Many-Body Perturbation Theory:
(3) More Examples and Further Issues

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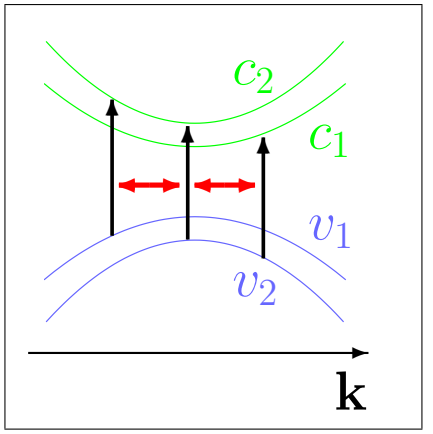
Fachbereich Physik
Universität Osnabrück

MASP, June 29, 2012

- Examples
- Interrelation with geometry

Coupled electron-hole excitations



- **Expansion of the excitations:** $|S\rangle = \sum_{v}^{\text{hole}} \sum_{c}^{\text{elec}} \sum_{\mathbf{k}} A^S_{vc\mathbf{k}} \, |vc\mathbf{k}\rangle$

$|vc\mathbf{k}\rangle := \hat{a}^\dagger_{v\mathbf{k}} \, \hat{b}^\dagger_{c\mathbf{k}+\mathbf{Q}} \, |0\rangle$ free electron-hole interband transition

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$E^{\text{QP}}_{v\mathbf{k}}$, $E^{\text{QP}}_{c\mathbf{k}+\mathbf{Q}}$ QP energies of the single-particle states

K^{eh} Electron-hole interaction

Ω_S Excitation energy

$\sim$ Single-excit. CI with W instead of v

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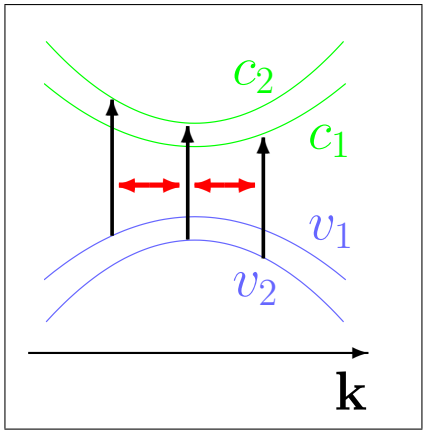

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K^{eh} Electr

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In here: Quasiparticle (QP) band-structure energies

$$G_1(E) = G_1^{(0)}(E) + G_1^{(0)}(E)\,\Sigma(E)\,G_1(E)$$

$\Sigma(E)$ = Self-energy operator

EOM for a single quasiparticle (= excited electron / hole):

$$\left\{-\nabla^2 + V_{\mathsf{ext}} + V^{[\rho]}_{\mathsf{Coul}} + \Sigma(E^{\mathsf{QP}}_{\mathsf{m}})\right\}\psi^{\mathsf{QP}}_{\mathsf{m}} = E^{\mathsf{QP}}_{\mathsf{m}}\psi^{\mathsf{QP}}_{\mathsf{m}}$$

$\Longrightarrow$ Quasiparticle wave functions $\psi^{\mathsf{QP}}_{\mathsf{m}}(\mathbf{r})$

Quasiparticle energies $E^{\mathsf{QP}}_{\mathsf{m}}$

$\mathrm{Re}(E^{\mathsf{QP}}_{\mathsf{m}})$ = Energy level / Band-structure energy

$\mathrm{Im}(E^{\mathsf{QP}}_{\mathsf{m}})$ = Spectral width γ_{m} / Inverse lifetime

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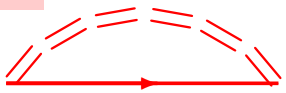
In here: GW Approximation (GWA) to $\Sigma(E)$

L. Hedin und S. Lundqvist, Sol. State Phys. 23, 1 (1969).

$$\Sigma \hat{=} G_1W + G_1WG_1WG_1 + \ldots$$

GWA: $\Sigma(1,2) = iG_1(1,2)W(1^+,2)$



$$\begin{aligned} W &= v + (W - v) \\ \Longrightarrow \Sigma &= iG_1v + iG_1(W - v) \\ &\equiv \Sigma_x^{\mathsf{HF}} + \Sigma_c \end{aligned}$$

Exchange + Correlation

Employ G_1 from DFT data:

$$G_1^{(0)}(\mathbf{x},\mathbf{x}',E) = \sum_m \frac{\psi_m^{\mathsf{DFT}}(\mathbf{x})\psi_m^{\mathsf{DFT}}(\mathbf{x}')^*}{E - E_m^{\mathsf{DFT}} \pm i0^+}$$

$\chi_0 = iG_1 \circ G_1$ **(Polarization)**

$\epsilon^{\mathsf{RPA}} = 1 - \chi_0 \circ v$ **(Diel. Func.)**

$W(1,2) = \int v(1,3)\epsilon^{-1}(3,2)d(3)$

(Screened Coulomb interaction)

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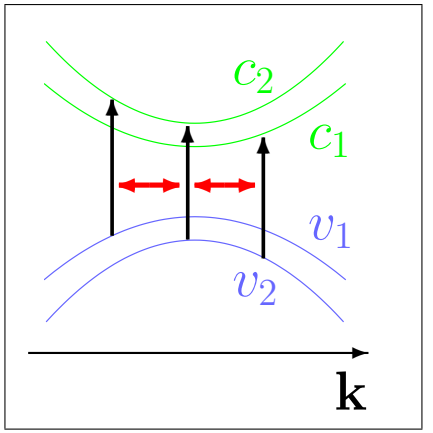

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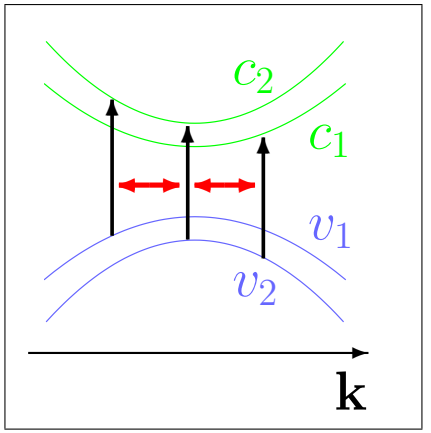

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In here: Electron-Hole Interaction K^{eh}

$$K^{eh}(12,34) = \frac{\delta[V_{\text{Coul}}(1)\delta(13) + \Sigma(13)]}{\delta G_1(42)}$$

$$\Sigma = iG_1W \text{ and } G_1 \frac{\delta W}{\delta G_1} \approx 0$$

$$\Longrightarrow K^{eh}(12,34) = -i\delta(13)\delta(2^-4)v(14) + i\delta(14)\delta(23)W(1^+3)$$

Repulsive exchange term (=:$K^{eh,x}$)

+ Attractive direct term (=:$K^{eh,d}$)

ıs

$$\rangle = \sum_v^{\text{hole}} \sum_c^{\text{elec}} \sum_{\mathbf{k}} A^S_{vc\mathbf{k}} |vc\mathbf{k}\rangle$$

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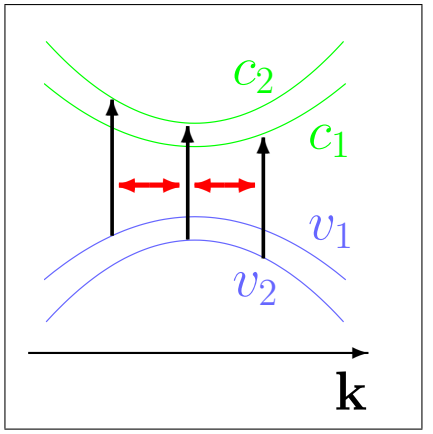


resp., |

$$\sum_{\mathbf{k}'} \langle vc\mathbf{k}|K^{eh}|v'c'\mathbf{k}'\rangle A^S_{v'c'\mathbf{k}'} = \Omega_S A^S_{vc\mathbf{k}}$$

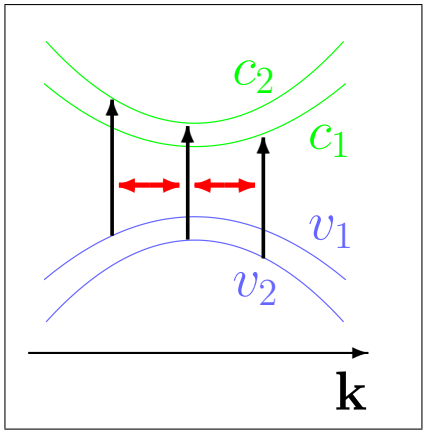
Single excit. CI

$$\langle vc\mathbf{k}|K^{eh}|v'c'\mathbf{k}'\rangle = \iint dxdx' \, \psi^*_{c\mathbf{k}+\mathbf{Q}}(\mathrm{x})\psi_{v\mathbf{k}}(\mathrm{x}) \, v(\mathbf{r},\mathbf{r}') \, \psi_{c'\mathbf{k}'+\mathbf{Q}}(\mathrm{x}')\psi^*_{v'\mathbf{k}'}(\mathrm{x}')$$

$$- \frac{i}{2\pi} \int d\omega e^{-i\omega 0^+} \iint dxdx' \, \psi^*_{c\mathbf{k}+\mathbf{Q}}(\mathrm{x})\psi_{c'\mathbf{k}'+\mathbf{Q}}(\mathrm{x}) \, W(\mathbf{r},\mathbf{r}',\omega) \, \psi_{v\mathbf{k}}(\mathrm{x}')\psi^*_{v'\mathbf{k}'}(\mathrm{x}')$$

$$\times \left[\frac{1}{\Omega_S - \omega - (E^{\text{QP}}_{c'\mathbf{k}'+\mathbf{Q}} - E^{\text{QP}}_{v\mathbf{k}}) + i0^+} + \frac{1}{\Omega_S + \omega - (E^{\text{QP}}_{c\mathbf{k}+\mathbf{Q}} - E^{\text{QP}}_{v'\mathbf{k}}) + i0^+} \right]$$

