

**Chapter 2**

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$$\left\langle \frac{\text{power}}{\text{volume}} \right\rangle = \left\langle \tilde{E}_y(t) \frac{d\tilde{P}_y(t)}{dt} \right\rangle = \frac{1}{2} \text{Re}[E(i\omega P)^*] \quad \text{eq. 2.1}$$

**Chapter 4**

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**4.2.3**

**1-D excitons**

Any object in the real world belongs to the physical Euclidean space and have 3 dimensions

(3D). The volume of this object, assuming a generalized parallelepiped shape is  $V=L_xL_yL_z$  where  $L_k$  is the dimension along  $k$  in a cartesian reference. (This is valid within a factor of  $\pi$  for most of the existing shapes.) We call one dimensional a solid having one dimension much larger than the others, like  $L_z \gg L_x$  and  $L_z \gg L_y$ . Here a generalized section is  $A=L_xL_y$ , with a section  $d = \sqrt{A}$  and the solid is 1D with axis along  $-z$ .

Let's consider now a pair of opposite charge particles, like electron and positron, free to move along an axis, as in a one dimensional space. This conceptual situation describes an electron-hole excitation in a one dimensional solid, like a carbon nanotube or a polymer chain, or, with less accuracy, a quantum wire. The study of the two particle motion in 1D has a fundamental limit when the separation distance between electron and hole,  $z_{eh}$ , becomes comparable or smaller than the section,  $z_{eh} \leq d$ . Indeed, from a simple geometrical point of view, if we consider a section of the solid  $dz \approx d$  the 1D approximation, as described above, breaks down.

The original problem of the hydrogen atom in 1D has been studied in 1950, as a particular case of the 3D hydrogen atom.

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The absorption spectrum of the 1D W-M exciton shows a very large intensity only in the first transition spectral line, and an almost suppressed band to band transition (**Figure 4.10**). This can be stated as a drastic reduction of the Sommerfeld factor,  $f_S$ , defined as the fraction of the band-

to-band oscillator strength,  $f_S = \frac{f_{BAND}}{f_{BAND} + f_{exc}}$ .

The peculiar features seen in the 1-D exciton stems from the effect of dimensionality onto the hydrogenoid atom. In 1D electron and hole cannot escape their mutual attraction (check in chapter 8 about random walk and dimensionality). The acceleration of the internal motion cannot counterbalance Coulomb attraction. Screening of the Coulomb interaction is ineffective because most of the force-lines of the interaction field (this is a 3D pattern!) are located “outside” the system, in the medium surrounding the nanotubes.

**Pag. 69 (end)**

Finally when the exciton level is degenerate, or embedded, in the band continuum, tunneling from the bound state to the free e-h continuum may occur spontaneously. This may lead to a Fano-like shape of the exciton resonance when the ionization rate is large enough (in the order of the exciton lifetime). An external electric field will facilitate this process, enhancing the auto ionization rate. For large field this may lead to a field induced modification of the resonance lineshape to a Fano lineshape. A tunneling probability can be estimated from the “leaking” of the exciton wavefunction, as evaluated from the exciton wavefunction amplitude at some large distance between electron and hole, enough to assume a free state. This probability amplitude can be converted into a tunneling rate, that can be eventually compared to experiments, by using

an approximate expression like  $E_b = h \nu_A$  where  $E_b$  is the exciton binding energy and  $\nu_A$  the attempt frequency of escape. The later expression is obtained by the following reasoning. The attempt frequency  $\nu_A$  can be written as  $\nu_A = v/2L_C$  where  $v$  is an averaged velocity describing the approaching at the potential wall of the internal particles. According to the Heisenberg uncertainty principle, an averaged momentum of the bound exciton is  $p = \frac{h}{L_C}$ . According to the virial theorem, the exciton binding energy  $E_b$  is proportional to the kinetic energy,  $E_k = p v/2$ . Assuming  $E_b = E_k$  one reach  $\nu_A = E_b/h$ . The attempt frequency can be used to estimate an effective dissociation rate when used together with a tunneling probability (for each attempt) as discussed in chapter 8.

