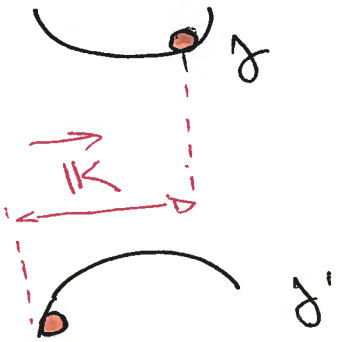
WANNIER EXCITONS

Lecture #11

EXCITON WAVE FUNCTION

$$|\vec{K}, \vec{r}\rangle = \sum_{\vec{k}_e + \vec{k}_h = \vec{K}} \Psi^{\vec{k}_e \vec{k}_h}_{jj'} \, |\vec{k}_{ej}; \vec{k}_{hj'}\rangle$$

- $\vec{K}$: EXCITON BLOCH WAVEVECTOR ASSOC. W/ CENTER OF MASS MOTION
- $\vec{r}$: RELATIVE COORDINATE
- $\Psi^{\vec{k}_e \vec{k}_h}_{jj'}$: CONSTANTS
- $|\vec{k}_{ej}; \vec{k}_{hj'}\rangle$: BLOCH STATE $1e + 1h^+$ EXCITATION



THE FOURIER TRANSFORM OF $\Psi^{\vec{k}_e \vec{k}_h}_{jj'}$ IS

$$\Phi(\vec{R}_{CM}, \vec{r}) \qquad \begin{cases} \vec{r} \equiv \vec{r}_e - \vec{r}_h \\ \vec{R}_{CM} = m_e \vec{r}_e + m_h \vec{r}_h / M \end{cases}$$

WHICH SATISFIES THE EFFECTIVE-MASS EQUATION:

$$H_{EMASS} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{\epsilon|\vec{r}_e - \vec{r}_h|}$$

PARABOLIC NON-DEGENERATE BANDS

NOTE: PROCEDURE IS MORE COMPLICATED FOR DEGENERATE BANDS - SET OF DIFF. EQS.

SOLUTIONS ARE OF THE FORM:

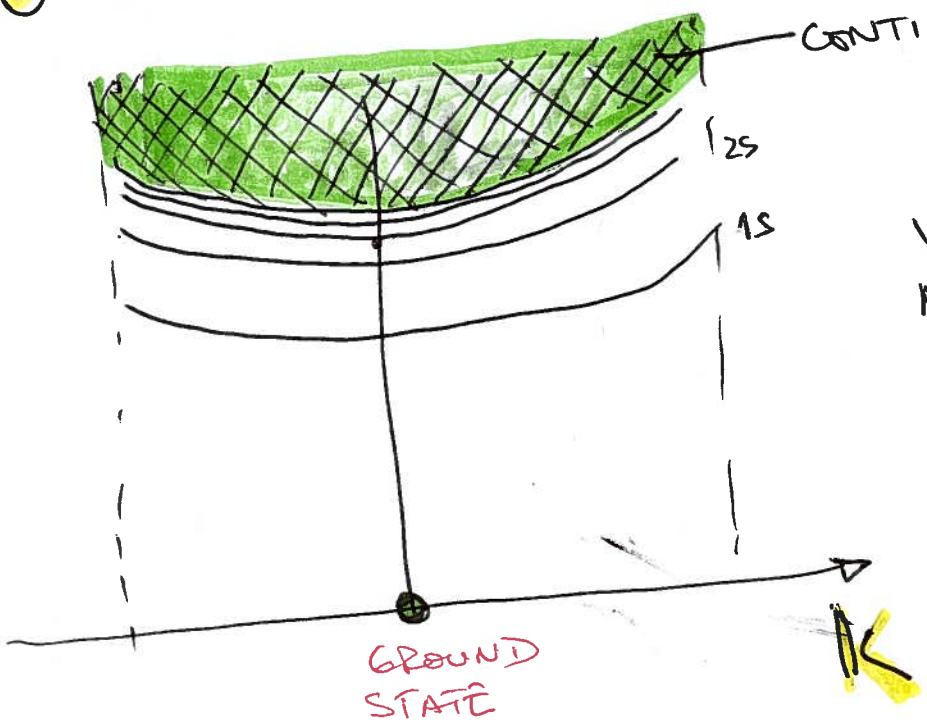
$$\Phi = \frac{1}{\sqrt{V_{CRYSTAL}}} e^{i \vec{K} \cdot \vec{R}_{CM}} \tilde{\phi}(\vec{r})$$

$\tilde{\phi}$: HYDROGENIC SOLUTIONS WITH $m^* = \frac{m_e m_h}{m_e + m_h}$

WITH EIGENENERGY

$$E = \frac{\hbar^2 K^2}{2(m_e + m_h)} + \mathcal{E}$$

$$\begin{cases} \mathcal{E} = -\dfrac{m^* e^4}{2\hbar^2 \epsilon^2} \dfrac{1}{n^2} & \text{BOUND STATES} \\ \mathcal{E} > 0 & \text{UNBOUND STATES} \end{cases}$$



VALID IN THE NEIGHBORHOOD OF $K \approx 0$

UNBOUND STATES:

$$\tilde{\phi}(\vec{r}) = e^{\pi/2\alpha}\,\left|\Gamma(l+1-i\alpha)\right|\,(2kr)^{l}\,Y_{l,m}(\theta,\varphi)$$

HYPERGEOMETRIC

$$\times\,\frac{e^{ibr}}{\sqrt{V_{CRYSTAL}}}\,\frac{F(-i\alpha+l+1;\,2l+2;\,-2ibr)}{(2l+1)!}$$