Coupled electron-hole excitations



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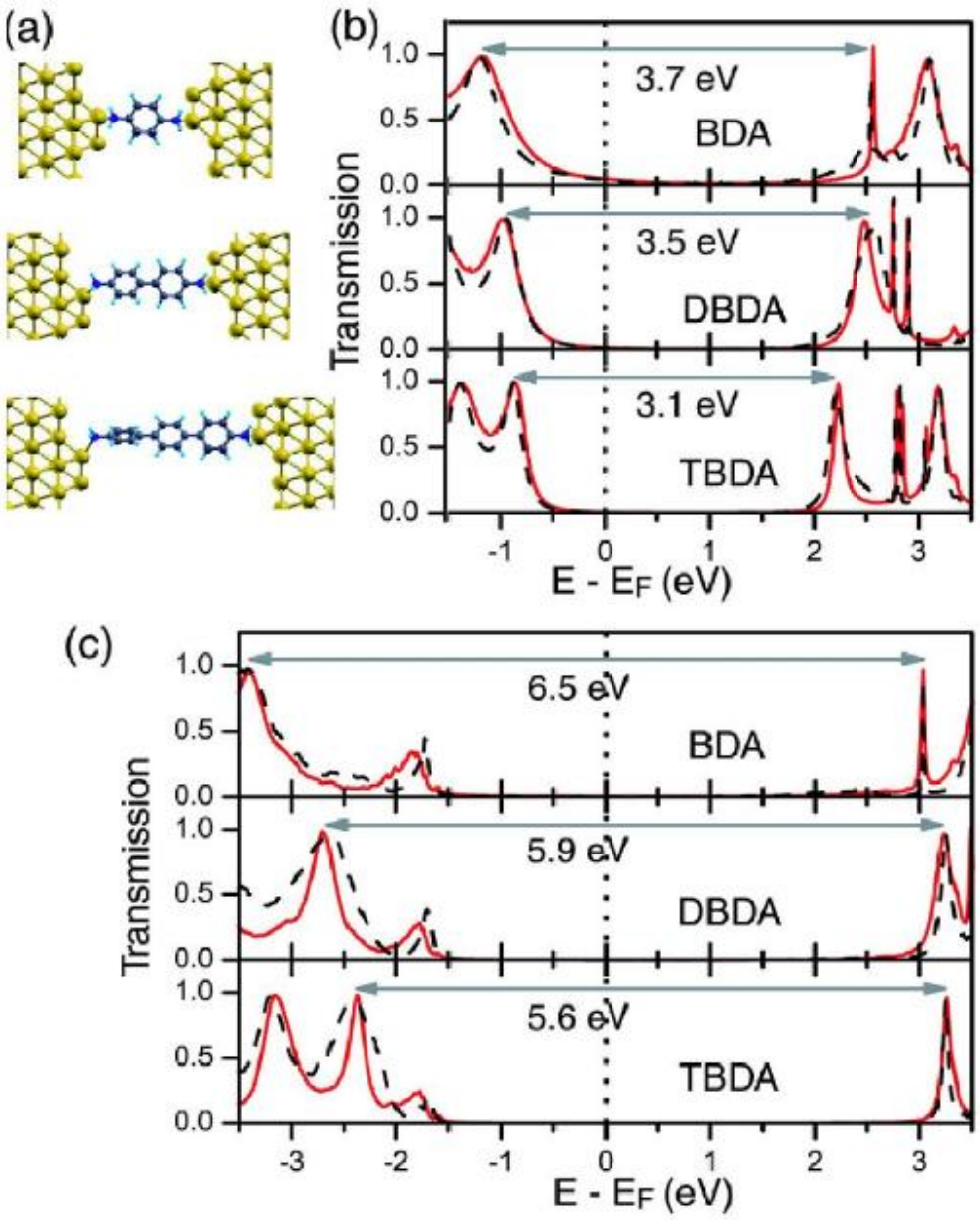
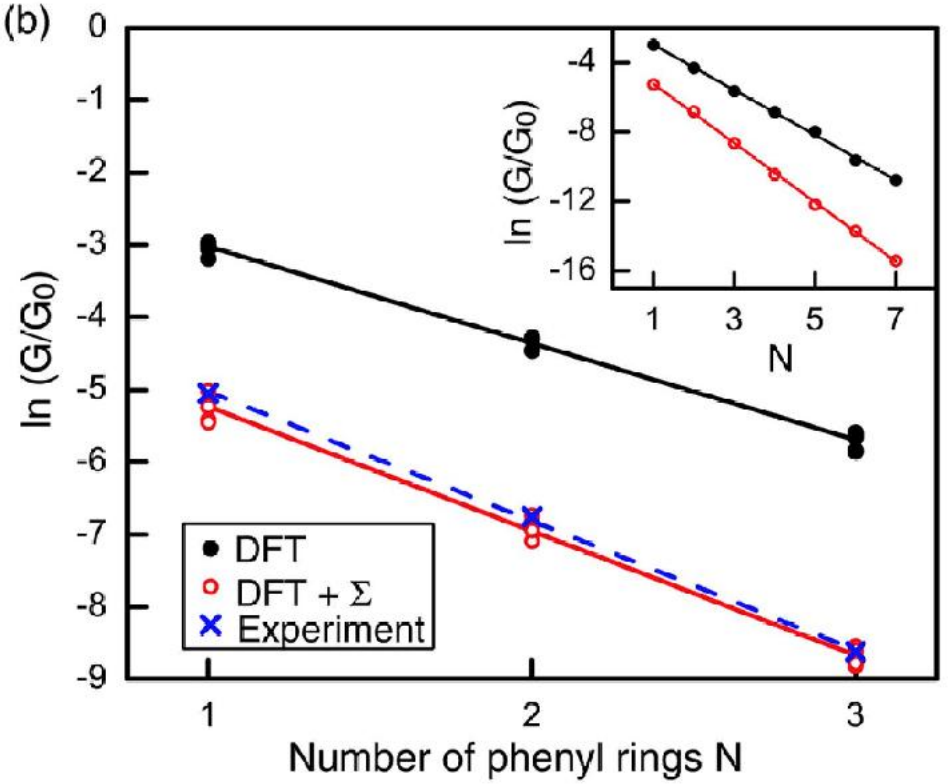
Relevance of molecular level alignment for electron conductance





- QP corrections move molecular states away from Fermi level
  $\Longrightarrow$ reduced transmission at E_F
- Include image-state effect in Σ !

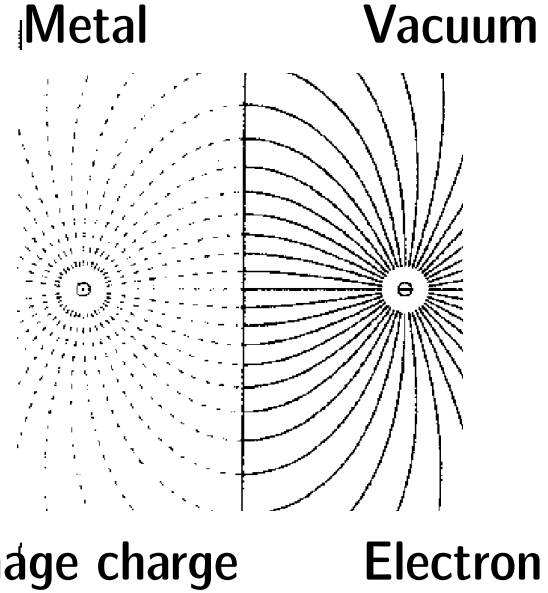
[S.Y. Quek, H.J. Choi, S.G. Louie, and J.B. Neaton, Nano Lett. 9, 3949 (2009).]

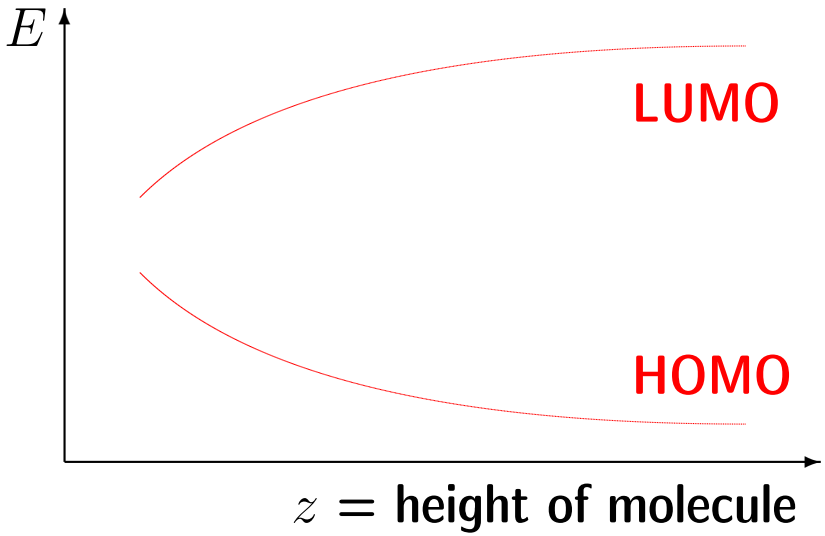
Image-Potential Effects

- Electron outside metal surface (at z)
  polarizes the metal substrate
  $\Longrightarrow$ Same field distribution as from an image charge

$\Longrightarrow$ attractive potential $V(z) = -\dfrac{e^2}{4z}$

- Modification of empty-state energies by $-\dfrac{e^2}{4z}$
- Opposite effect on occupied states: $+\dfrac{e^2}{4z}$
- Also valid in front of non-metals: $\pm\dfrac{\epsilon_0 - 1}{\epsilon_0 + 1}\dfrac{e^2}{4z}$
- Automatically included in GW self energy !