## Chapter 8

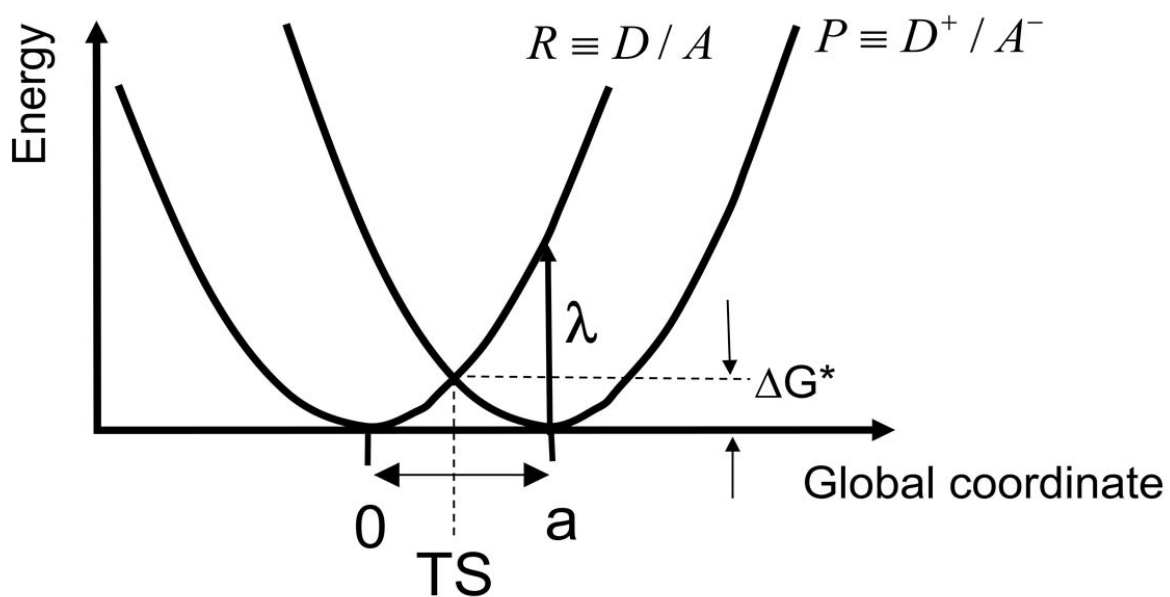
**Pag.146** (following “.....that provides the proper scaling for the rate.)

Essentially it is dictated by the time scale of the slowest coupled mode, typically a collective solvent reorganizational mode.

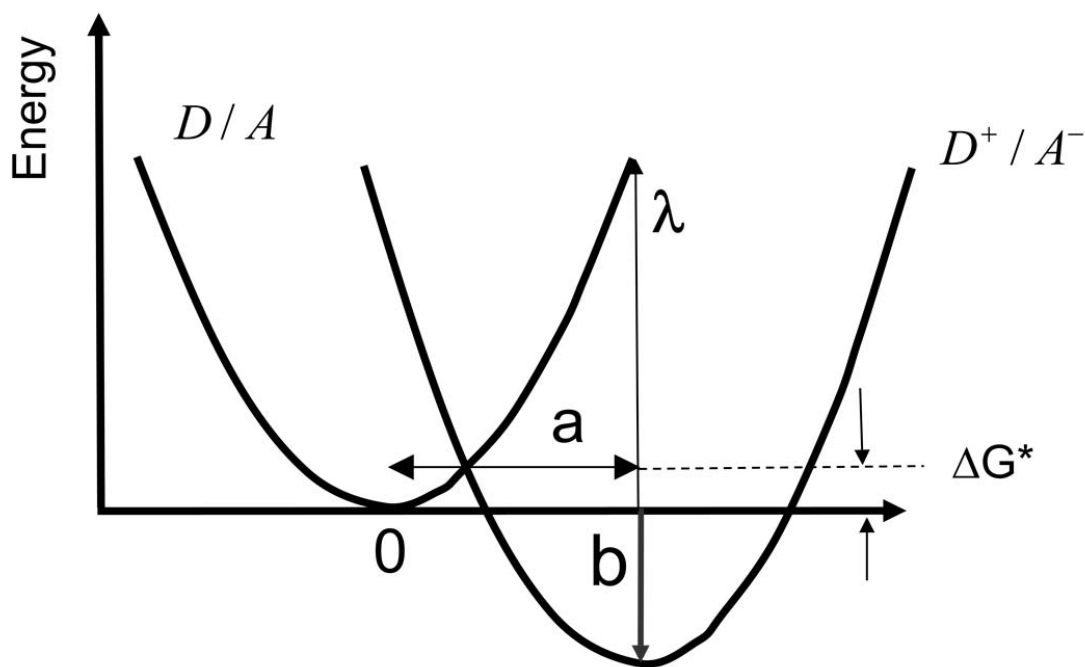
(before Now we consider....)

