: $\lambda^2\hbar\Omega \ll W$, $\lambda^2\hbar\Omega \approx W$ and $\lambda^2\hbar\Omega \gg W$, respectively.

2   One intramolecular phonon mode

2.1   Hamiltonian - One intramolecular phonon mode

In the framework of the Frenkel-Davydov theory, molecules in a crystal are treated as two level systems where the excited state corresponds to the presence of a Frenkel exciton. When interactions between different molecules are taken into account, optical properties are determined by the eigenstates of the whole crystal and they strongly depend on molecular packing. Since intermolecular interactions are much smaller than the molecular transition energy, coupling between crystal states with different numbers of excitons can be neglected. This is called the Heitler- London approximation. Typically, molecular excitations occur in the UV-visible range of the spectrum and optical properties are mainly determined by crystal states with a single exciton. Within the above approximations we will now consider a molecular crystal made of N cells, each containing σ molecules.[1]

We initially assume an infinite 3D crystal in which each molecule has one vibrational and one electronic degree of freedom. Molecules are labeled according to the unit cell they belong to (indicated by $\mathbf{n}$) and to their position inside the cell (indicated by α). Vibrationally each molecule $\mathbf{n}, \alpha$ has one effective configuration coordinate $Q_{\mathbf{n},\alpha}$. The vibrational potential is $V_{\mathbf{n},\alpha}^{gr} = \hbar\Omega Q_{\mathbf{n},\alpha}^2$ in the electronic ground state and $V_{\mathbf{n},\alpha}^{ex} = \hbar\Omega \left(Q_{\mathbf{n},\alpha} - \lambda\right)^2$ in the excited state, where $\hbar\Omega$ is the energy of the intramolecular vibrational (phonon) mode and λ^2 is the corresponding Huang-Rhys factor (cfr Appendix A).

When we include the interaction between all the molecules of the infinite crystal the Hamiltonian for one phonon mode reads (in a similar notation to [2])

$$H_1 = H_1^{FE} + H_1^{ph} + H_1^{FE-ph}, \tag{1}$$

with

$$H_1^{FE} = \hbar\omega \sum_{\mathbf{n},\alpha} a_{\mathbf{n},\alpha}^\dagger a_{\mathbf{n},\alpha} + {\sum_{\mathbf{n},\alpha,\mathbf{m},\beta}}' J_{\alpha\beta}(\mathbf{r_n} - \mathbf{r_m}) a_{\mathbf{n},\alpha}^\dagger a_{\mathbf{m},\beta}, \tag{2}$$

$$H_1^{ph} = \hbar\Omega \sum_{\mathbf{n},\alpha} b_{\mathbf{n},\alpha}^\dagger b_{\mathbf{n},\alpha}, \tag{3}$$

$$H_1^{FE-ph} = \hbar\Omega \sum_{\mathbf{n},\alpha} a_{\mathbf{n},\alpha}^\dagger a_{\mathbf{n},\alpha} \left[-\lambda \left(b_{\mathbf{n},\alpha}^\dagger + b_{\mathbf{n},\alpha}\right) + \lambda^2\right]. \tag{4}$$

In the above formulas $\mathbf{n} \equiv \{n_a, n_b, n_c\}$ denotes the crystal vector $\mathbf{r_n} \equiv n_a\mathbf{a} + n_b\mathbf{b} + n_c\mathbf{c}$ and $J_{\alpha\beta}(\mathbf{r_n} - \mathbf{r_m})$ is the interaction energy between a molecule of type α in cell $\mathbf{r_n}$ and a molecule of type β in cell $\mathbf{r_m}$, which only depends on the type of molecule and the relative position of the two unit cells. The primed summation in eq.(2) indicates that self-interaction must be excluded, i.e. if $\alpha = \beta$ then $\mathbf{r_n} \neq \mathbf{r_m}$. Operators $b_{\mathbf{n},\alpha}^\dagger$ create a phonon excitation localized on a α molecule in the unit cell $\mathbf{n}$ in its ground state. Operators $a_{\mathbf{n},\alpha}^\dagger$ create an electronic excitation localized on a α molecule in the unit cell $\mathbf{n}$.

2.2   Phonon cloud basis functions - One intramolecular phonon mode

As basis functions, we use the eigenstates $|\mathbf{n}, \alpha; \underline{\nu}\rangle$ from the limiting case of zero intermolecular interaction, i.e. $J_{\alpha\beta} = 0$. We call this the molecular limit, since all intermolecular interaction terms are turned off now. In the molecular limit, an exciton localized at site n is stationary and the vibrational wave functions at this site are given by oscillator functions in the displaced potential V^{ex}. At all other sites, which we count relative to the position of the exciton, the vibrational wave functions are oscillator functions in the ground state potential V^{gr}. The multiparticle basis states are denoted by [2]

$$
\begin{aligned}
|\mathbf{n}, \alpha; \underline{\nu}\rangle \quad &\equiv \quad &(5)\\
&\equiv \quad |\mathbf{n}, \alpha\rangle | \cdots \nu_{\{-1,0,0\};1} \cdots \nu_{\{-1,0,0\};\sigma} \nu_{\mathbf{0};1} \cdots \tilde{\nu}_{\mathbf{0};\alpha} \cdots \nu_{\mathbf{0};\sigma} \nu_{\{1,0,0\};1} \cdots \nu_{\{1,0,0\};\sigma} \cdots \rangle\\
&\equiv \quad a_{\mathbf{n},\alpha}^\dagger |0^{el}\rangle \times \frac{1}{\sqrt{\nu_{\mathbf{0};\alpha}!}} \left(\tilde{b}_{\mathbf{n},\alpha}^\dagger\right)^{\nu_{\mathbf{0};\alpha}} |\tilde{0}_{\mathbf{n},\alpha}\rangle \times \prod_{(\delta\mathbf{n},\beta)\neq(\mathbf{0};\alpha)} \frac{1}{\sqrt{\nu_{\delta\mathbf{n},\beta}!}} \left(b_{\mathbf{n}+\delta\mathbf{n},\beta}^\dagger\right)^{\nu_{\delta\mathbf{n},\beta}} |0_{\mathbf{n}+\delta\mathbf{n},\beta}\rangle,
\end{aligned}
$$