M. Rohlfing et al., PRL 91, 256802 (2003).
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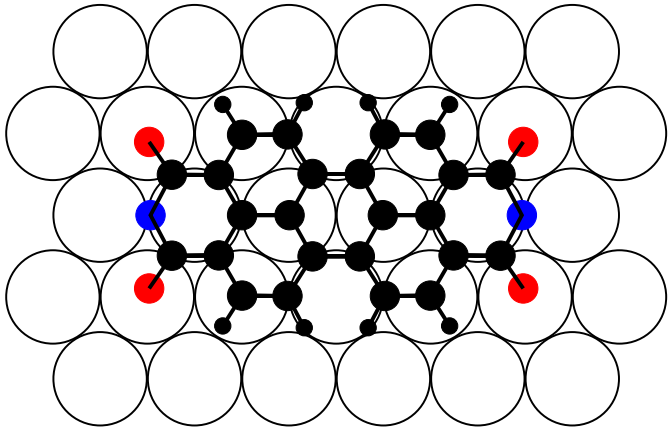
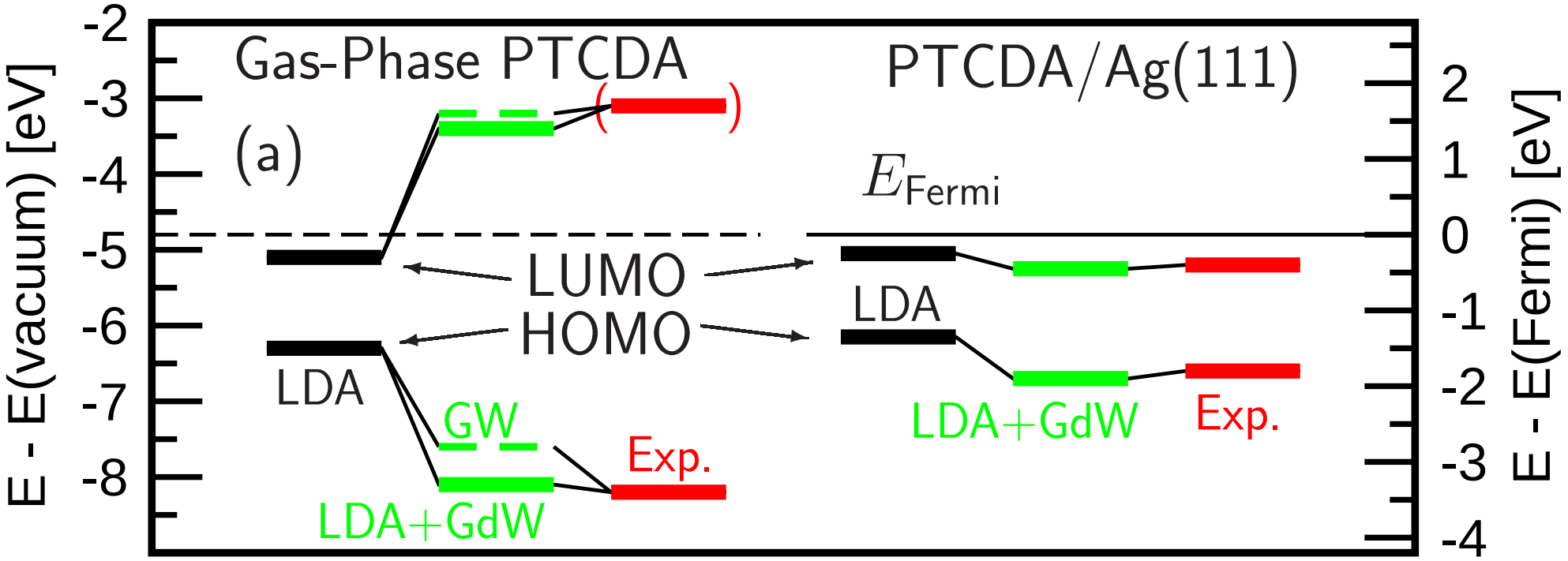
K.S. Thygesen and A. Rubio, PRL 102, 046802 (2009).
J.M. Garcia-Lastra and K.S. Thygesen, PRL 106, 187402 (2011).

PTCDA: electronic spectrum

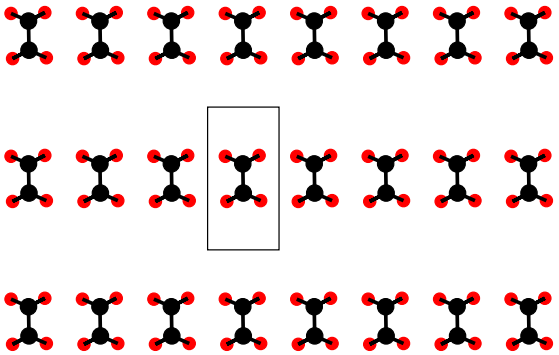


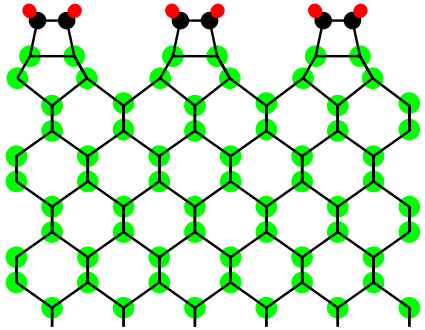


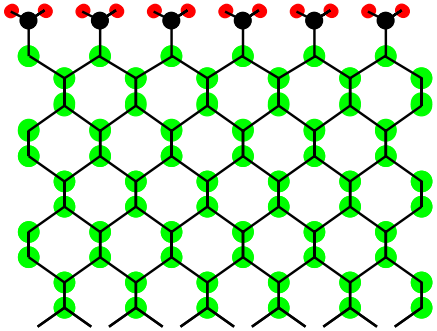
Metal surface reduces the fundamental gap

The C_2H_4:Si(001)-(2x1) surface

Top View:







C_2H_4: occupied molecular orbitals:

E_{vac}–23.4 eV	E_{vac}–18.7 eV	E_{vac}–15.7 eV	E_{vac}–14.3 eV	E_{vac}–12.5 eV	E_{vac}–10.2 eV (HOMO)
Top View					
Side View					
PDOS on Si					

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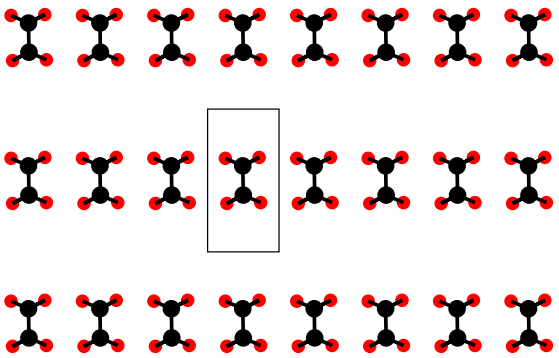
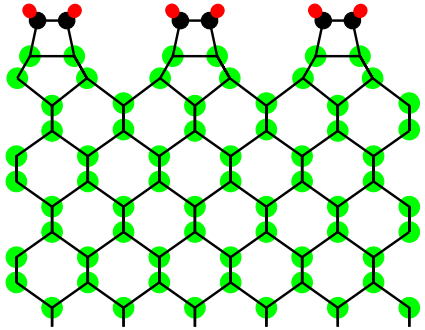
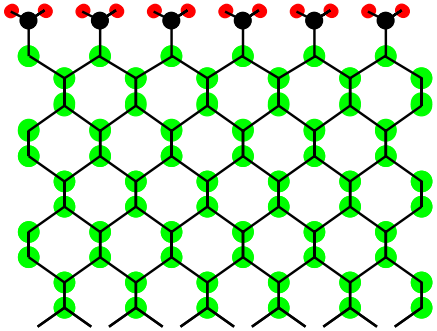