RUTHERDORF PROBLEM

$$\epsilon = \frac{\hbar^2 k^2}{2m^*} \qquad \alpha^2 = \frac{m^* e^4}{2\hbar^2\epsilon^2}\,\frac{1}{\epsilon}$$

CALCULATE MATRIX ELEMENTS FOR OPTICAL TRANSITIONS:

$$\vec{P}\cdot\vec{A} \propto \vec{P}\cdot\vec{A}_0$$

ELECTRIC-DIPOLE APPROXIMATION

$$\langle \vec{K}, \vec{r}\,|\,\vec{P}\cdot\vec{A}_0\,|\,0\rangle =$$

electron transition

$$= \sum_{\substack{k_e+k_h=K \\ JJ'}} \Psi_{k_e k_h} \left\langle \psi_{k_e;J}\left|-i\hbar\vec{\nabla}\right|\psi_{k_h;J'}\right\rangle \cdot\vec{A}_0$$

ASSUME THAT

$$\langle .. | -i\hbar\vec{\nabla} | .. \rangle$$

DEPENDS WEAKLY ON $\vec{k}_e$ (IT MAINLY OPERATES ON PERIODIC PART OF BLOCH STATE)

$$\langle k, \vec{r} | \vec{p}\cdot\vec{A}_0 | 0 \rangle \approx \langle \psi_{k_e} | -i\hbar\vec{\nabla} | \psi_{-k_h} \rangle$$

@ $k_e = 0$

{ SAME AS FOR INTERBAND TRANSITIONS

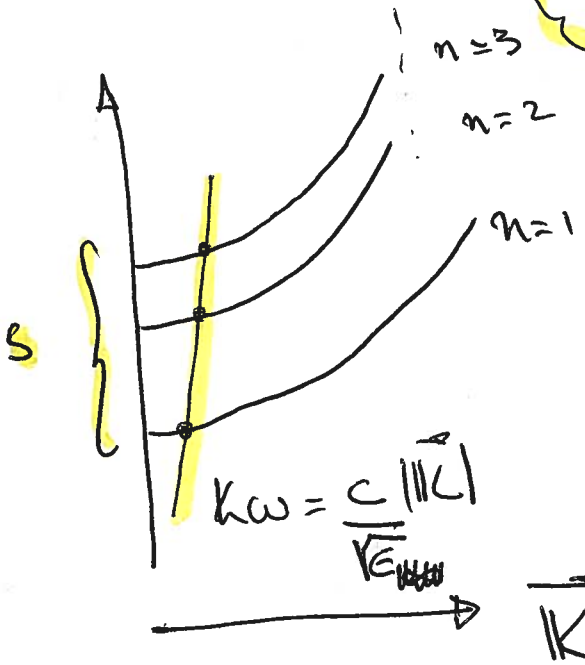
$$\times \sum_{k_e} \psi_{k_e, -k_h}$$

$\phi(\vec{r}=0)$

HENCE, ONLY S-STATES COUPLE TO LIGHT !

$$|\phi_n|^2 \propto \frac{1}{n^3}$$

- BOUND STATES



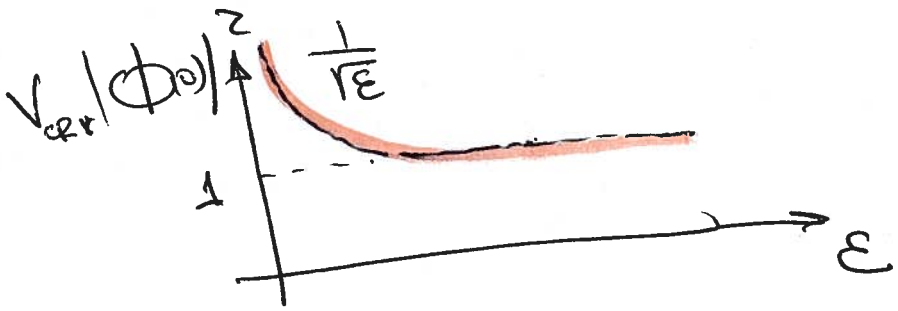
~~BOUND~~ EXCITONS @ $\vec{k}$ COUPLE ONLY TO $\vec{k}$ PHOTON

- COUPLED OSCILLATORS

FOR UNBOUND STATES

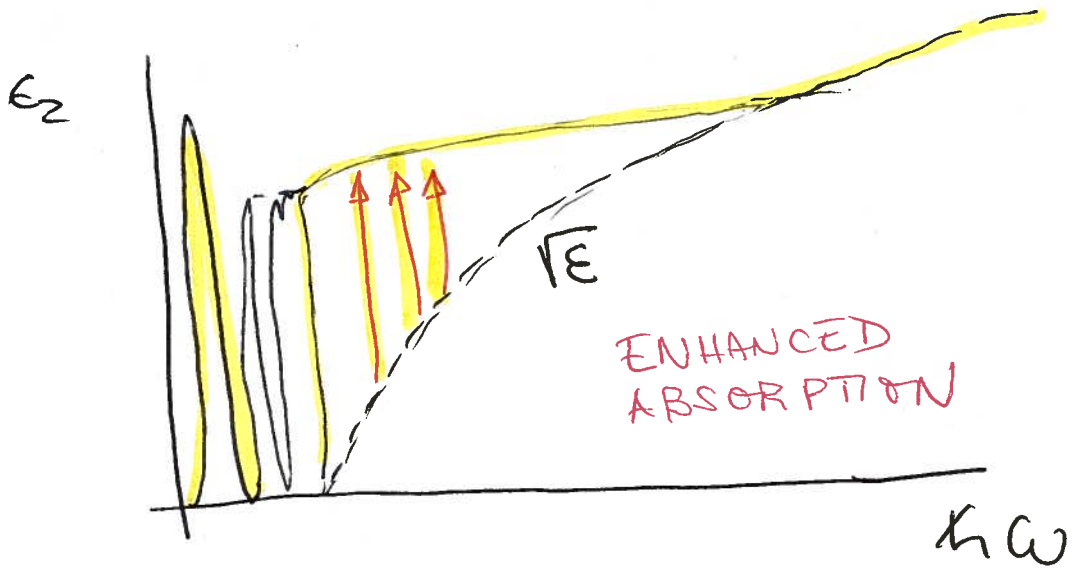
$$|\phi(0)|^2 = \frac{\pi\alpha\, e^{\pi\alpha}}{V_{CRYSTAL}\, \sinh(\pi\alpha)}$$