where $\mathbf{n} \equiv \{n_a, n_b, n_c\}$, again, denotes the crystal vector $\mathbf{r_n} = n_a\mathbf{a} + n_b\mathbf{b} + n_c\mathbf{c}$ (the notation $\mathbf{0} = \{0,0,0\}$ was also used); $\alpha = 1, \ldots, \sigma$ labels the translationally non-equivalent molecules in the unit cell
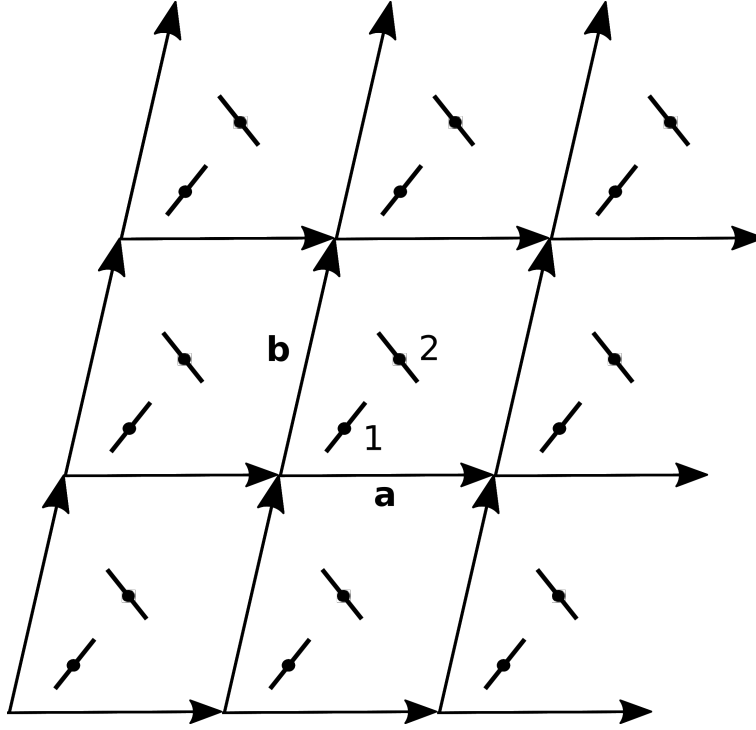
Figure 1: Lattice example.

placed at $\mathbf{r}_{\mathbf{n},\alpha} = \mathbf{r}_{\mathbf{n}} + \mathbf{r}_\alpha$, where $\mathbf{r}_\alpha$ denotes the position inside the cell. Operators $b^\dagger_{\mathbf{n},\alpha}$ create a phonon excitation localized on a α molecule in its ground state, while $\tilde{b}^\dagger_{\mathbf{n},\alpha} = b^\dagger_{\mathbf{n},\alpha} - \lambda$ create a phonon excitation localized on a α molecule in its excited state. It follows that $\underline{\nu}$ can be interpreted as a phonon cloud. Note that in the above notation the position of the phonons in the phonon cloud is relative to the electronic excitation.

The choice of the displaced basis functions corresponds to applying the polaron canonical transformation (Lang-Firsov transformation) to a set of basis functions, in which all vibrational functions (including the site n of the exciton) are oscillator functions in the ground state potential. This transformation simplifies the matrix elements of the exciton-phonon interaction part of the Hamiltonian.

With the restriction that phonon clouds be localized around the purely electronic excitation we Fourier transform the basis states and we need a single wave vector that describes the delocalization of the electronic excitation surrounded by the phonon cloud:

$$|\mathbf{k},\alpha;\underline{\nu}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \exp(i\mathbf{k}\mathbf{r}_{\mathbf{n}})|\mathbf{n},\alpha;\underline{\nu}\rangle. \tag{6}$$

We emphasize that in contrast to the real space basis, the momentum-space basis functions are not Born-Oppenheimer separable into a product of a purely electronic and a purely vibrational part.

2.3 Matrix elements in real space

First we compute matrix elements in real space, i.e.

$$\langle \mathbf{n},\alpha;\underline{\nu}|H_1|\mathbf{m},\beta;\underline{\mu}\rangle. \tag{7}$$