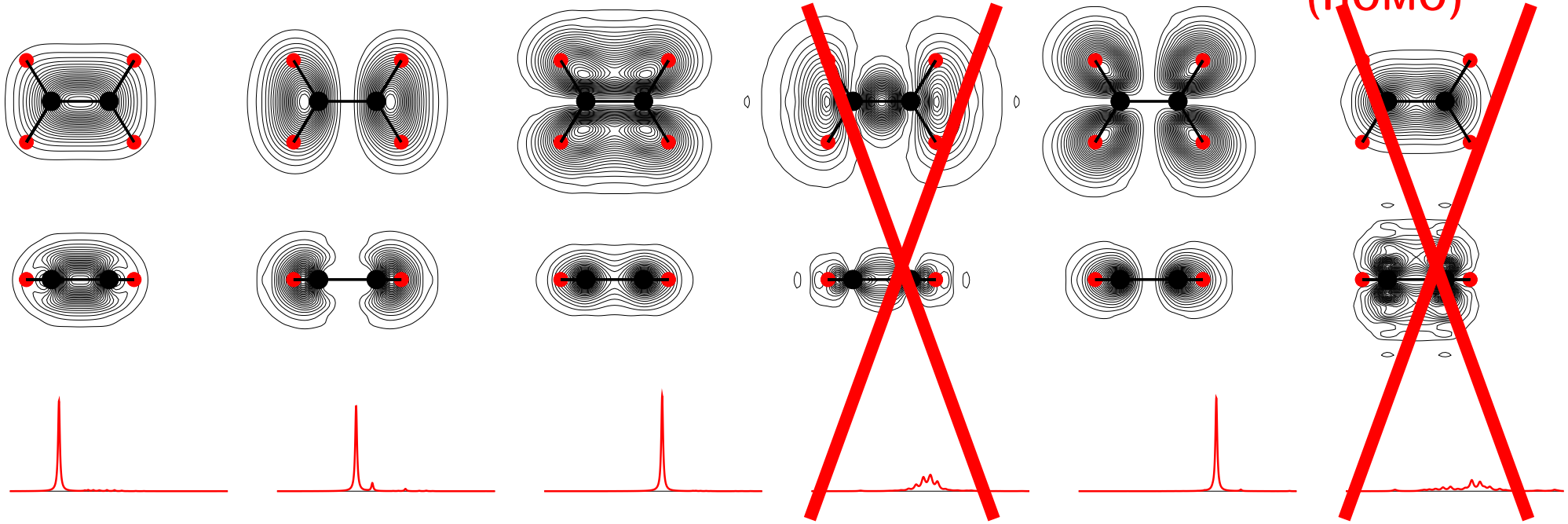
C_2H_4: occupied molecular orbitals:

E_{vac}–23.4 eV | E_{vac}–18.7 eV | E_{vac}–15.7 eV | E_{vac}–14.3 eV | E_{vac}–12.5 eV | E_{vac}–10.2 eV (HOMO)

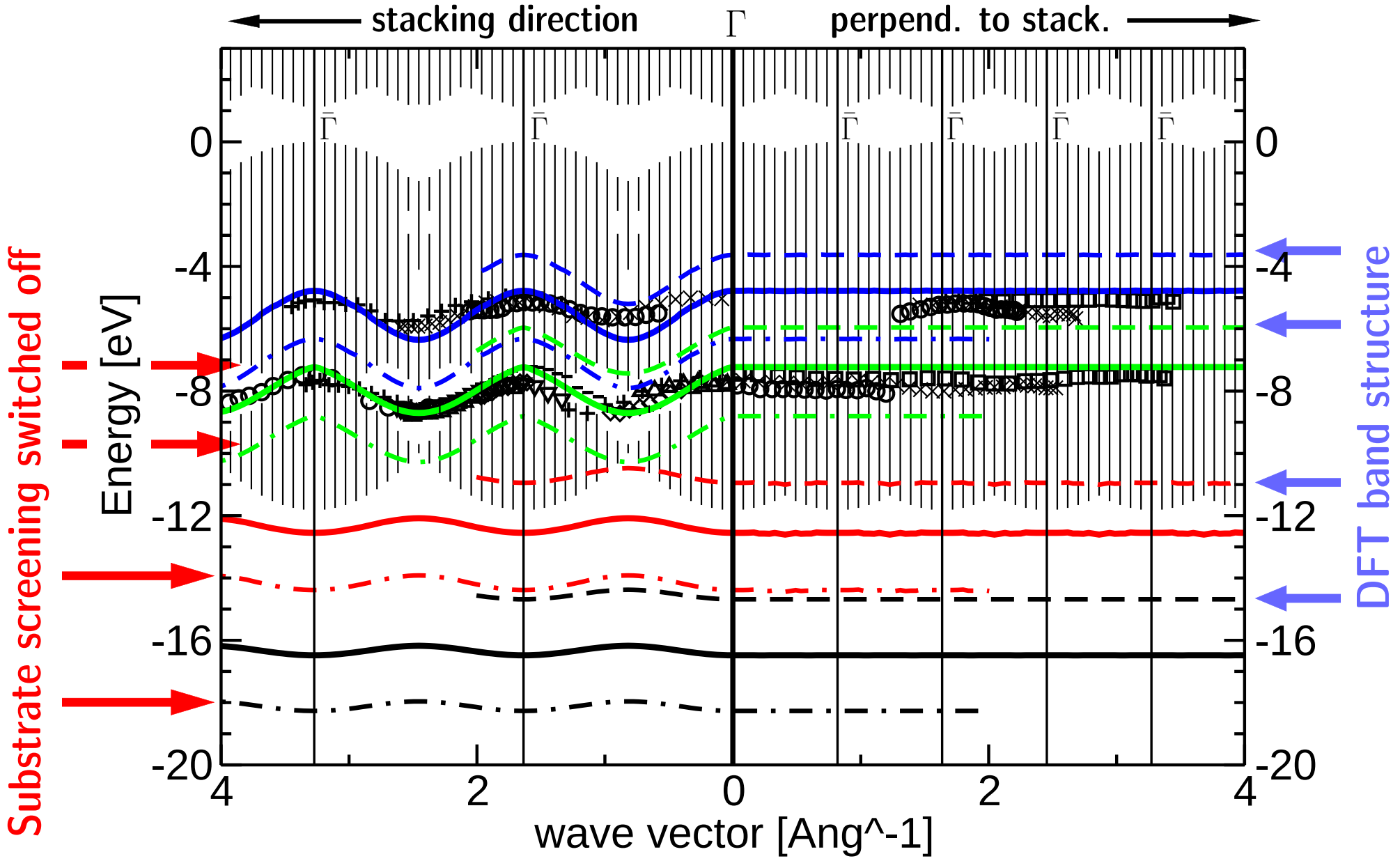
Top View

Side View

PDOS on Si

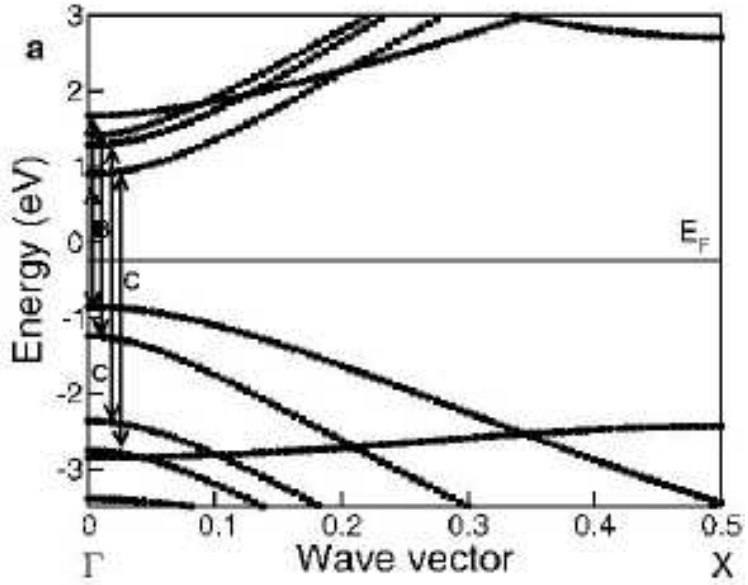


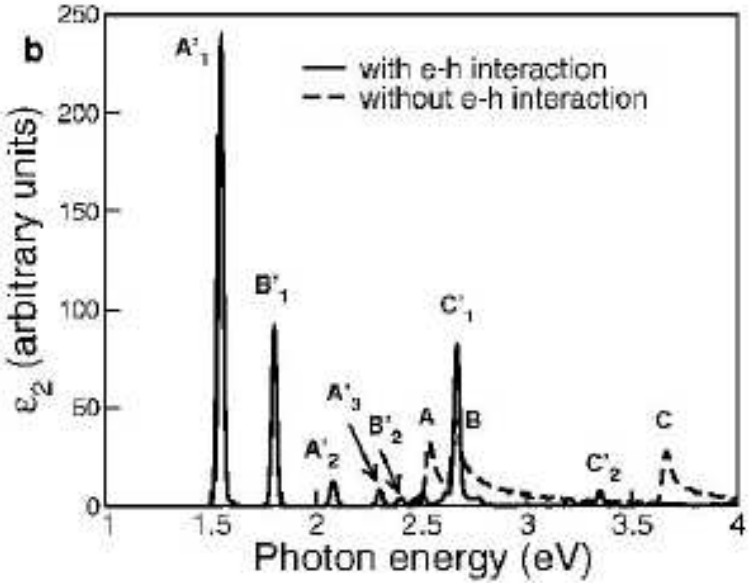
LDA+GdW Electronic spectrum of the C2H4:Si(001)-(2x1) surface

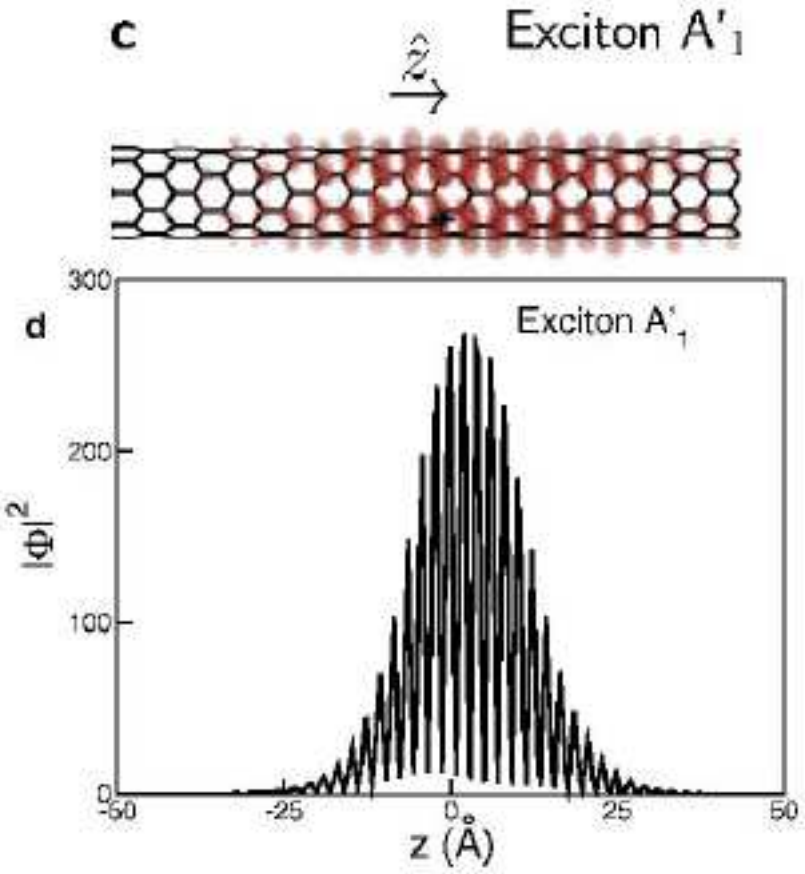


Exp.: W. Widdra et al., PRL 80, 4269 (1998).

