Distinguished Visiting Scientist Program

Prof. Leonas Valkunas
Department of Theoretical Physics
Vilnius University, Lithuania

Series Title: *Excitons*

Lecture-2: *Excitons in Molecular Crystals and Aggregates*
Excitons in Molecular Crystals and Aggregates

Leonas Valkunas
Institute of Physics, Vilnius
Department of Theoretical Physics, Vilnius
University
A separate molecule

\[ H_n \phi^i_n = \varepsilon^i_n \phi^i_n \]

- \( n \) enumerates molecules and \( i \) refers to the ground (0) or excited (1) states
Two coupled molecules (dimer)

\[ \psi^f = c_{f1} \varphi_1^1 \varphi_2^0 + c_{f2} \varphi_2^1 \varphi_1^0 \]

- The excited state

\[ |c_{f1}|^2 + |c_{f2}|^2 = 1 \]

\[ (H_1 + H_2 + V)\psi^f = E^f \psi^f \]
Optical transitions

\[ \psi^f = c_{f1}\phi_1^1\phi_2^0 + c_{f2}\phi_2^1\phi_1^0 \]

- In the case of the dimer

\[ W_{01} \propto \left| \langle \psi^1 | H_1 | \psi^0 \rangle \right|^2 = E_0^2 \left| \hat{E} \cdot (c_{11}\vec{\mu}_1 + c_{12}\vec{\mu}_2) \right|^2 \]

\[ \vec{\mu}_i = \langle \phi_i^1 | \vec{\mu} | \phi_i^0 \rangle \]
Excitons

Frenkel  CT  Vannier-Mott

Self-trapped exciton
Excitons in larger systems

\[ \psi^f = \sum_n c_{fn} \varphi_n^1 \prod_{m \neq n} \varphi_m^0 \]

\[ H_{nm} = \delta_{nm} \varepsilon_n + V_{nm} \]

\[ \tilde{\mu}_f = \sum_n c_{fn} \tilde{\mu}_n \]

- Exciton wave function
- Hamiltonian
- Transition dipole moment
Translational symmetry

- \( \vec{r}_n \) is the coordinate of the \( n \)-th molecule
- \( k \) is the exciton quantum number
- The optical transition is allowed into a single exciton state \( k=0 \)

\[
C_{fn} \propto e^{ik\vec{r}_n}
\]

\[
\sum_{n=1}^{N} e^{ik\vec{r}_n} = N \delta_{\vec{k},0}
\]
Excitons in ring-like structure

Hamiltonian of monomeric LH2

\[
H = \begin{bmatrix}
    E_1 & V_{1,2} & V_{1,3} & \cdots & \cdots & V_{1,18} \\
    V_{2,1} & E_2 & V_{2,3} & \cdots & \cdots & V_{2,18} \\
    V_{3,1} & V_{3,2} & E_3 & \cdots & \cdots & V_{3,18} \\
    V_{18,1} & V_{18,2} & \cdots & \cdots & \cdots & V_{17,18} \\
    V_{17,18} & \cdots & \cdots & \cdots & \cdots & E_{18}
\end{bmatrix}
\]

\( E_i \) and \( V_{ij} \) must be taken from a Gaussian Distribution

Proteins are disordered

\( P(E) \)
Excitons

N- interacting molecules. Neglecting nuclear motions:

\[ |0\rangle = \prod_n |\varphi_n^0\rangle \]

\[ |n, f\rangle = |\varphi_n^f\rangle \prod_{m \neq n} |\varphi_m^0\rangle \]

\[
H = H_0 |0\rangle\langle 0| + \sum_n \epsilon_n |n, f\rangle\langle f, n| + \sum_{n,m} V_{nm} |n, f\rangle\langle f, m| + |m, f\rangle\langle f, n| \equiv H_0 |0\rangle\langle 0| + H_{exc}
\]
Excitons