We separate the Hamiltonian into two terms and obtain respectively

$$\langle \mathbf{n},\alpha;\underline{\nu}|H_1^{ph} + H_1^{FE-ph}|\mathbf{m},\beta;\underline{\mu}\rangle = \hbar\Omega\delta_{\{\mathbf{n},\alpha\},\{\mathbf{m},\beta\}}\delta_{\underline{\nu},\underline{\mu}} \sum_{\delta\mathbf{n},\gamma} \nu_{\delta\mathbf{n},\gamma} \tag{8}$$
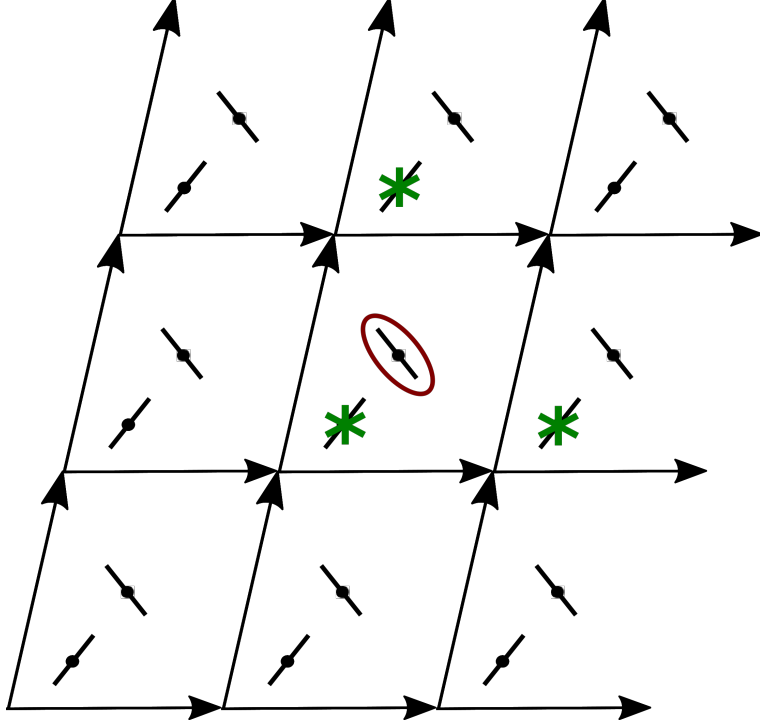
and

3

Figure 2: Phonon cloud example.

$$\langle \mathbf{n}, \alpha; \underline{\nu} | H_1^{FE} | \mathbf{m}, \beta; \underline{\mu} \rangle \quad = \quad \hbar\omega \delta_{\{\mathbf{n},\alpha\},\{\mathbf{m},\beta\}} \delta_{\underline{\nu},\underline{\mu}} + \tag{9}$$

$$+ J_{\alpha\beta}(\delta\mathbf{r}) S \left(\begin{array}{c} \nu_{\mathbf{0},\alpha} \\ \mu_{\delta\mathbf{r},\alpha} \end{array} \right) S \left(\begin{array}{c} \mu_{\mathbf{0},\beta} \\ \nu_{-\delta\mathbf{r},\beta} \end{array} \right) \prod_{\{\mathbf{r},\gamma\} \neq \{\mathbf{0},\alpha\} \neq \{-\delta\mathbf{r},\beta\}} \langle \nu_{\mathbf{r},\gamma} | \mu_{\mathbf{r}+\delta\mathbf{r},\gamma} \rangle, \tag{10}$$

where

$$\delta\mathbf{r} \equiv \mathbf{r_n} - \mathbf{r_m}, \tag{11}$$

$$J_{\alpha\alpha}(\mathbf{0}) = 0. \tag{12}$$

The symbol $\delta_{\underline{\nu},\underline{\mu}}$ is different from 0 only if the two phonon clouds are identical and localized on the same molecule. Moreover we have

$$S \left(\begin{array}{c} \mu \\ \nu \end{array} \right) \quad \equiv \quad \left\langle \frac{1}{\sqrt{\mu!}} (b^\dagger)^\mu 0 \, \middle| \, \frac{1}{\sqrt{\nu!}} (\tilde{b}^\dagger)^\nu 0 \right\rangle = \tag{13}$$

$$= \quad \frac{\exp(-\lambda^2/2)}{\sqrt{\mu!\nu!}} \sum_{i=0}^{\min(\mu,\nu)} \frac{(-1)^{\nu-i} \lambda^{\mu+\nu-2i} \mu!\nu!}{i!(\mu-i)!(\nu-i)!} \tag{14}$$

and

$$\langle \nu_{\mathbf{r},\gamma} | \mu_{\mathbf{r}+\delta\mathbf{r},\gamma} \rangle = \delta_{\nu,\mu} \tag{15}$$

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2.4 Matrix elements in k space

We want to compute

$$\langle \mathbf{k}, \alpha; \underline{\nu} | H_1 | \mathbf{k}', \beta; \underline{\mu} \rangle \tag{16}$$

Using the results of the previous section and equation (6) we find

$$\langle \mathbf{k}, \alpha; \underline{\nu} | H_1^{ph} + H_1^{FE-ph} | \mathbf{k}', \beta; \underline{\mu} \rangle = \hbar\Omega \delta_{\{\mathbf{k},\alpha\},\{\mathbf{k}',\beta\}} \delta_{\underline{\nu},\underline{\mu}} \sum_{\delta\mathbf{n},\gamma} \nu_{\delta\mathbf{n},\gamma} \tag{17}$$

and

$$\langle \mathbf{k}, \alpha; \underline{\nu} | H_1^{FE} | \mathbf{k}', \beta; \underline{\mu} \rangle = \hbar\omega \delta_{\{\mathbf{k},\alpha\},\{\mathbf{k}',\beta\}} \delta_{\underline{\nu},\underline{\mu}} + \tag{18}$$

$$+ \delta_{\mathbf{k},\mathbf{k}'} \sum_{\delta\mathbf{r}} J_{\alpha\beta}(\delta\mathbf{r}) \exp(i\mathbf{k}\delta\mathbf{r}) S \begin{pmatrix} \nu_{\mathbf{0},\alpha} \\ \mu_{\delta\mathbf{r},\alpha} \end{pmatrix} S \begin{pmatrix} \mu_{\mathbf{0},\beta} \\ \nu_{-\delta\mathbf{r},\beta} \end{pmatrix} \prod_{\{\mathbf{r},\gamma\} \neq \{\mathbf{0},\alpha\} \neq \{-\delta\mathbf{r},\beta\}} \langle \nu_{\mathbf{r},\gamma} | \mu_{\mathbf{r}+\delta\mathbf{r},\gamma} \rangle,$$