According to this picture the electron transfer process is suppressed at low temperature, because the encounter probability reduce to zero as the solvent modes get frozen.

**Pag.146 Figure 8.1**



**Pag.147 Figure 8.2**



**Pag.150.** (after ... energy is  $\lambda = S_s \hbar \omega_s + S \hbar \omega_e$  .)

In the adiabatic regime, when  $\nu_e = \frac{2\pi}{\hbar} V^2$  is large respect to the phonon frequencies, the total pre-exp factor A will be given by  $A = \left( \frac{1}{\nu_n} + \frac{1}{\nu_e} \right)^{-1} \xrightarrow{\nu_e \gg \nu_n} \nu_n$ . It should be noted that even weak electronic coupling (e.g.  $V=10 \text{ cm}^{-1}$  giving  $\nu_e^{-1} = 5.3 \text{ ps}$  ) is sufficient to reach the adiabatic limit. Equation 8.9 is thus the classical limit of the quantum mechanical expression. When the coupling is small the non adiabatic regime sets in and tunneling becomes important.

**Pag. 156** (Following Dimensionality has an important role)

The probability of return to the origin for a random walker in 3D is  $P(3D) \cong 0.34$ . Remember

however that a random walker in 1D and 2D always go back to the origin,  $P(2D)=P(1D)=1$ . In

1D the averaged distance travelled after N jumps is  $\langle D \rangle = \sqrt{N} a$  if "a" is the single jump

distance. Assuming a constant jump rate, the time dependent survival probability of the random

walker in 1D is  $\propto t^{-1/2}$  .

**Pag.156** (following “Figure 8.7 summarizes these considerations”)

The Onsager theory is instructive in describing the dissociation process, but it faces the problem of quantitative fitting. In order to reproduce experimental results in solids one should plug in values for the initial CT radius, or thermalization distance, of several nm, while a CT state is usually occurring between nearest neighbor, with separation  $< 1$  nm. This discrepancy can be rationalized considering hot dissociation and the role of excess energy in pushing away the initial charges, as described for amorphous semiconductors in the paragraph above. A second weakness of the model is that geminate recombination to the ground state of the dissociated carriers seems in contrast with the existence of a metastable intermediate CT state. According to Braun the Onsager equation should be corrected to take into account the dynamic balance between CT

dissociation and CT regeneration,  $GS \xrightleftharpoons[k_{CT}]{k_d} CT \xrightleftharpoons[\gamma N_{FC}]{k_d} FC$ , where  $k_d$  is the dissociation rate of the

bound pair,  $\gamma N_{FC}$  is the recombination rate constant of the population of free carriers (either polarons or electron and holes), and  $k_{CT}$  is the CT rate of back recombination to the ground state.

Here  $\gamma$  is the bimolecular recombination constant of the free carriers. We first analyze the dynamical equilibrium in zero electric field. At equilibrium the rate of dissociation and bimolecular recombination are equal,  $k_d = \gamma N_{FC}$ . Let's assume a population of CT states (ion pairs in the original Braun paper) with average electron-hole distance “ $a$ ” (thermalization distance in Onsager model) that occupies all the space. Their density at zero external field ( $F=0$ ),

will be  $N_{CT}^{F=0} = V^{-1} = \frac{3}{4\pi a^3}$ . At equilibrium the population of bound pairs ( $N_{CT}^{F=0}$  at distance “ $a$ ”)

versus free pairs ( $N_{FC}^{F=0}$  at infinite distance) is:

$$\frac{N_{FC}^{F=0}}{N_{CT}^{F=0}} = e^{-\Delta E / KT} \quad \text{eq. 8.16}$$

where  $\Delta E = \frac{e^2}{4\pi\epsilon a}$  and we use the Boltzman statistics. According to equation 8.16