Where

\[ H_0 = \sum_i \varepsilon_0^i \]

\[ V_{nm} = \frac{\vec{\mu}_n \cdot \vec{\mu}_m - 3(\vec{\mu}_n \cdot \vec{R}_{nm})(\vec{\mu}_m \cdot \vec{R}_{nm})}{R_{nm}^3}, \quad \varepsilon_n = \varepsilon_n^1 - \varepsilon_n^0 \]

\[ H_{exc} = \begin{pmatrix} \varepsilon_1 & & \\ & \varepsilon_2 & V_{mn} \\ & & \varepsilon_N \end{pmatrix} \]
Excitons

For diagonalization $H_{exc}$

$$|k\rangle_{exc} = \sum_n c_{kn} |n, f\rangle,$$

where expansion coefficients have to fulfil the following equation:

$$H_{exc} |k\rangle_{exc} = E_{exc}(k) |k\rangle_{exc}$$
Excitons

\[ E_{exc}(k) = \mathcal{E} + \Delta + L(k) \]

\[ \Delta = \sum_m \{ \langle n, f, m, 0 | V_{nm} | n, f, m, 0 \rangle - \langle n, 0, m, 0 | V_{nm} | n, 0, m, 0 \rangle \} \]

\[ L(k) = \sum_m J_{0m} e^{i \kappa \tilde{m}} \]

\[ J_{nm} = \langle n, f, m, 0 | V_{nm} | n, 0, m, f \rangle \]

- the exciton spectrum for the equivalent molecules
- the resonance interaction
Excitons

\[ k_s = \frac{2\pi}{N_s} j_s \]

\[ -\frac{N_s}{2} < j_s \leq \frac{N_s}{2} \]

\[ E_{\text{exc}}(s, k_s) = E_{\text{exc}}(s) + \frac{\hbar^2 k_s^2}{2m_s} \]

\[ m_s = -\frac{\hbar^2}{\sum_n n_s^2 J_{0n}} \]

- for the periodic boundary conditions
- for small \( k \) values
Excitons

\[ c_{kn\alpha} = \frac{1}{\sqrt{N}} u_{\alpha\nu} e^{ik \vec{r}_{n\alpha}} \]

\[ \vec{r}_{n\alpha} = \vec{n} + \vec{\rho}_\alpha \]

- for \( \sigma \) molecules per unit cell, \( u_{\alpha\nu} \) is the unitary matrix and \( \alpha \) enumerates molecules in the unit cell

\[ \sum_{\beta=1}^{\sigma} \{[\varepsilon + \Delta_{\alpha}] \delta_{\alpha\beta} + L_{\alpha\beta}(k)\} u_{\beta\nu}(k) = E_{\nu}(k) u_{\alpha\nu}(k) \]
Excitons

$$\Delta_\alpha = \sum_{m_\beta} \{ \langle n\alpha, f, m\beta, 0 | V_{n\alpha m_\beta} | n\alpha, f, m\beta, 0 \rangle - \langle n\alpha, 0, m\beta, 0 | V_{n\alpha m_\beta} | n\alpha, 0, m\beta, 0 \rangle \}$$

the displacement energy

$$L_{\alpha\beta}(k) = \sum_{m_\beta} \langle n\alpha, f, m\beta, 0 | V_{n\alpha m_\beta} | n\alpha, 0, m\beta, f \rangle e^{ik(r_{m_\beta} - r_{n\alpha})}$$

the resonance interaction

$$\det \{ L_{\alpha\beta}(k) + \delta_{\alpha\beta} [\varepsilon + \Delta_\alpha - E(k)] \} = 0$$

the characteristic equation
Two molecules per unit cell

\[ u_{av}(k) = \begin{bmatrix} \cos \phi(k) & \sin \phi(k) \\ -\sin \phi(k) & \cos \phi(k) \end{bmatrix} \]