where

$$J_{\alpha\alpha}(\mathbf{0}) = 0. \tag{19}$$

3 Two intramolecular phonon modes

3.1 Hamiltonian - Two intramolecular phonon mode

When we include the interaction between all the molecules of the infinite crystal the Hamiltonian reads

$$H_2 = H_2^{FE} + H_2^{ph} + H_2^{FE-ph}, \tag{20}$$

with

$$H_2^{FE} = \hbar\omega \sum_{\mathbf{n},\alpha} a_{\mathbf{n},\alpha}^\dagger a_{\mathbf{n},\alpha} + \sum_{\mathbf{n},\alpha,\mathbf{m},\beta}' J_{\alpha\beta}(\mathbf{r_n} - \mathbf{r_m}) a_{\mathbf{n},\alpha}^\dagger a_{\mathbf{m},\beta}, \tag{21}$$

$$H_2^{ph} = \hbar\Omega_0 \sum_{\mathbf{n},\alpha} b_{\mathbf{n},\alpha}^{0\dagger} b_{\mathbf{n},\alpha}^0 + \hbar\Omega_1 \sum_{\mathbf{n},\alpha} b_{\mathbf{n},\alpha}^{1\dagger} b_{\mathbf{n},\alpha}^1, \tag{22}$$

$$H_2^{FE-ph} = \hbar\Omega_0 \sum_{\mathbf{n},\alpha} a_{\mathbf{n},\alpha}^\dagger a_{\mathbf{n},\alpha} \left[-\lambda_0 \left(b_{\mathbf{n},\alpha}^{0\dagger} + b_{\mathbf{n},\alpha}^0 \right) + \lambda_0^2 \right] + \hbar\Omega_1 \sum_{\mathbf{n},\alpha} a_{\mathbf{n},\alpha}^\dagger a_{\mathbf{n},\alpha} \left[-\lambda_1 \left(b_{\mathbf{n},\alpha}^{1\dagger} + b_{\mathbf{n},\alpha}^1 \right) + \lambda_1^2 \right]. \tag{23}$$

In the above formulas we used the same notation of the previous section, but introduced two phonon modes, labeled 0 and 1, respectively, with their own energy and Huang-Rhys factor.

3.2 Phonon cloud basis functions - Two intramolecular phonon modes

The multiparticle basis states are denoted by

$$|\mathbf{n}, \alpha; \underline{\nu}^0; \underline{\nu}^1 \rangle \tag{24}$$

where the same notation has been used and there are now two phonon clouds corresponding to the two modes.

With the restriction that phonon clouds be localized around the purely electronic excitation we Fourier transform the basis states and we need a single wave vector that describes the delocalization of the electronic excitation surrounded by the phonon cloud:

$$|\mathbf{k}, \alpha; \underline{\nu}^0; \underline{\nu}^1 \rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \exp(i\mathbf{k}\mathbf{r_n}) |\mathbf{n}, \alpha; \underline{\nu}^0; \underline{\nu}^1 \rangle. \tag{25}$$

3.3 Matrix elements in real space

First we compute matrix elements in real space, i.e.

$$\langle \mathbf{n}, \alpha; \underline{\nu}^0; \underline{\nu}^1 | H_2 | \mathbf{m}, \beta; \underline{\mu}^0; \underline{\mu}^1 \rangle. \tag{26}$$

We separate the Hamiltonian into two terms and obtain respectively

$$\langle \mathbf{n}, \alpha; \underline{\nu}^0; \underline{\nu}^1 | H_2^{ph} + H_2^{FE-ph} | \mathbf{m}, \beta; \underline{\mu}^0; \underline{\mu}^1 \rangle = \tag{27}$$

$$\delta_{\{\mathbf{n},\alpha\},\{\mathbf{m},\beta\}} \delta_{\underline{\nu}^0,\underline{\mu}^0} \delta_{\underline{\nu}^1,\underline{\mu}^1} \left[\hbar\Omega_0 \sum_{\delta\mathbf{n},\gamma} \nu^0_{\delta\mathbf{n},\gamma} + \hbar\Omega_1 \sum_{\delta\mathbf{n},\gamma} \nu^1_{\delta\mathbf{n},\gamma} \right] \tag{28}$$

and

$$\langle \mathbf{n}, \alpha; \underline{\nu}^0; \underline{\nu}^1 | H_2^{FE} | \mathbf{m}, \beta; \underline{\mu}^0; \underline{\mu}^1 \rangle = \hbar\omega \delta_{\{\mathbf{n},\alpha\},\{\mathbf{m},\beta\}} \delta_{\underline{\nu}^0,\underline{\mu}^0} \delta_{\underline{\nu}^1,\underline{\mu}^1} + \tag{29}$$

$$+ J_{\alpha\beta}(\delta\mathbf{r}) S_0 \begin{pmatrix} \nu^0_{\mathbf{0},\alpha} \\ \mu^0_{\delta\mathbf{r},\alpha} \end{pmatrix} S_0 \begin{pmatrix} \mu^0_{\mathbf{0},\beta} \\ \nu^0_{-\delta\mathbf{r},\beta} \end{pmatrix} \prod_{\{\mathbf{r},\gamma\}\neq\{\mathbf{0},\alpha\}\neq\{-\delta\mathbf{r},\beta\}} \langle \nu^0_{\mathbf{r},\gamma} | \mu^0_{\mathbf{r}+\delta\mathbf{r},\gamma} \rangle \times \tag{30}$$