$$\alpha^2 = \frac{m^* e^4}{2\hbar^2\epsilon^2}\,\frac{1}{\mathcal{E}} \rightarrow \text{energy}$$



LARGE ENHANCEMENT OF ABSORPTION NEAR THE EDGE

$$K \propto |\phi(0)|^2 N_{DOS}$$

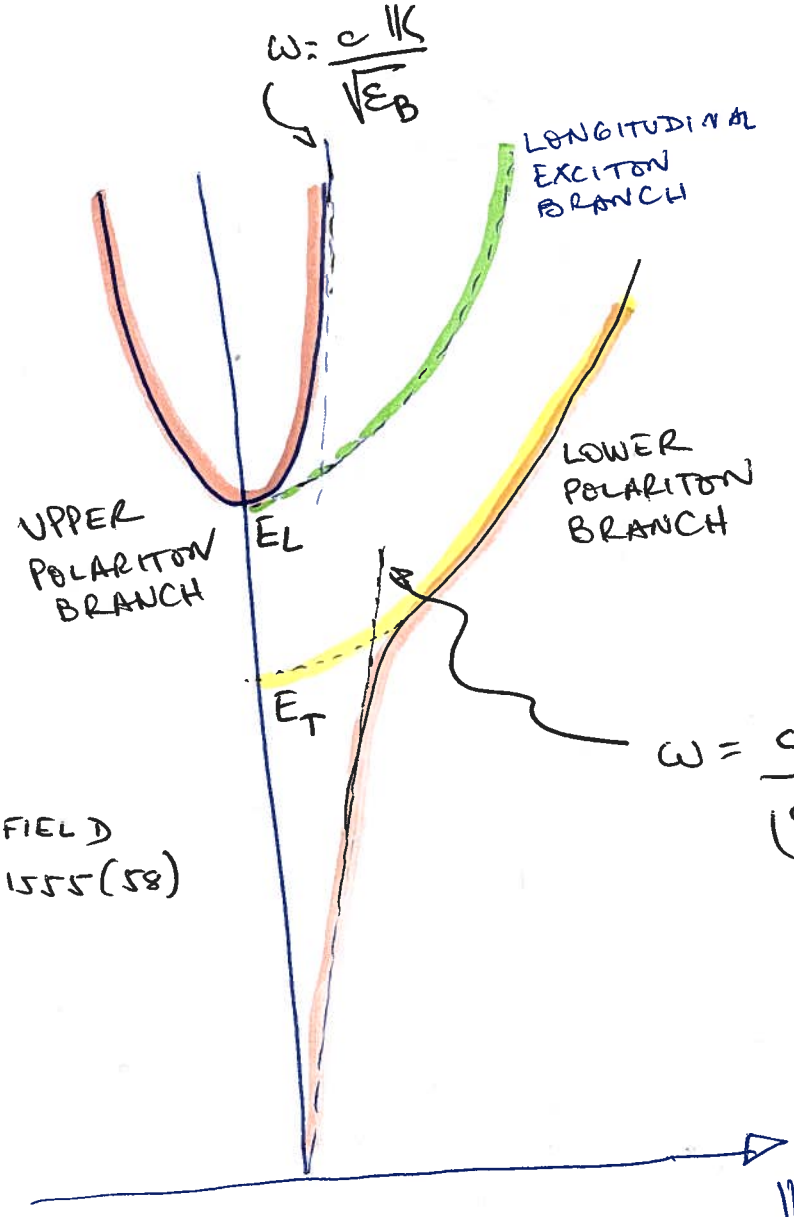


CONSIDER ONLY IS STATE DEFINED BY $\omega_{1S}(\vec{K})$. THEN, USING SAME PROCEDURE USED FOR LATTICE VIBRATIONS

SPATIAL DISPERSION

$$\varepsilon(\omega, \vec{K}) = \frac{c^2 K^2}{\omega^2(\vec{K})} = \varepsilon_B + \frac{4\pi\alpha\omega_{1S}^2(\vec{K})}{\omega_{1S}^2(\vec{K}) - \omega^2(\vec{K})}$$

PLAYS ROLE OF ε_∞ IN LATTICE



	$E_L - E_T$ (meV)
GaAs	0.08
CdS	2-3
GaSe	1.5
PbI_2	7

JJ HOPFIELD PR 112, 1555 (58)