- The characteristic equation

\[ \begin{vmatrix} \varepsilon + \Delta_1 + L_{11}(k) - E_{\nu}(k) & L_{12}(k) \\ L_{21}(k) & \varepsilon + \Delta_2 + L_{22}(k) - E_{\nu}(k) \end{vmatrix} = 0 \]
Two molecules per unit cell

\[ E_\nu(k) = \varepsilon + \frac{\Delta_1 + \Delta_2}{2} - (-1)^\nu \sqrt{\left(\frac{L_{11}(k) - L_{22}(k) + \Delta_1 - \Delta_2}{2}\right)^2 + (L_{12}(k))^2} \]

- The solution of the characteristic equation

\[ \tan \phi_\nu(k) = \frac{\varepsilon + \Delta_1 + L_{11}(k) - E_\nu(k)}{L_{12}(k)} \]
Two molecules per unit cell

When

\[ \Delta_1 = \Delta_2 \]

\[ L_{11}(k) = L_{22}(k) \]

\[ \Delta E(k) = 2L_{12}(k) \]  Davydov splitting
Cyclic molecular aggregate

\[ L_{11}(k) = L_{22}(k) = 0 \]

\[ L_{12}(k) = J_b e^{-i\bar{k}b} + J_a e^{i\bar{k}a} \]

\[ |L_{12}(k)|^2 = J_b^2 + J_a^2 + 2J_a J_b \cos \bar{k}(\bar{a} + \bar{b}) \]
Cyclic molecular aggregate

\[ E_\nu(k) = \varepsilon + \frac{\Delta_1 + \Delta_2}{2} - (-1)^\nu \sqrt{\frac{(\Delta_1 - \Delta_2)^2}{2} + J_b^2 + J_a^2 + 2J_aJ_b \cos k(\vec{a} + \vec{b})} \]

- In the case when \( \Delta_1 = \Delta_2 = \Delta \)
  \( J_a = J_b = J \)

\[ E_\nu(k) = \varepsilon + \Delta - (-1)^\nu 2J \sqrt{\frac{1}{2} + \frac{1}{2} \cos 2k\vec{a}} = \]
\[ \varepsilon + \Delta - (-1)^\nu 2J \cos k\vec{a} \]

- Both Davydov subbands have merged
Cyclic molecular aggregate
Linear molecular aggregate

\[ c_{fn}(j) = \sqrt{\frac{2}{N+1}} \sin\left(\frac{\pi j n}{N+1}\right) \]

- free edges (zero boundary conditions) for one molecule per unit cell

\[ j = 1, \ldots, N \]

\[ L(j) = \sum_{n=0}^{N+1} J_{n,n+1} \sin\left(\frac{\pi j n}{N+1}\right) \sin\left(\frac{\pi j (n+1)}{N+1}\right) = J \cos\left(\frac{\pi j}{N+1}\right) \]

- in the “nearest neighbor” approximation
Linear molecular aggregate

\[ E(j) = \varepsilon + \Delta + 2J \cos\left(\frac{\pi j}{N + 1}\right) \]

- exciton energies
Excitons

Frenkel\quad CT\quad Vannier-Mott

\begin{align*}
a_{ex} &<< a_L \\
a_{ex} &>> a_L
\end{align*}

Self-trapped exciton
Wannier-Mott excitons

\[ H_{ex} = -\frac{\hbar^2}{2m_e} \nabla^2_e - \frac{\hbar^2}{2m_h} \nabla^2_h - \frac{e^2}{\varepsilon r_{eh}} = \]

\[ -\frac{\hbar^2}{2M} \nabla^2_R - \frac{\hbar^2}{2\mu} \nabla^2_\rho - \frac{e^2}{\varepsilon \rho} \]

\[ \vec{R} = \vec{r}_e + \vec{r}_h \quad M = m_e + m_h \]

\[ \vec{\rho} = \vec{r}_e - \vec{r}_h \quad \mu = \frac{m_e \cdot m_h}{m_e + m_h} \]
Exciton wave functions and Schrödinger equation

\[ \Psi(\tilde{R}, \tilde{\rho}) = \frac{1}{L^{d/2}} e^{i\tilde{K}\tilde{R}} \varphi(\tilde{\rho}) \]

\[ \left\{ -\frac{\hbar^2}{2\mu\rho^{d-1}} \frac{\partial}{\partial \rho} [\rho^{d-1} \frac{\partial}{\partial \rho}] + \frac{l^2}{2\mu\rho^2} - \frac{e^2}{\varepsilon\rho} \right\} \varphi(\rho, \vartheta) = (E - E_g) \varphi(\rho, \vartheta) \]
Exciton parameters