$$S_1 \begin{pmatrix} \nu^1_{\mathbf{0},\alpha} \\ \mu^1_{\delta\mathbf{r},\alpha} \end{pmatrix} S_1 \begin{pmatrix} \mu^1_{\mathbf{0},\beta} \\ \nu^1_{-\delta\mathbf{r},\beta} \end{pmatrix} \prod_{\{\mathbf{r},\gamma\}\neq\{\mathbf{0},\alpha\}\neq\{-\delta\mathbf{r},\beta\}} \langle \nu^1_{\mathbf{r},\gamma} | \mu^1_{\mathbf{r}+\delta\mathbf{r},\gamma} \rangle, \tag{31}$$

where

$$\delta\mathbf{r} \equiv \mathbf{r_n} - \mathbf{r_m}, \tag{32}$$
$$J_{\alpha\alpha}(\mathbf{0}) = 0. \tag{33}$$

The symbol $\delta_{\underline{\nu},\underline{\mu}}$ is different from 0 only if the two phonon clouds are identical and localized on the same molecule. Moreover we have

$$S_m \begin{pmatrix} \mu \\ \nu \end{pmatrix} \equiv \left\langle \frac{1}{\sqrt{\mu!}} (b^{m\dagger})^\mu 0 \middle| \frac{1}{\sqrt{\nu!}} (\tilde{b}^{m\dagger})^\nu 0 \right\rangle = \tag{34}$$

$$= \frac{\exp(-\lambda_m^2/2)}{\sqrt{\mu!\nu!}} \sum_{i=0}^{\min(\mu,\nu)} \frac{(-1)^{\nu-i}\lambda_m^{\mu+\nu-2i}\mu!\nu!}{i!(\mu-i)!(\nu-i)!} \tag{35}$$

and

$$\langle \nu_{\mathbf{r},\gamma} | \mu_{\mathbf{r}+\delta\mathbf{r},\gamma} \rangle = \delta_{\nu,\mu} \tag{36}$$

3.4 Matrix elements in k space

Similar.

4 Absorption

The dielectric tensor can be obtained from the computed excitonic states from the following formula

$$\epsilon_{ij}(\omega) = \epsilon_\infty \delta_{ij} + \frac{2}{\epsilon_0 \upsilon \hbar} \sum_n \frac{(\mathbf{d}_n)_i (\mathbf{d}_n)_j \omega_n}{\omega_n^2 - \omega^2 - i\gamma\omega}, \tag{37}$$

where υ is the cell volume, $\hbar\omega_n$ and $\mathbf{d}_n$ are the energy and transition dipole of the n-th state respectively; γ is a damping factor which can also depend on the frequency ω. We recall that there is an extra factor 2 due to the spin degeneracy, which is appropriate to excitonic singlet states, which must be included in the dipole moment value $\mathbf{d}_n$. The above expression corresponds to an oscillator strength of

$$f_n = \frac{2m\omega_n \mathbf{d}_n^2}{e^2\hbar}, \tag{38}$$

for each excitonic transition, where again the extra factor 2 must be included in the dipole moment value $\mathbf{d}_n$ and it is appropriate to excitonic singlet states. This can be seen by comparing the above expression for ϵ with its general form:

$$\epsilon = \epsilon_b + \sum_n \frac{f_n \omega_p^2}{\omega_n^2 - \omega^2}, \tag{39}$$

where we neglected damping, ϵ_b is a background dielectric constant and

$$\omega_p^2 = \frac{e^2}{v m \epsilon_0}. \tag{40}$$

If dipoles are expresses in Debyes, energies in eV and lengths in Å, formula (37) reduces to

$$\epsilon_{ij}(\omega) = \epsilon_\infty \delta_{ij} + \frac{8\pi}{1.602 v} \sum_n \frac{(\mathbf{d}_n)_i (\mathbf{d}_n)_j E_n}{E_n^2 - E^2 - i\Gamma E}, \tag{41}$$

where $E_n = \hbar\omega_n$, $E = \hbar\omega$ and $\Gamma = \hbar\gamma$. We obtained the above coefficient by using the following constants and conversions

$$
\begin{aligned}
\epsilon_0 &= 8.8541 \times 10^{-12} C^2 m^{-2} N^{-1} & (42)\\
1D &= 3.336 \times 10^{-30} Cm = e10^{-20} m & (43)\\
1eV &= 1.602 \times 10^{-19} J & (44)\\
\hbar c &= 1.97327 \times 10^{-7} m \cdot eV & (45)\\
mc^2 &= 0.511 \times 10^6 eV & (46)
\end{aligned}
$$

The above formulas are equivalent to the gaussian units expression

$$\epsilon_{ij}(\omega) = \epsilon_\infty \delta_{ij} + \frac{8\pi}{v\hbar} \sum_n \frac{(\mathbf{d}_n)_i (\mathbf{d}_n)_j \omega_n}{\omega_n^2 - \omega^2 - i\gamma\omega}, \tag{47}$$

where dipoles are in statC $\cdot$ cm, energies in erg, lengths in cm and statC $= $ cm $\sqrt{dyn}$. We recall that gaussian units expressions can be obtained substituting each SI charge q with $q\sqrt{4\pi\epsilon_0}$.

We finally note that the oscillator strength indicated by Gaussian is $f_n^{(Gaussian)} = f_n/3$ and gives a dipole moment in Debyes of

$$|\mathbf{d}_n| = \sqrt{\frac{3}{2} 175.8 \frac{f_n^{(Gaussian)}}{E_n}} = 16.239 \sqrt{\frac{f_n^{(Gaussian)}}{E_n}}, \tag{48}$$

where E_n is expressed in eV.