Excitons in Semiconducting Carbon Nanotubes





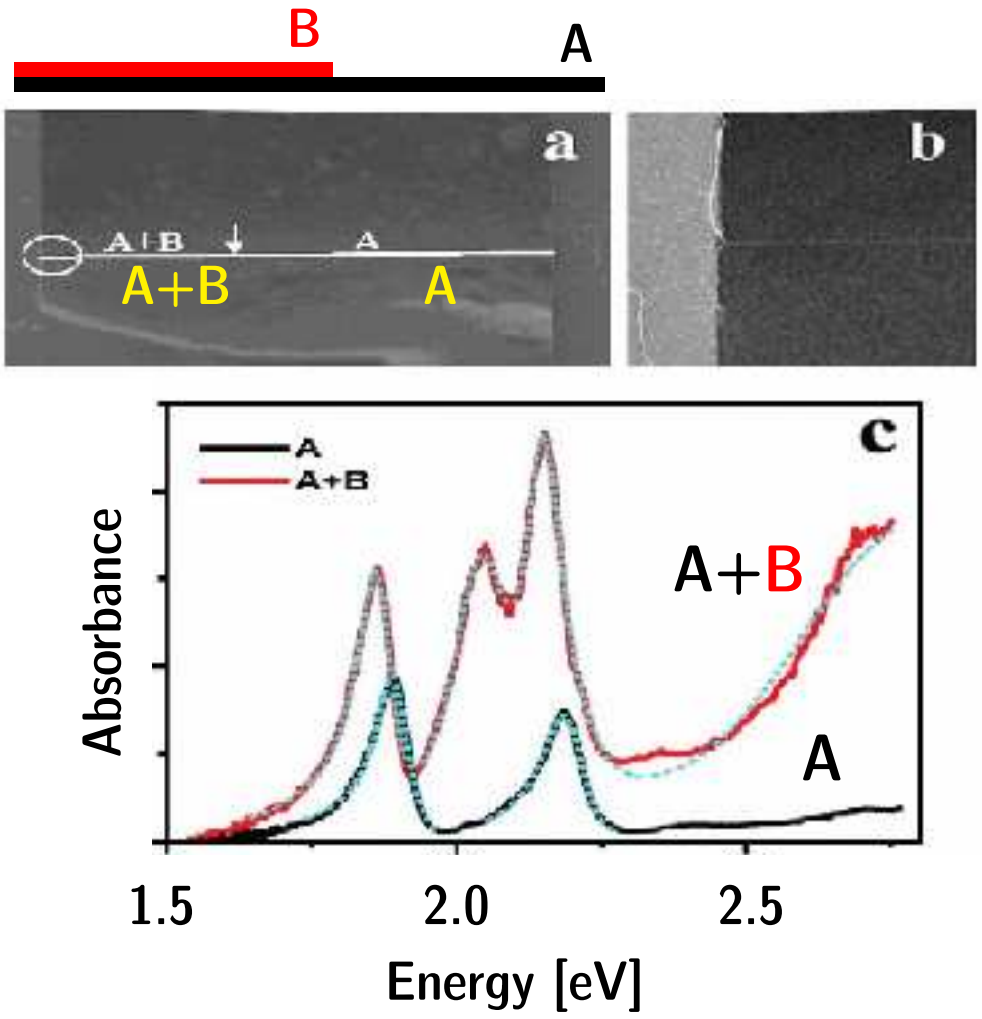


- Reduced dimensionality
  $\Longrightarrow$ strong e-h interaction
- Anisotropic e-h wave function

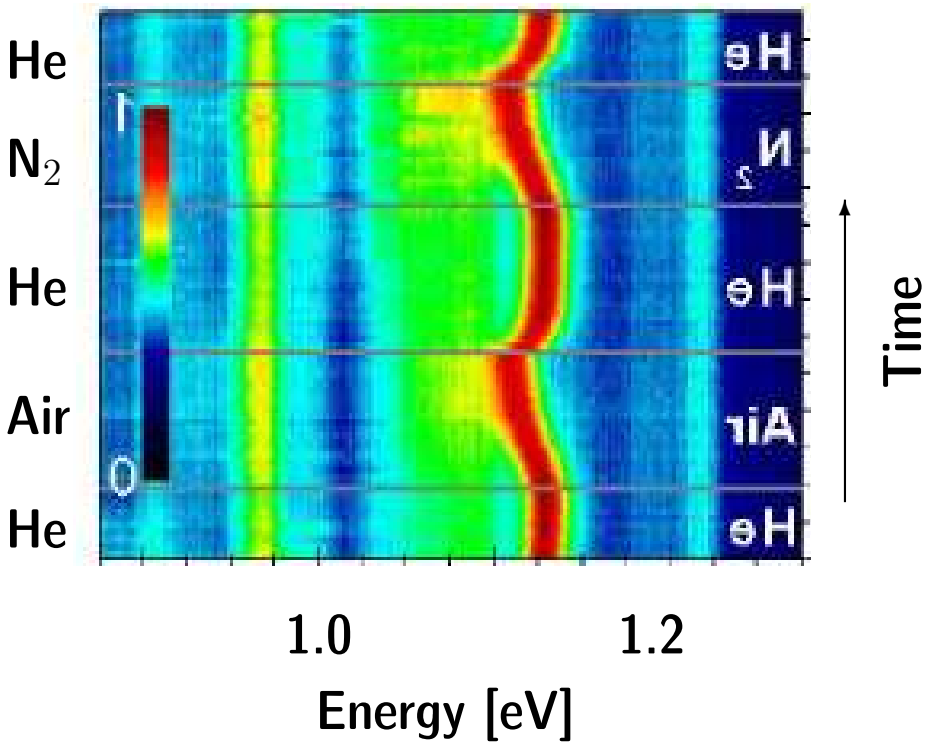
[C.D. Spataru, S. Ismail-Beigi, L.X. Benedict, and S.G. Louie, PRL 92, 077402 (2004).]

Red-shift of CNT Excitons from Physical Environment

F. Wang et al., PRL 96, 167401 (2006):

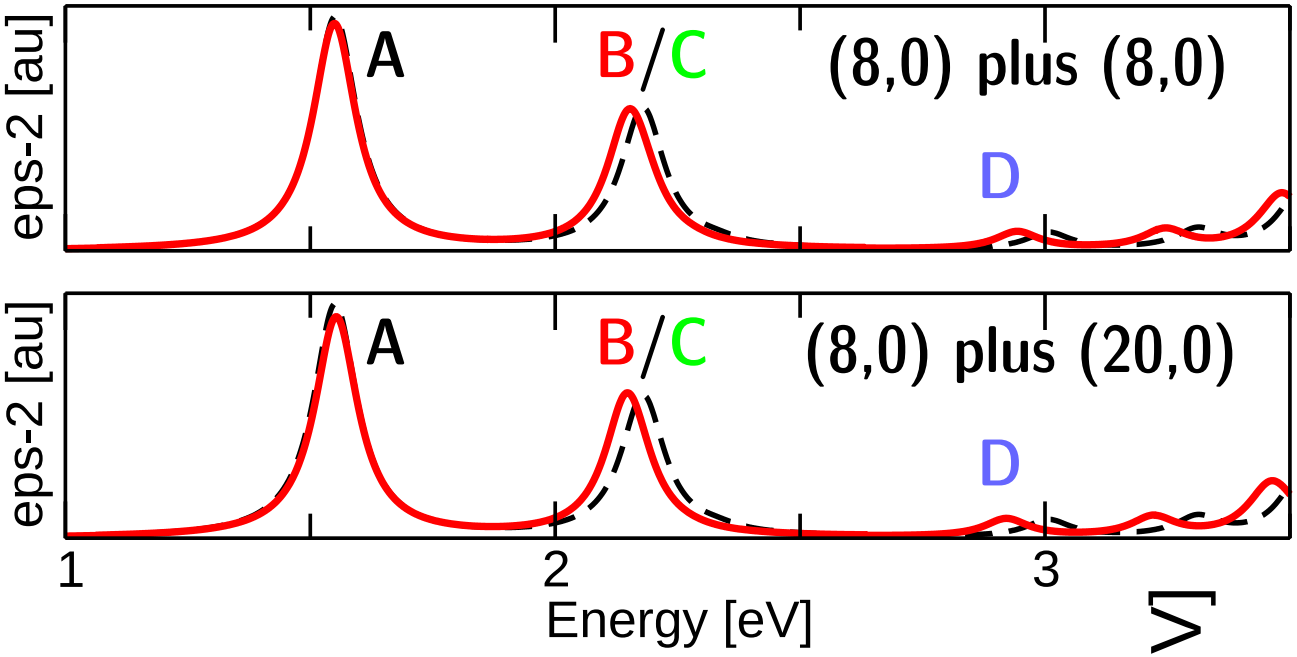


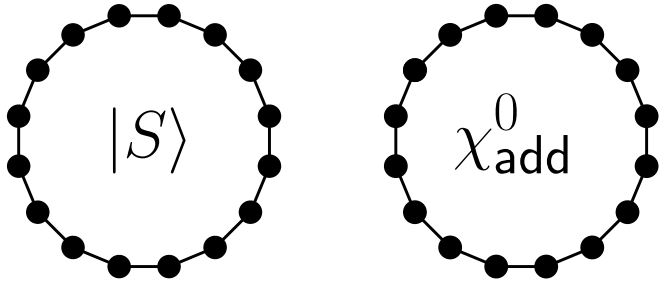
P. Finnie et al., PRL 94, 247401 (2005):
CNT in He / Air / N_2 (at room temp.)