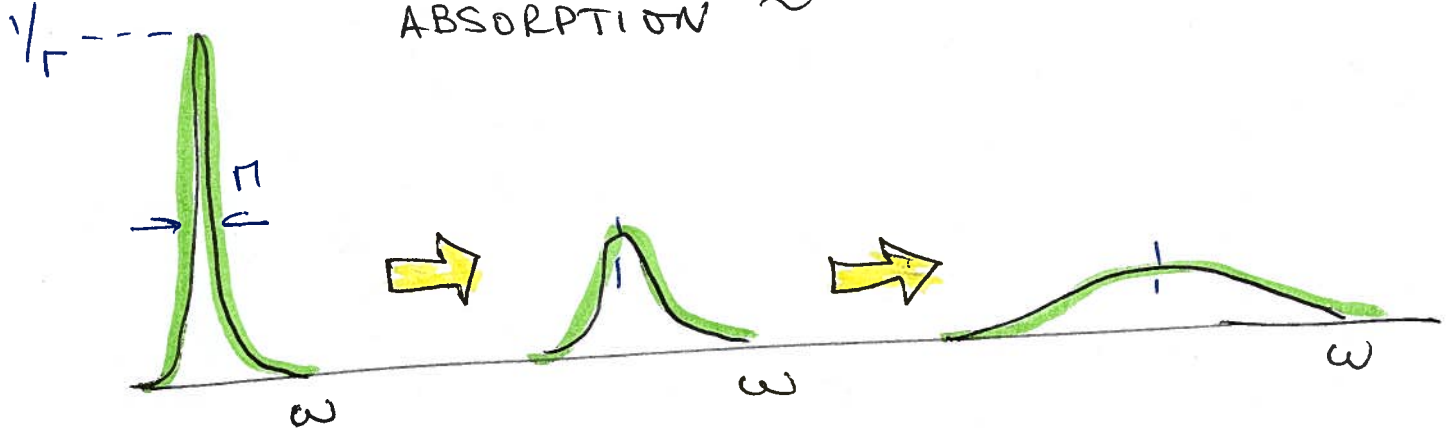
EXCITON POLARITONS

NOTE: ABOVE E_L, THERE ARE 2 STATES FOR 1 ENERGY

CLASSICAL VS. POLARITON ABSORPTION

CLASSICAL:

INTEGRATED ABSORPTION $\simeq$ CONSTANT



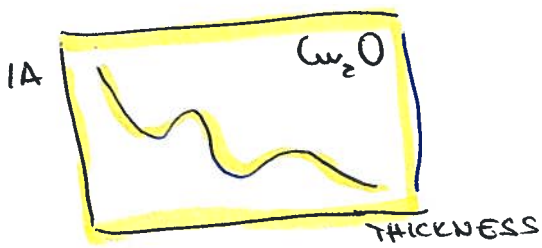
SINCE

$$\epsilon_1 - \epsilon_\infty = \frac{2}{\pi} \int_0^\infty \frac{\epsilon_2(\omega')\,\omega'}{\omega'^2 - \omega^2}\, d\omega'$$

$$\Rightarrow \boxed{8 \int_0^\infty \frac{\sigma_1(\omega)}{\omega^2}\, d\omega \equiv \epsilon_0 - \epsilon_\infty}$$

→ INDEPENDENT OF Γ

POLARITONS



INTEGRATED ABSORPTION DEPENDS ON THICKNESS

$1/\delta$

ON Γ

CONTROVERSIAL FOR GaSe
PRL 36, 1086 (76)
PRL 39, 671 (77)

- RELATIONSHIP BETWEEN $\vec{P}$ & $\vec{E}$ CANNOT BE LOCAL (IF IT WERE, KK WOULD APPLY)

$$\varepsilon(K,\omega) = \varepsilon_b + \frac{4\pi\alpha\,\omega_{is}^2(K)}{\omega_{is}^2(K) - \omega^2}$$

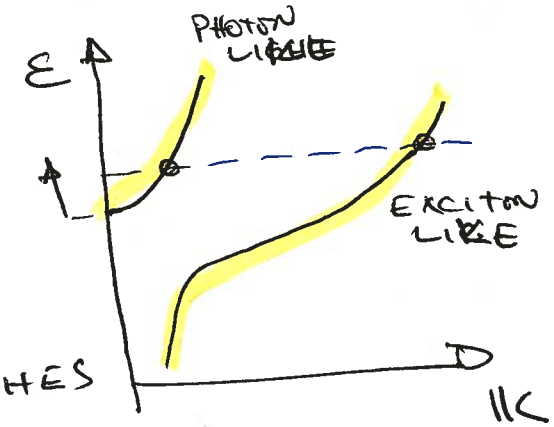
NON-LOCAL

$$\hbar\omega_{is} = \frac{\hbar^2 K^2}{2\,(m_e + m_h)} + \Delta - E_B$$

DETAILED DISCUSSION BEYOND SCOPE OF COURSE.