- Exciton energies and radii

\[ E_n = E_g - \frac{E_e}{(n + \frac{d - 3}{2})^2} \]

\[ a_n = (n + \frac{d - 3}{2})^2 a_e \]

- \( E_e \) is the effective Rydberg constant and \( a_e \) is the effective Bohr radius:

\[ E_e = (\frac{\mu}{m_e \varepsilon}) \text{Ry} \]

\[ a_e = (\frac{m_e \varepsilon}{\mu}) a_B \]
Exciton parameters

• The exciton binding energy:

\[ E_b \equiv E_1 = \left( \frac{2}{d-1} \right)^2 E_e \]

• and the exciton radius:

\[ r_{ex} \equiv a_1 = \left( \frac{d-1}{2} \right)^2 a_e \]
Disorder

\[ H = H_{ex} + H_{dis} \]

\[ H_{dis} = \sum_{nm} \Delta_{nm} |n, f \rangle \langle m, f| \]

\[ H_{dis} = \sum_{n} \Delta_{n} |n, f \rangle \langle n, f| \]  

- Diagonal disorder
Impurity

\[ \Delta_n = \Delta \delta_{n,0} \]

\[ (E - H_{ex}) \psi = \Delta |0, f \rangle \langle 0, f| \psi \]

\[ \psi = (E - H_{ex})^{-1} \Delta |0, f \rangle \langle 0, f| \psi \]

- A single impurity
- the Schrödinger equation
- the formal solution
Impurity

\[ G = \frac{1}{E - H_{ex}} = \sum_k |k\rangle \frac{1}{E - E(k)} \langle k| \]

- Green’s operator

\[ \psi^f = \sum_n c_{fn} \varphi^1_n \prod_{m \neq n} \varphi^0_m \]

\[ c_{fn} = \Delta \cdot G_{n0} c_{f0} \]

\[ G_{nm} = \frac{1}{N} \sum_k \frac{e^{ik(\bar{n} - \bar{m})}}{E - E(k)} \]
Impurity

\[ G_{00} = \frac{1}{\Delta} \]

- the energy localized on the impurity, the local exciton

\[ G_{00} = \frac{1}{N} \sum_k \frac{1}{E - E(k)} = \int \frac{\rho(\varepsilon)}{E - \varepsilon} d\varepsilon \]

\[ \rho(\varepsilon) = \frac{1}{N} \sum_k \delta(\varepsilon - E(k)) \]

- the density of states
Impurity
Diagonal disorder of the ring-like structure
Anderson localization

• $\Delta_n$ is randomly in the energy interval 
  \{-W/2, W/2\} 
  $W_{cr}$, which is of the order of the exciton 
  bandwidth, determines the Anderson transition
Optical transitions

\[ \vec{P} = \sum_{n} \vec{P}_n \]

\[ \langle 0 | \vec{P} | k \rangle = \frac{1}{\sqrt{N}} \sum_{n\alpha} u_{\alpha \nu}(k) \mu_{n\alpha} e^{i\vec{k}\vec{r}_{n\alpha}} \]

\[ \mu_{n\alpha} = \langle n\alpha, 0 | \vec{P}_{n\alpha} | n\alpha, f \rangle \]