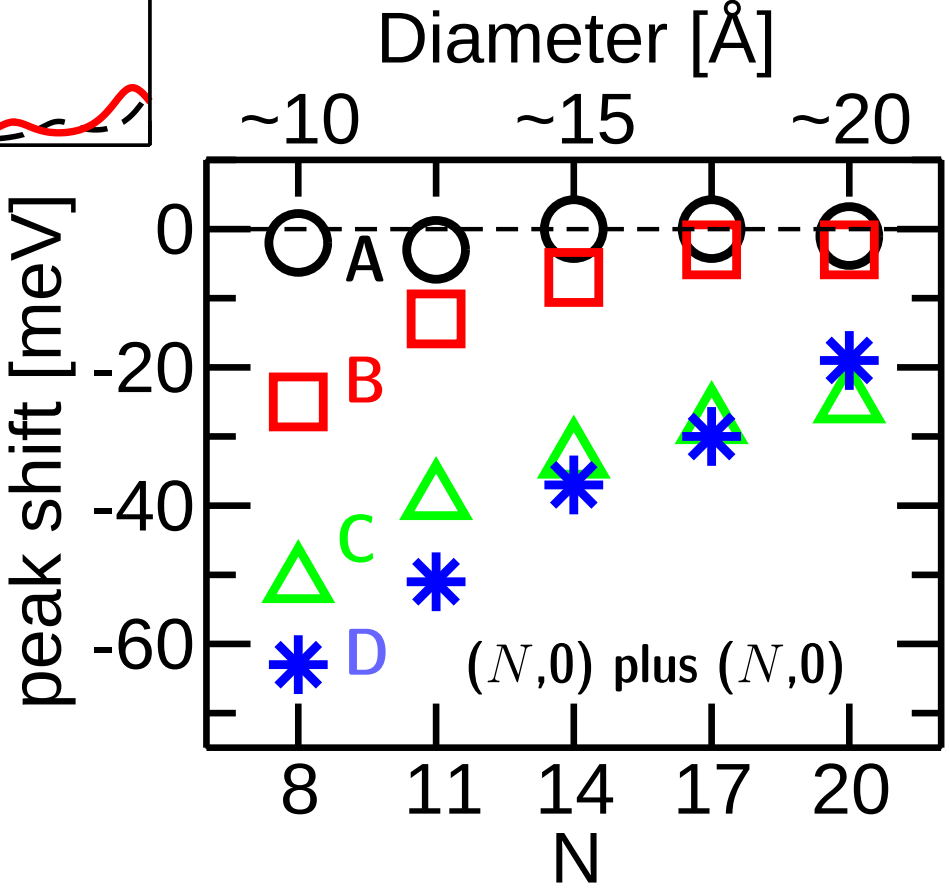


- Red-shifts of 20-50 meV
- Band-gap renormalization?
- Electronic coupling between excitons?
- Environmental polarizability?

Polarizability effect from a neighboring tube





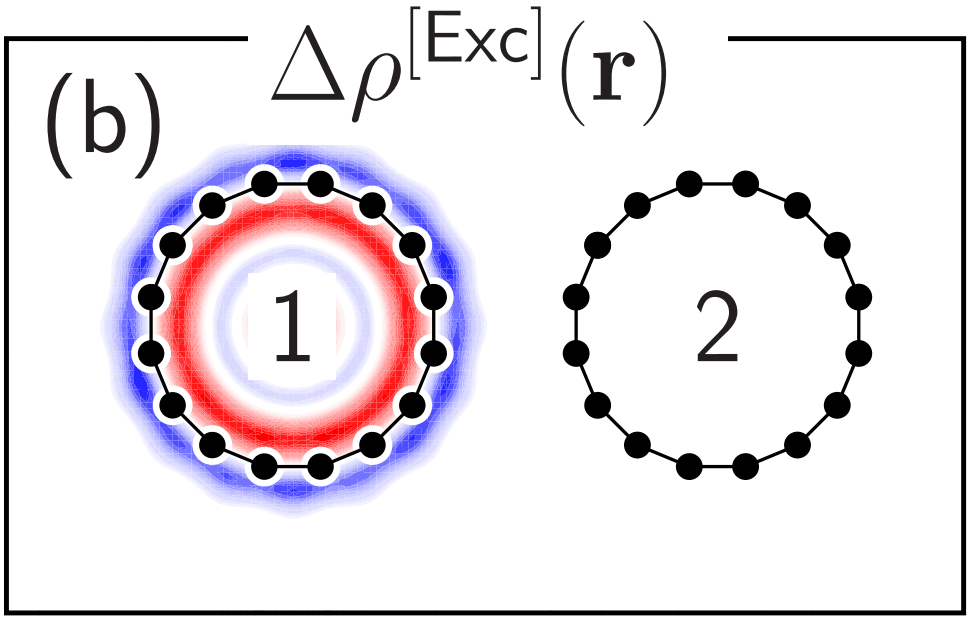


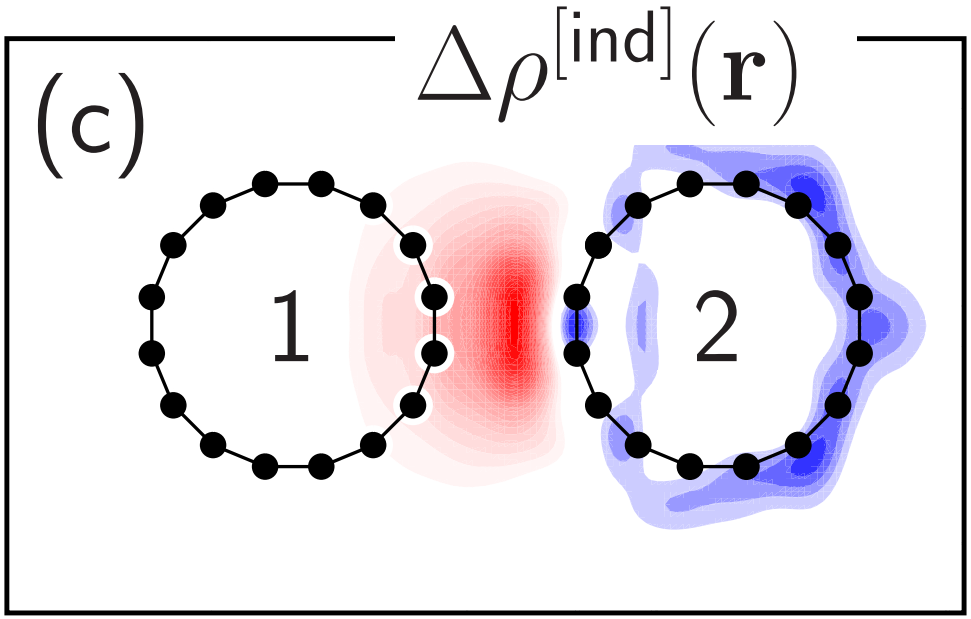
- Exp.: Red-shift of 30-50 meV

  [F. Wang et al., PRL 96, 167401 (2006).]

[PRL 108, 087402 (2012).]