5 Emission

5.1 General definitions

Emission polarized along direction $\mathbf{u}$ is given by

$$S_{\mathbf{u}}(\hbar\omega) = R(T) \frac{1}{Z} \sum_{\mathbf{k}, dc, n} e^{-\frac{E_{\mathbf{k}, dc, n} - E_{LBE}}{k_B T}} S_{\mathbf{u}}^{(\mathbf{k}, dc, n)}(\hbar\omega), \tag{49}$$

where the partition function is

$$Z \equiv \sum_{\mathbf{k}, dc, n} e^{-\frac{E_{\mathbf{k}, dc, n} - E_{LBE}}{k_B T}} \tag{50}$$

$$S_{\mathbf{u}}^{(\mathbf{k}, dc, n)}(\hbar\omega) = \sum_{\nu_t = 0, 1, \dots} I_{\mathbf{u}}^{0 - \nu_t}(\mathbf{k}, dc, n) \left[\frac{E_{\mathbf{k}, dc, n} - \nu_t \hbar\omega_0}{E_{LBE}} \right]^3 \frac{W_e(\hbar\omega - E_{\mathbf{k}, dc, n} + \nu_t \hbar\omega_0)}{W_e(0)} \tag{51}$$

$$I_{\mathbf{u}}^{0-\nu_t}(\mathbf{k}, dc, n) = \sum_{\{\nu_{\mathbf{n},\alpha}\}}{}' \left| \langle \psi_{\mathbf{k},dc,n} | \hat{\mathbf{D}} \cdot \mathbf{u} \prod_{\mathbf{n},\alpha} | g_{\mathbf{n},\alpha}, \nu_{\mathbf{n},\alpha} \rangle \right|^2, \tag{52}$$

$$\hat{\mathbf{D}} = \sum_{\mathbf{n},\alpha} \mathbf{d}_\alpha |\mathbf{n}, \alpha\rangle \langle g| + h.c. \tag{53}$$

$$R(T) = \frac{P}{\gamma_r + \gamma_{nr}(T)} \tag{54}$$

5.2 Weak electronic coupling: two-particle approximation

Conditions: $W \ll \hbar\omega_0$ and $k_B T \ll \hbar\omega_0$. We assume that the emitting states are only the σ lowest energy states in each Davydov subspace. We now consider a multi particle basis set containing one- and two-particle states. The eigenstates are written as

$$\psi_{\mathbf{k},dc,n=0} = \sum_{\alpha,\underline{\mu}} c_{\alpha,\underline{\mu}}(\mathbf{k}, dc) |\mathbf{k}, \alpha, \underline{\mu}\rangle = \sum_{\alpha,\underline{\mu},\mathbf{n}} c_{\alpha,\underline{\mu}}(\mathbf{k}, dc) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{kn}} |\mathbf{n}, \alpha, \underline{\mu}\rangle \tag{55}$$

$$|\mathbf{k}, \alpha, \underline{\mu}\rangle \equiv \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} \sum_{\mathbf{n}} e^{i\mathbf{kn}} |\mathbf{n}, \alpha, \underline{\mu}\rangle. \tag{56}$$

Following Spano we write

$$I_{\mathbf{u}}^{0-\nu_t}(\mathbf{k}, dc, n) = \delta_{\nu_t,0} I_{\mathbf{u}}^{(0)}(\mathbf{k}, dc, n) + (1 - \delta_{\nu_t,0}) \left\{ I_{\mathbf{u}}^{(1)}(\nu_t; \mathbf{k}, dc, n) \right. \tag{57}$$

$$\left. + \sum_{\nu_1=1}^{\nu_t-1} I_{\mathbf{u}}^{(2)}(\nu_1, \nu_t - 1; \mathbf{k}, dc, n) \right\}, \tag{58}$$

where $I_{\mathbf{u}}^{(p)}$ is the line strength corresponding to emission to ground electronic states with a total of ν_t quanta spread over p molecules. The 0-0 emission line only contains terms due to one-particle states

$$I_{\mathbf{u}}^{(0)}(\mathbf{k}, dc, n) = \left| \langle \psi_{\mathbf{k},dc,n} | \hat{\mathbf{D}} \cdot \mathbf{u} | 0 \rangle \right|^2 = \left| \langle \psi_{\mathbf{k},dc,n} | \hat{\mathbf{D}} | 0 \rangle \cdot \mathbf{u} \right|^2 \tag{59}$$

$$= \left| \sum_{\alpha,\tilde{\mu},\mathbf{n}} \sum_{\mathbf{m},\beta} c_{\alpha,\tilde{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{kn}} \langle \mathbf{n}, \alpha | \mathbf{m}, \beta \rangle_{\mathrm{el}} \langle \tilde{\mu} | 0 \rangle_{\mathrm{ph}} \mathbf{d}_\beta \cdot \mathbf{u} \right|^2 \tag{60}$$

$$= \left| \sum_{\alpha,\tilde{\mu},\mathbf{n}} c_{\alpha,\tilde{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{kn}} S_{\tilde{\mu}0} \mathbf{d}_\alpha \cdot \mathbf{u} \right|^2 \tag{61}$$

$$= \delta(\mathbf{k}) \left| \sum_{\alpha,\tilde{\mu}} c_{\alpha,\tilde{\mu}}(\mathbf{k}, dc, n) \sqrt{N} e^{-i\mathbf{k}\rho_\alpha} S_{\tilde{\mu}0} \mathbf{d}_\alpha \cdot \mathbf{u} \right|^2 \tag{62}$$

$$= N\delta(\mathbf{k}) \left| \sum_{\alpha,\tilde{\mu}} c_{\alpha,\tilde{\mu}}(\mathbf{k}=0, dc, n) S_{\tilde{\mu}0} \mathbf{d}_\alpha \cdot \mathbf{u} \right|^2 \tag{63}$$

$$\tag{64}$$

where we used the relation

$$\sum_{\mathbf{n}} \frac{1}{N} e^{i\mathbf{kn}} = \delta(\mathbf{k}). \tag{65}$$