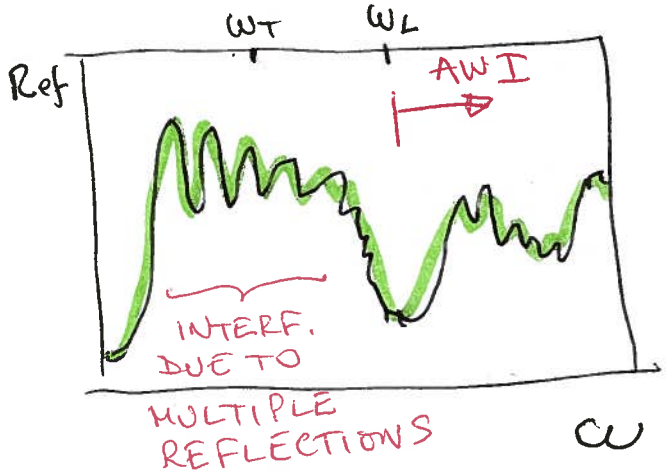
- NEED ADDIT. BOUNDARY CONDITIONS (ABC)

TWO BRANCHES ABOVE E_L !
THIS LEADS TO "ADITIONAL WAVE INTERFERENCES" IF THICKNESS < DECAY LENGTH OF BOTH BRANCHES ($\lesssim 20\mu m$)



GENERAL ABC

$$\vec{P} + \lambda \frac{d\vec{P}}{dz}\bigg|_{z=0} = 0$$



FRENKEL EXCITONS

WRITE FOR GROUND STATE (ANSATZ)

CHARGE TRANSFER NOT INCLUDED

$$\Phi_0 = \hat{A}\{\phi_{0,R_1}(\vec{r}_1)\cdots\phi_{0,R_N}(\vec{r}_N)\}$$

ANTISYMM. OPERATOR

EXCITATION OF ATOM @ $\vec{R}_i$ TO LEVEL n

$$\Phi_{n,R_i} = \hat{A}\{\Phi_{0,R_1}\cdots\Phi_{n,R_i}\cdots\Phi_{0,R_N}\}$$

FROM HERE TO BLOCH STATES, USE

$$\Phi_n(\vec{k}) = \frac{1}{\sqrt{N}}\sum_{R_i} e^{i\,k\cdot R_i}\Phi_{n,R_i}$$

ONE SINGLE ATOM EXCITED TO LEVEL "n"

$$E_n = \langle\Phi_n|\hat{H}_0|\Phi_n\rangle =$$

$$= E_{0n} + \sum_{R_i} e^{i\,k\cdot R_i} V^n_{R_i,0}$$

SIMILAR TO TIGHT BINDING

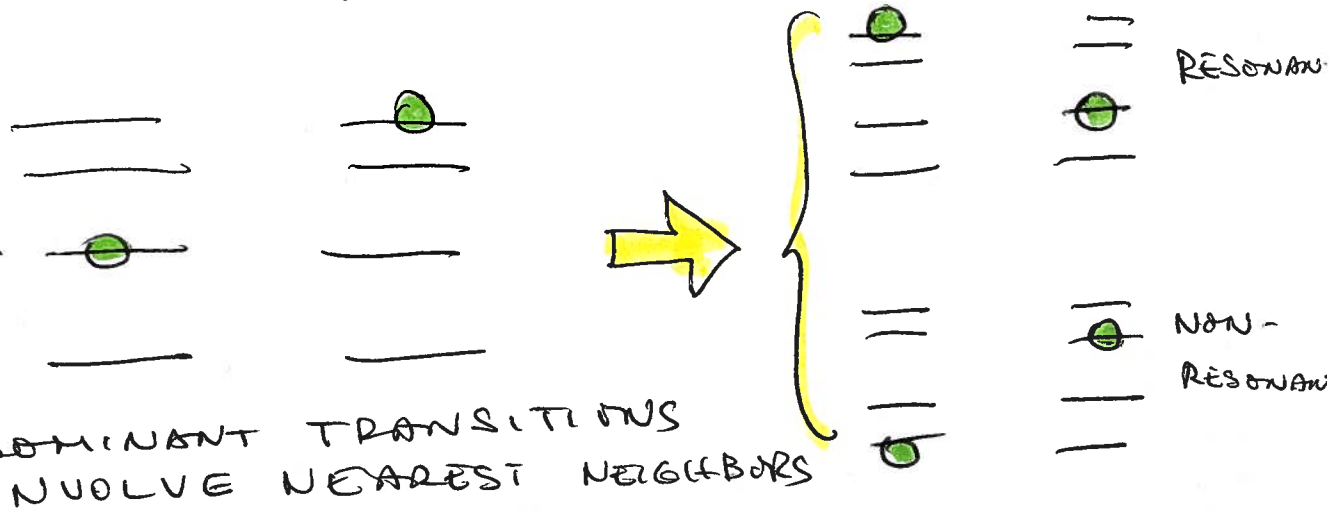
FOURIER EXPANSION OF ENERGY

FORMALLY, ONE CAN USE THE FOLLOWING EFFECTIVE HAMILTONIAN:

$$\hat{H} = \sum_i \hat{H}_{IR_i} + \sum_{\substack{nm \\ ij \\ n'm'}} V^{nm}_{IR_i IR_j n'm'} \left| \phi^{m'}_{IR_i} \phi^{n'}_{IR_j} \right\rangle \left\langle \phi^{m}_{IR_i} \phi^{n}_{IR_j} \right|$$

WHERE

$$\hat{H}_{IR_i} \left| \phi^{(n)}_{IR_i} \right\rangle = \varepsilon_n \left| \phi^{(n)}_{IR_i} \right\rangle$$



DOMINANT TRANSITIONS INVOLVE NEAREST NEIGHBORS

LOWEST-LYING $\begin{cases} m = 0, 1 \\ n = 0, 1 \end{cases}$

L-T SPLITTING - FRENKEL EXCITONS

CONSIDER S-LIKE GROUND STATE

+ EXCITED P-LIKE STATES

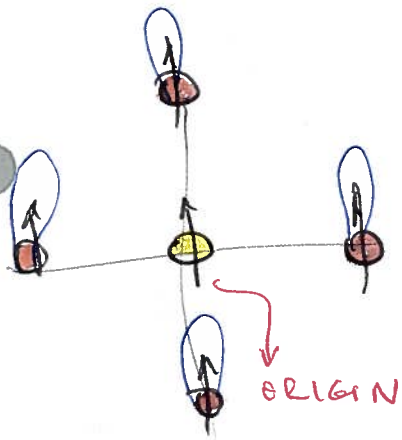
VAN DER WAALS (DIPOLE - DIPOLE) INTERACTION