Polarizability effect from a neighboring tube (2)





Exciton on tube 1:

Effective charge of the exciton

$$\Delta\rho^{[Exc]}(\mathbf{r}) := \rho_v(\mathbf{r}) - \rho_c(\mathbf{r})$$

(Slightly positive inside, negative outside)

Induced charge on tube 2:

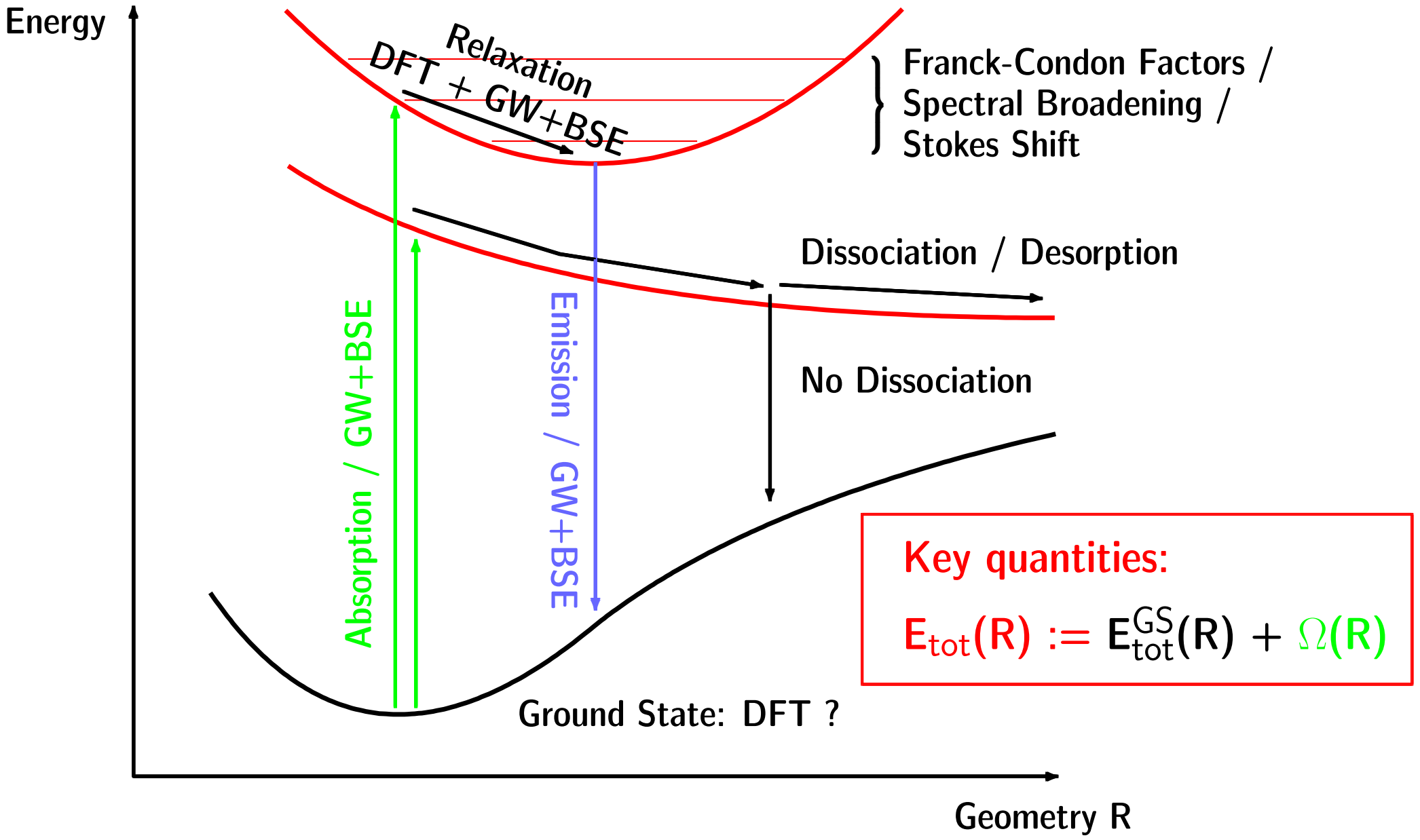
Positive in contact area,

Negative elsewhere

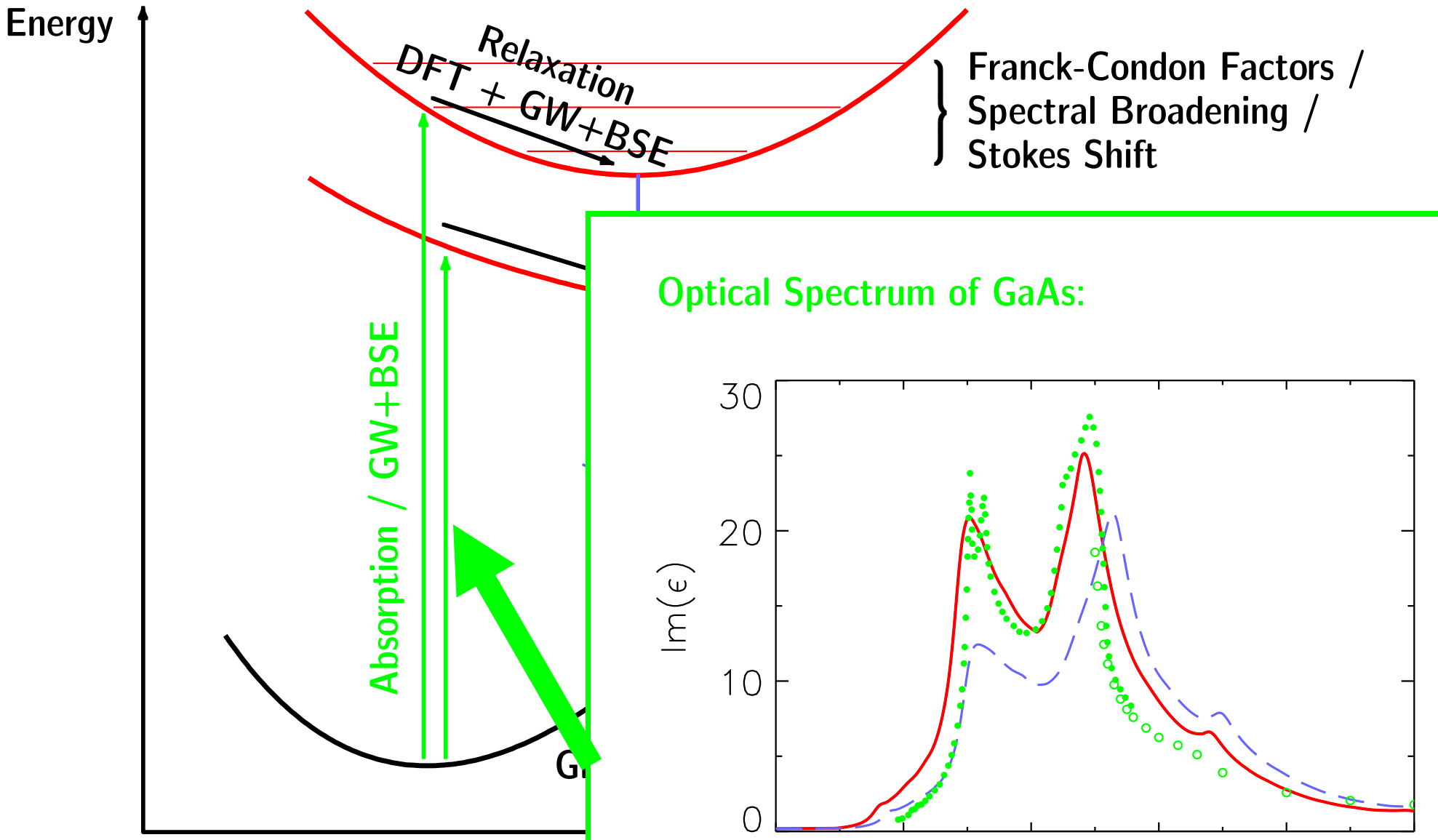
$\Longrightarrow$ Interaction $\Longrightarrow$ Redshift

- Significant effect for touching systems, even without dipoles
- Should always lead to redshift