Now we give the expression for $I_{\mathbf{u}}^{(1)}(\nu_t; \mathbf{k}, dc, n)$, which consider emission ending on states $|g; \nu_t, \mathbf{l}, \gamma\rangle \equiv |g\rangle_{\mathrm{el}} |\nu_{t\mathbf{l},\gamma}\rangle_{\mathrm{ph}}$ in which all molecules are in their electronic ground state and there are ν_t vibrational quanta

on molecule $(\mathbf{l}, \gamma)$. Here we have an additional contribution due to two-particle states. The phonon cloud in this case is indicated for convenience as $\underline{\mu} \equiv \{\tilde{\mu}; \nu, \mathbf{p}, \sigma\}$, where $\tilde{\mu}$ indicates the number of phonons on the (electronically) excited molecule and ν indicates the number of phonons in the (electronic) ground state molecule residing at the relative position $(\mathbf{p}, \sigma)$ with respect to the (electronically) excited molecule.

$$I_{\mathbf{u}}^{(1)}(\nu_t; \mathbf{k}, dc, n) = \tag{66}$$

$$= \sum_{\mathbf{l}, \gamma} \left| \langle \psi_{\mathbf{k}, dc, n} | \hat{\mathbf{D}} \cdot \mathbf{u} | g; \mathbf{l}, \gamma, \nu_t \rangle \right|^2$$

$$= \sum_{\mathbf{l}, \gamma} \left| \sum_{\mathbf{n}, \alpha, \tilde{\mu}, \nu, \mathbf{p}, \sigma} \sum_{\mathbf{m}, \beta} c_{\alpha, \underline{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} \langle \mathbf{n}, \alpha | \mathbf{m}, \beta \rangle_{\mathrm{el}} \langle \mathbf{n}, \alpha, \tilde{\mu}; \mathbf{n}+\mathbf{p}, \sigma, \nu | \mathbf{l}, \gamma, \nu_t \rangle_{\mathrm{ph}} \mathbf{d}_\beta \cdot \mathbf{u} \right|^2$$

$$= \sum_{\mathbf{l}, \gamma} \left| \sum_{\tilde{\mu}} c_{\gamma, \tilde{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\gamma}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{l}} S_{\tilde{\mu}\nu_t} \mathbf{d}_\gamma \cdot \mathbf{u} + \sum_{\mathbf{p}, \alpha, \tilde{\mu}} c_{\alpha, \{\tilde{\mu}, \mathbf{p}, \gamma, \nu_t\}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{l}} e^{-i\mathbf{k}\mathbf{p}} S_{\tilde{\mu}0} \mathbf{d}_\alpha \cdot \mathbf{u} \right|^2$$

$$= \sum_{\gamma} \left| \sum_{\tilde{\mu}} c_{\gamma, \tilde{\mu}}(\mathbf{k}, dc, n) e^{-i\mathbf{k}\rho_\gamma} S_{\tilde{\mu}\nu_t} \mathbf{d}_\gamma \cdot \mathbf{u} + \sum_{\mathbf{p}, \alpha, \tilde{\mu}} c_{\alpha, \{\tilde{\mu}, \mathbf{p}, \gamma, \nu_t\}}(\mathbf{k}, dc, n) e^{-i\mathbf{k}\rho_\alpha} e^{-i\mathbf{k}\mathbf{p}} S_{\tilde{\mu}0} \mathbf{d}_\alpha \cdot \mathbf{u} \right|^2$$

where the first term is due to one-particle states and the second to two-particle states. We made use of the relation

$$\langle \mathbf{n}, \alpha, \tilde{\mu}; \mathbf{n}+\mathbf{p}, \sigma, \nu | \mathbf{l}, \gamma, \nu_t \rangle_{\mathrm{ph}} = \delta_{\mathbf{n}, \mathbf{l}} \delta_{\alpha\gamma} \delta_{\nu 0} S_{\tilde{\mu}\nu_t} + \delta_{\mathbf{n}+\mathbf{p}, \mathbf{l}} \delta_{\sigma\gamma} \delta_{\nu\nu_t} S_{\tilde{\mu}0}(1 - \delta_{\nu 0}) \tag{67}$$

$$I_{\mathbf{u}}^{(2)}(\nu_1, \nu_2; \mathbf{k}, dc, n) = \tag{68}$$

$$= \sum_{\mathbf{l}, \gamma, \mathbf{j}, \xi} \left| \langle \psi_{\mathbf{k}, dc, n} | \hat{\mathbf{D}} \cdot \mathbf{u} | g; \mathbf{l}, \gamma, \nu_1; \mathbf{j}, \xi, \nu_2 \rangle \right|^2$$