- Dipole moment
- Transition dipole moment
Optical transitions

- Different Davydov components correspond to different transition frequencies

\[
\bar{\mu}_\nu(k) = \frac{1}{\sqrt{N}} \sum_\alpha u_{\alpha \nu}(k) e^{i k \rho_\alpha} \sum_n \hat{\mu}_{n \alpha} e^{i k \hat{n}}
\]

\[
\bar{r}_{n \alpha} = \hat{n} + \hat{\rho}_\alpha
\]
Optical transitions

- When \( \vec{\mu}_{n, \alpha} = \vec{\mu}_{\alpha} \)

\[
\vec{\mu}_v (k) = F(k) \sum_\alpha u_{\alpha v} (k) e^{i k \vec{p}_\alpha} \vec{\mu}_{\alpha}
\]

\[
F(k) = \frac{1}{\sqrt{N}} \sum_n e^{i k \vec{n}} = \sqrt{N} \delta_{\vec{k}, \vec{0}}
\]

- Selection rule
Optical transitions

\[ u_{\alpha \nu}(k) = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} \]

- Two equivalent molecules per unit cell with \( k \)-vectors perpendicular to the plane

\[ \tilde{\mu}_\nu = \sqrt{\frac{N}{2}} (\tilde{\mu}_{\alpha=2} - (-1)^\nu \tilde{\mu}_{\alpha=1}) \]
Optical transitions

- \( j=0 \) corresponds to \( k=0 \)
Optical transitions

\[ \mu_n = \mu \cos(\gamma n) \]

\[ \gamma = \frac{2\pi}{N} \]

- For cyclic molecular aggregate
Optical transitions

\[ \mu(k) = \frac{1}{\sqrt{N}} \sum_n \mu_n e^{ikn} = \frac{1}{\sqrt{N}} \sum_n \mu \cos(\gamma n) e^{ikn} = \frac{\mu}{2} (F_+(k) + F_-(k)) \]

\[ F_{\pm}(k) = \frac{1}{\sqrt{N}} \sum_n e^{i(k \pm \gamma)n} = \sqrt{N} \delta_{k, \pm \gamma} \]
Optical transitions

\[
\mu(j) = \mu \sqrt{\frac{2}{N+1}} \sum_{n=0}^{N+1} \sin\left(\frac{\pi j n}{N+1}\right)
\]

- Linear molecular aggregate

\[
\mu(j) = \mu \sqrt{\frac{2}{N+1}} \cot\left(\frac{\pi j}{N+1}\right)
\]

- Leading to
- when \( j \) is odd and
- when \( j \) is even
- \( j=1 \) contains 81% of the oscillator strength when \( N \gg 1 \)

\[
\mu(j) = 0
\]
Optical transitions

\[ c_{fn} = \Delta \cdot G_{n0} c_{f0} \quad \text{• for the local exciton} \]

\[ G_{nm} = \frac{1}{N} \sum_k e^{ik(\bar{n}-\bar{m})} \]

\[ \tilde{\mu}_{loc} = \frac{\tilde{\mu} \Delta c_{f0}}{\sqrt{N}} \sum_k \frac{F(k)}{E - E(k)} = \frac{\tilde{\mu} \Delta c_{f0}}{E - E(0)} \]
Optical transitions

\[ \sum_{n} \left| c_{fn} \right|^2 = 1 \]

- normalization of the wavefunction

\[ \left| \Delta \right|^2 \left| c_{fn} \right|^2 = \frac{1}{\sum_{n} \left| G_{n0} \right|^2} \]

- taking into account that

\[ G_{00} = \frac{1}{\Delta} \]
Optical transitions

\[ |c_{f0}|^2 = \frac{1}{|\Delta|^2} \left| \frac{\partial G_{00}}{\partial E} \right|^{-1} = \left| \frac{d}{dE} \frac{1}{G_{00}} \right|^{-1} = \frac{dE}{d\Delta} \]

• The dipole strength

\[ D_{loc} = d \frac{|\Delta|^2}{(E - E(0))^2} \cdot \frac{dE}{d\Delta} \]

• for a shallow local exciton in a 1D crystal

\[ D_{loc} = 2d \cdot \frac{E_{\text{band}}}{\Delta} \]

• giant oscillator strength – Rashba effect