CLASSICALLY,

$$H_{DD} = \frac{-\mu_0}{4\pi R^5}\left[(\hat{\mu}^A_{m0}\cdot\hat{\mu}^B_{0m'})R^2 - 3(\hat{\mu}^A_{m0}\cdot\vec{R})(\hat{\mu}^B_{0m'}\cdot\vec{R})\right]$$

$$\mu_{m0} = \frac{e}{\sqrt{2}}\langle\phi_m|\vec{r}|\phi_0\rangle \qquad \mu_{0m'} = \frac{e}{\sqrt{2}}\langle\phi_0|\vec{r}|\phi_{m'}\rangle$$

CONSIDER AN ARRAY OF DIPOLES, ALL ORIENTED ALONG THE SAME DIRECTION



CALCULATE

$$\sum_{i\neq 0} e^{i\vec{k}\cdot\vec{R}_i}\,\frac{\mu^2 R_i^2 - 3(\vec{\mu}\cdot\vec{R}_i)^2}{R_i^5}$$

- SLOWLY CONVERGING LATTICE SUM THAT IS SINGULAR @ $k=0$, i.e., $\sum$ DEPENDS ON ANGLE BETWEEN $\vec{k}$ & $\vec{\mu}$

- NOTE: FOR SIMPLE CUBIC LATTICE

$$\sum_{NN} \mu^2 R_i^2 - 3(\vec{\mu}\cdot\vec{R}_i)^2 = 0$$

CONSIDER TWO CASES:

1. $\vec{k} \perp \vec{\mu}$ PARALLEL TO $\hat{z}$

$$\Rightarrow \Sigma_{\parallel} \approx \frac{2\pi\mu^2}{a_L^3} \int_0^{\pi} e^{ikr\cos\theta} \frac{(1-3\cos^2\theta)}{r} \sin\theta \, d\theta \, dr$$

2. $\vec{k} \parallel \hat{z}$ BUT $\vec{\mu} \parallel \hat{x}$

$$\Rightarrow \Sigma_{\perp} \approx \frac{\mu^2}{a_L^3} \int_0^{\pi} e^{ikr\cos\theta} \frac{(1-3\sin^2\theta\cos^2\varphi)}{r} \sin\theta \, d\theta \, d\varphi \, dr$$

$$\equiv \frac{\mu^2}{a_L^3} \int_0^{\pi} e^{ikr\cos\theta} \frac{(2\pi - 3\sin^2\theta\,\pi)}{r} \sin\theta \, d\theta \, dr$$

$$\equiv 2\pi\frac{\mu^2}{a_L^3} \int_0^{\pi} e^{ikr\cos\theta} \underbrace{\left(1 - \frac{3}{2}\sin^2\theta\right)}_{-\frac{1}{2}(1-3\cos^2\theta)} \frac{\sin\theta \, d\theta \, dr}{r}$$

Phys. Rev. 99, 1128

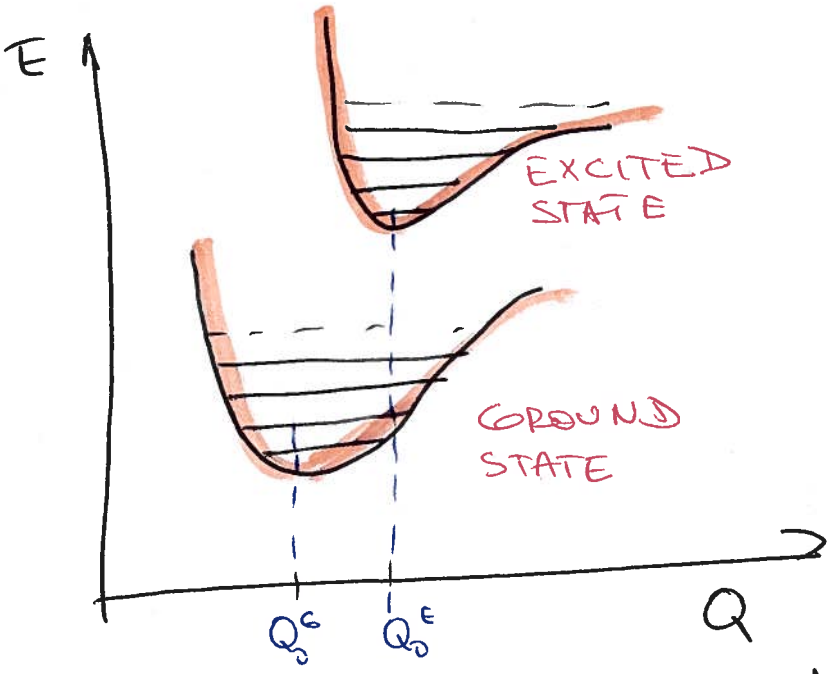
$$\Sigma_{\perp} \equiv -\frac{1}{2}\Sigma_{\parallel}$$

{ SAME ARGUMENTS APPLY TO OPTICALLY ACTIVE PHONONS

$$\begin{cases} \Sigma_{\parallel} = +\frac{8\pi}{3}\mu^2/a^3 \\ \Sigma_{\perp} = -4\pi/3\,\mu^2/a^3 \end{cases}$$