$N_{FC}^{F=0} = N_{CT}^{F=0} e^{-\Delta E / KT}$ . Recalling that the free carriers can undergo bimolecular recombination, at equilibrium the dissociation rate is  $k_d^{F=0} = \gamma N_{FC}^{F=0} = \gamma N_{CT}^{F=0} e^{-\Delta E / KT}$ .

The bimolecular recombination constant can be expressed according to Langevin model,  $\gamma = \frac{\mu e}{\epsilon}$

, to get the final result

$$k_d^{F=0} = \frac{3\mu e}{4\pi\epsilon a^3} e^{-\Delta E / KT} \quad \text{eq.8.17}$$

This contains explicitly the role of transport (through mobility) in the dissociation dynamics.

In presence of the electric field the equilibrium population will be different, due to the possibility of field assisted dissociation. We note that eq.8.13 can be written as the product of two terms,

$$\Omega = \Omega_0 \Omega^F \quad \text{where } \Omega_0 \text{ is the dissociation probability at zero field and } \Omega^F = 1 + \frac{e}{KT} \frac{r_c E}{2!} + \dots$$

is the field dependent dissociation probability. Assuming valid the Onsager model for the field

effect, the free carrier population in presence of the field can be expressed as  $N_{FC}^{F \neq 0} = \Omega^F N_{FC}^{F=0}$ ,

in order to account for the non-null field assisted escape probability. Again at kinetic equilibrium

the dissociation and bimolecular recombination rates will be equal,  $k_d^{F \neq 0} = \gamma \Omega^F N_{FC}^{F=0} = \Omega^F k_d^{F=0}$ .

This provides the dissociation rate in presence of electric field:

$$k_d^{F \neq 0} = \frac{3\mu e}{4\pi\epsilon a^3} \Omega^F e^{-\Delta E/KT} \quad \text{eq. 8.18}$$

The final result of the Braun Onsager model is an yield of dissociation  $\Omega_{BO} = \frac{k_d(F)}{k_d(F) + k_{CT}}$ . The crucial difference of this theory with respect to the pure Onsager model, based on eq. 8.13, is that free carrier recombination leads to CT regeneration and subsequent re-dissociation, while in Onsager model the dissociated pairs never come back and the recombined pair disappears from the system. In other term pure Onsager is described by  $GS \xleftarrow{k_{CT}} CT \xrightarrow{k_d} FC$  while Braun Onsager describes the dynamical equilibrium between CT and FC according to  $GS \xleftarrow{k_{CT}} CT \xrightleftharpoons[N_{FC}]{k_d} FC$ . The modified dissociation rate according to Braun is consistent with thermalization distances sizably smaller than those needed when fitting the original Onsager model. The explicit dependence on mobility also suggests that better transport might help dissociation of the initial CT pair.

*Poole-Frenkel.....*

### Box 8.1

The matrix element appearing (squared) into the golden rule rate are:

$$\beta_C = \langle \phi_D^*(1)\phi_A(2) | V | \phi_D(1)\phi_A^*(2) \rangle$$

$$\beta_E = \langle \phi_D^*(1)\phi_A(2) | V | \phi_D(2)\phi_A^*(1) \rangle$$

Energy transfer can be seen as an exchange of a virtual photon. In energy transfer a vertical transition can conserve energy due to the contribution of the photon field. For this reason the reorganization energy does not lead to a barrier in the process. In addition the external reorganization energy is small because the states are overall neutral. In energy transfer reorganization energy appears as relaxation energy following the event.

The exchange (Dexter) matrix element requires the overlap between  $\phi_D^*(1)\phi_A^*(1)$ , that are on two different molecules, introducing the exponential dependence on distance.

$$\beta_{CT} = \langle \phi_D(1)\phi_A(0) | V | \phi_{D^+}(0)\phi_{A^-}^*(1) \rangle$$