$$= \sum_{\mathbf{l}, \gamma, \mathbf{j}, \xi} \left| \sum_{\mathbf{n}, \alpha, \tilde{\mu}, \nu, \mathbf{p}, \sigma} \sum_{\mathbf{m}, \beta} c_{\alpha, \underline{\mu}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\alpha}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{n}} \langle \mathbf{n}, \alpha | \mathbf{m}, \beta \rangle_{\mathrm{el}} \langle \mathbf{n}, \alpha, \tilde{\mu}; \mathbf{n}+\mathbf{p}, \sigma, \nu | \mathbf{l}, \gamma, \nu_1; \mathbf{j}, \xi, \nu_2 \rangle_{\mathrm{ph}} \mathbf{d}_\beta \cdot \mathbf{u} \right|^2$$

$$= \sum_{\mathbf{l}, \gamma, \mathbf{j}, \xi} \left| \sum_{\tilde{\mu}} c_{\gamma, \{\tilde{\mu}, \mathbf{j}-\mathbf{l}, \xi, \nu_2\}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\gamma}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{l}} S_{\tilde{\mu}\nu_1} \mathbf{d}_\gamma \cdot \mathbf{u} + \sum_{\tilde{\mu}} c_{\xi, \{\tilde{\mu}, \mathbf{l}-\mathbf{j}, \gamma, \nu_1\}}(\mathbf{k}, dc, n) \frac{e^{-i\mathbf{k}\rho_\xi}}{\sqrt{N}} e^{i\mathbf{k}\mathbf{j}} S_{\tilde{\mu}\nu_2} \mathbf{d}_\xi \cdot \mathbf{u} \right|^2$$

$$= \sum_{\gamma, \mathbf{r}, \xi} \left| \sum_{\tilde{\mu}} c_{\gamma, \{\tilde{\mu}, \mathbf{j}-\mathbf{l}, \xi, \nu_2\}}(\mathbf{k}, dc, n) e^{-i\mathbf{k}\rho_\gamma} S_{\tilde{\mu}\nu_1} \mathbf{d}_\gamma \cdot \mathbf{u} + \sum_{\tilde{\mu}} c_{\xi, \{\tilde{\mu}, \mathbf{l}-\mathbf{j}, \gamma, \nu_1\}}(\mathbf{k}, dc, n) e^{-i\mathbf{k}\rho_\xi} e^{i\mathbf{k}\mathbf{r}} S_{\tilde{\mu}\nu_2} \mathbf{d}_\xi \cdot \mathbf{u} \right|^2$$

where all terms are due to two-particle states. We defined

$$\mathbf{r} \equiv \mathbf{j} - \mathbf{l} \tag{69}$$

and made use of the relation

$$\langle \mathbf{n}, \alpha, \tilde{\mu}; \mathbf{n}+\mathbf{p}, \sigma, \nu | \mathbf{l}, \gamma, \nu_1; \mathbf{j}, \xi, \nu_2 \rangle_{\mathrm{ph}} = \delta_{\mathbf{n}, \mathbf{l}} \delta_{\alpha\gamma} \delta_{\mathbf{n}+\mathbf{p}, \mathbf{j}} \delta_{\sigma, \xi} \delta_{\nu\nu_2} S_{\tilde{\mu}\nu_1} + \delta_{\mathbf{n}, \mathbf{j}} \delta_{\alpha\xi} \delta_{\mathbf{n}+\mathbf{p}, \mathbf{l}} \delta_{\sigma, \gamma} \delta_{\nu\nu_1} S_{\tilde{\mu}\nu_2} \tag{70}$$

Appendix A. Harmonic oscillator

Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \tag{71}$$

Eigenfunctions

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right) \tag{72}$$

with eigenenergies $E_n = \hbar\omega(n + 1/2)$. We can introduce creation and destruction operators

$$a = \sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{i}{m\omega}p\right) \tag{73}$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(x - \frac{i}{m\omega}p\right) \tag{74}$$

which operate on the eigenfunctions as

$$a|\psi_n\rangle = \sqrt{n}|\psi_{n-1}\rangle \tag{75}$$
$$a^\dagger|\psi_n\rangle = \sqrt{n+1}|\psi_{n+1}\rangle \tag{76}$$

so that Hamiltonian reads $H = \hbar\omega(a^\dagger a + 1/2)$ with $[a, a^\dagger] = 1$. If we measure energy in units of $\hbar\omega$ and lengths in units of $\sqrt{\frac{2\hbar}{m\omega}}$ the Hamiltonian reads

$$H = -\frac{1}{4}\frac{\partial^2}{\partial Q^2} + Q^2 \tag{77}$$

and eigenfunctions become

$$\psi_n(Q) = \frac{1}{\sqrt{2^n n!}} (\pi/2)^{-1/4} \exp\left(-Q^2\right) H_n\left(\sqrt{2}Q\right). \tag{78}$$

A harmonic oscillator displaced by λ in "natural" coordinates has Hamiltonian

$$H = -\frac{1}{4}\frac{\partial^2}{\partial Q^2} + (Q - \lambda)^2 \tag{79}$$

and eigenfunctions

$$\psi_{n,\lambda}(Q) = \frac{1}{\sqrt{2^n n!}} (\pi/2)^{-1/4} \exp\left(-(Q-\lambda)^2\right) H_n\left(\sqrt{2}(Q-\lambda)\right). \tag{80}$$

Overlaps between these functions are usually defined as

$$S_{\mu\nu} = \langle\psi_{\mu,0}|\psi_{\nu,\lambda}\rangle \tag{81}$$

Franck-Condon factors are then given by

$$S_{0\nu}^2 = \langle\psi_{0,0}|\psi_{\nu,\lambda}\rangle^2 = \frac{\exp(-\lambda^2)\lambda^{2\nu}}{\nu!} \tag{82}$$

A Huang-Rhys factor has also been defined as $S = \lambda^2$.

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