LATTICE CALCULATION:

- ELECTRON-PHONON COUPLING
MOLECULAR CRYSTALS



CONFIGURATION COORDINATE DIAGRAM

EM FIELD CAN COUPLE TO VIBRATIONAL MODES WITHIN SAME e-STATE OR BETWEEN "VIBRONIC" LEVELS ± e-STATES

BORN-OPPENHEIMER ADIABATIC APPROXIMATION

$$\hat{H} = \hat{T}_e + \hat{T}_N + U(\vec{r}_e, \vec{R}_N)$$

→ NUCLEI

$$\Psi = \psi(\vec{r}, \vec{R}) \varphi(\vec{R})$$

WHERE

$$\left[\hat{T}_e + U(\vec{r}_e, \vec{R})\right]\psi = V(\vec{R})\psi$$

FIX POSITIONS OF NUCLEI

GIVES MANY $V(\vec{r}_N)$'s

$$\left[T_N + V(\vec{R})\right]\varphi = E\varphi$$

CONSIDER TRANSITIONS

$$\psi_G(\vec{r}_e, Q)\,\varphi_G^{n_G}(Q) \rightarrow \psi_u(\vec{r}_e, Q)\,\varphi_u^{n_u}(Q)$$

THE RELEVANT MATRIX ELEMENT IS

$$\left| \langle n_u | \vec{\mu}_e(Q) | n_G \rangle \right|^2$$

WHERE $\vec{\mu}_e(Q) = \langle \psi_u | \vec{\mu}_e | \psi_G \rangle$

$\vec{\mu}_e$ → electron electric-dipole operator

CONSIDER THE EXPANSION

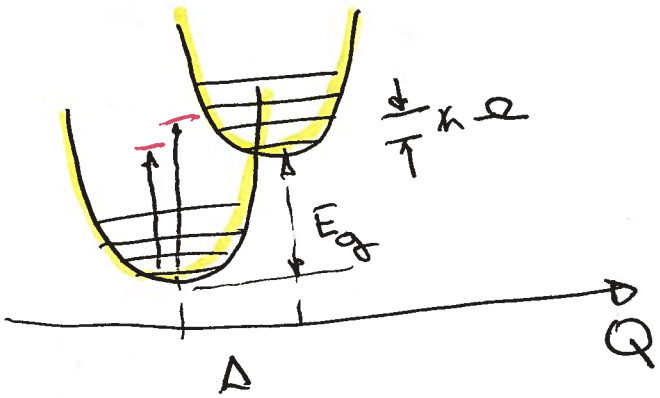
$$\vec{\mu}_e(Q) = \underbrace{\vec{\mu}_e(Q_0)}_{\text{VALUE @ EQUILIBRIUM}} + \sum_{Q_i} \left.\frac{\partial \vec{\mu}_e}{\partial Q_i}\right|_{Q_i = Q_i^{(e)}} Q_i + \cdots$$

FRANCK-CONDON APPROXIMATION $\vec{\mu}_e \approx \vec{\mu}_e(Q_0)$

See Sov. Phys. Usp. 18, 391
BEYOND FC APPROXIMATION

$$\Rightarrow \left| \langle 1 | \vec{\mu} | \rangle \right|^2 \approx \left| \langle \psi_u(Q_0) | \vec{\mu}_e | \psi_G(Q_0) \rangle \right|^2 \left| \langle n_u | n_G \rangle \right|^2$$

CONSIDER DISPLACED OSCILLATOR PROBLEM:



ABSORPTION (T=0K)

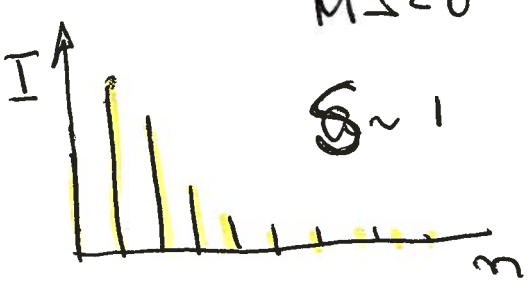
CAN BE CALCULATED EXACTLY

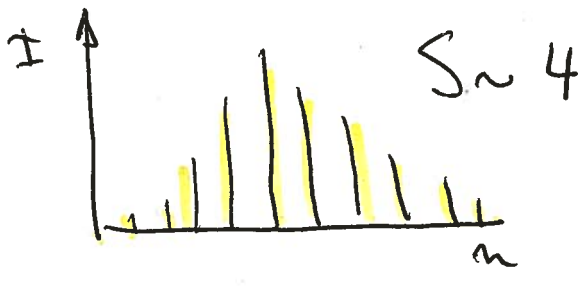
$$\sum_n \frac{|\langle \vec{\mu}_1 \rangle|^2 \; |\langle n_v | 0_6 \rangle|^2}{\left[\omega^2 - (E_g + \hbar\Omega n)^2\right]^2 + \omega^2 \Gamma_n^2}$$

$$|\langle n_v | 0_6 \rangle|^2 = e^{-S^2/2} \frac{(S^2/2)^n}{n!}$$

HUANG-RHYS MODEL (F-centers)

$$\Delta = \frac{S\hbar}{M\Omega_0} \quad \text{(displacement)}$$





WHAT IS THE HAMILTONIAN ?

$$H_e = E_0 |\psi_k\rangle\langle\psi_k|$$

TWO-LEVEL SYSTEM

$$H_{LATTICE} = \hbar\Omega_0 \underbrace{b^+ b}_{\#\ \text{PHONONS}}$$

$$H_{e-L} = \lambda |\psi_v\rangle\langle\psi_k| \underbrace{(b + b^+)}_{\text{DISPLACEMENT}}$$

- GOOD FOR SINGLE MOLECULES OR DEFECTS IN SOLIDS.
- TO DESCRIBE FRENKEL EXCITONS WE NEED TO CONSIDER INTERSITE TRANSFER. THUS

$$\hat{H} = \sum_i H_{R_i} + \sum_{ij} V_{R_i R_j} |\phi_{R_i}\phi_{R_j}\rangle\langle\phi_{R_i}\phi_{R_j}|$$

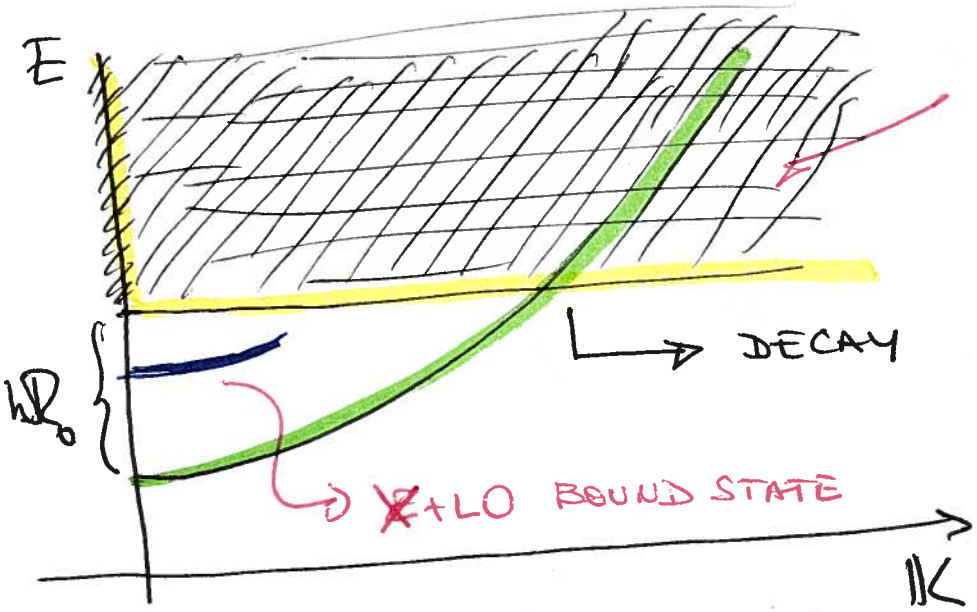
HOLSTEIN HAMILTONIAN
(ONE DIMENSIONAL MODEL)

PRB 66, 024305

e-phonon COUPLING
WANNIER EXCITONS

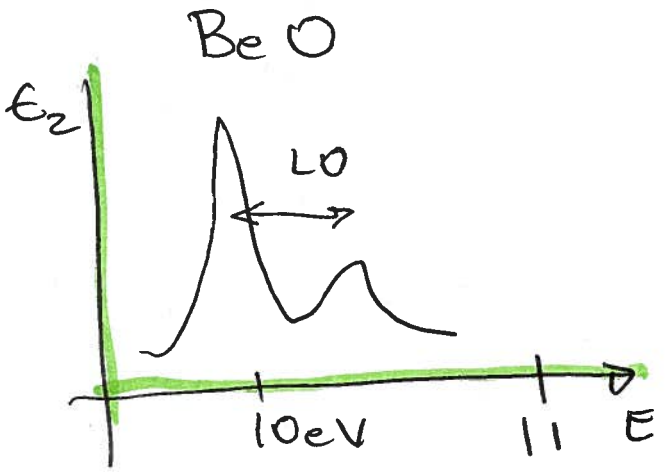
CONSIDER COUPLING TO LO PHONONS (THEY CARRY AN $\vec{E}$-FIELD) — ASSUME PHONON DISPERSION IS DISPERSIONLESS

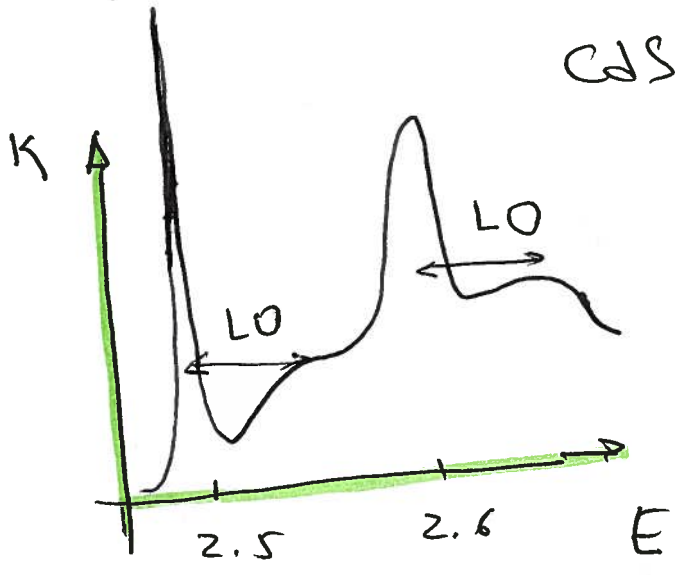
LOOKS LIKE MOLECULES !



1 EXCITON +1 LO PHONON CONTINUUM

CLOSELY RELATED TO POLARON PROBLEM





IMPORTANT IF $\epsilon_B \approx \hbar\Omega_{LO}$