Interplay between Electrons and Structure

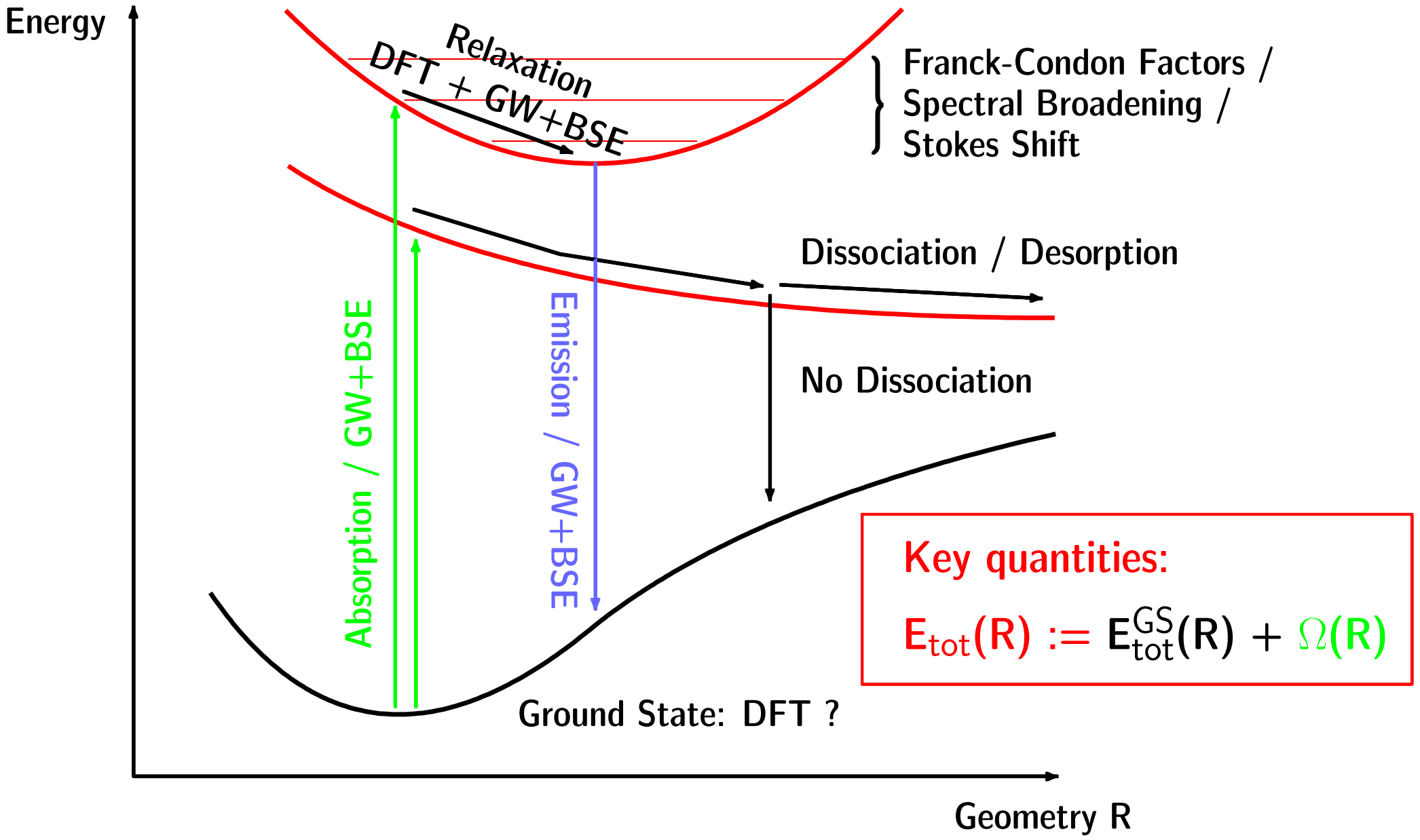


Interplay between Electrons and Structure

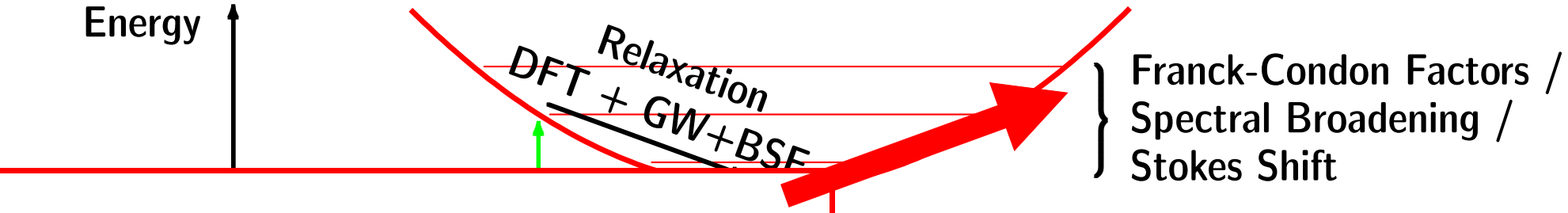


Optical Spectrum of GaAs:

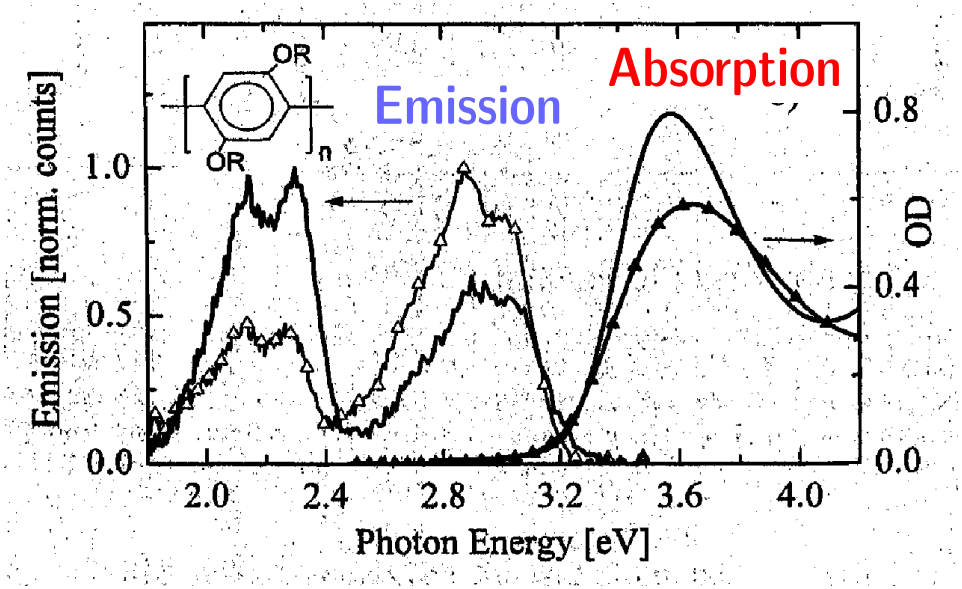
Interplay between Electrons and Structure



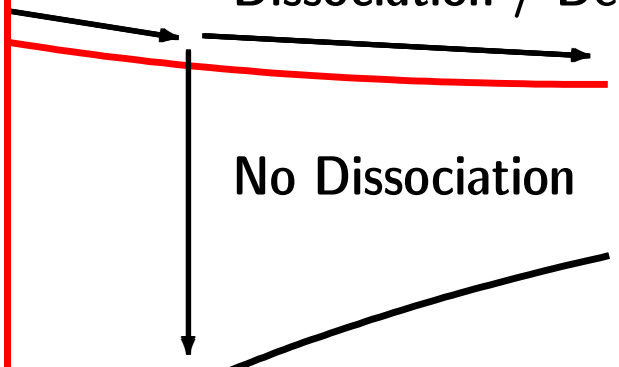
Interplay between Electrons and Structure



Absorption + Emission
Spectrum of PPP:



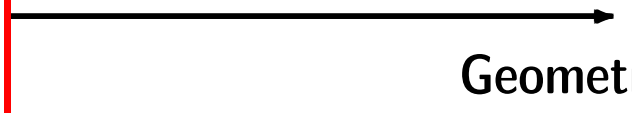
[D. Hertel et al., Adv.Mat. 13, 65 (2001)]



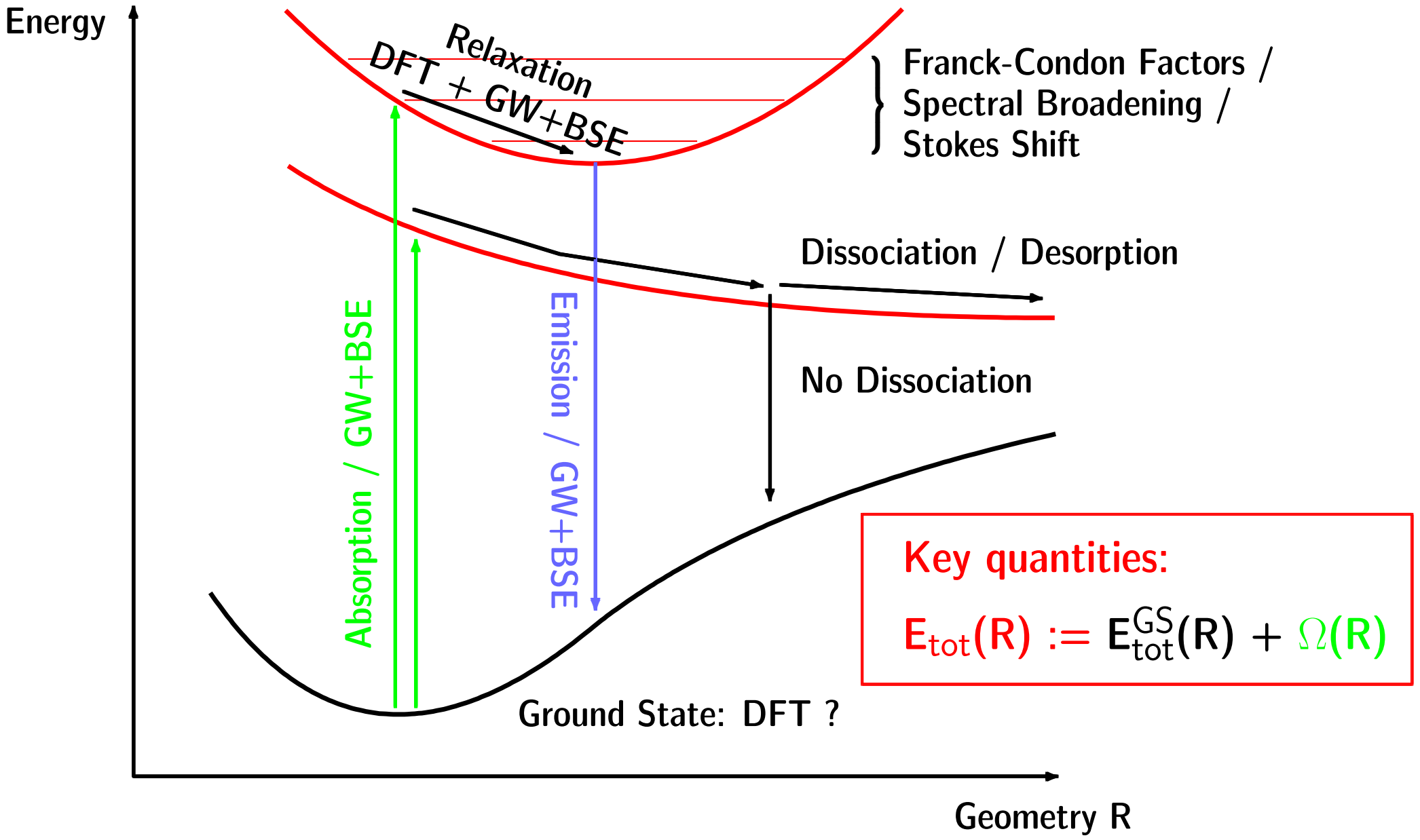
Key quantities:

$E_{tot}(R) := E^{GS}_{tot}(R) + \Omega(R)$

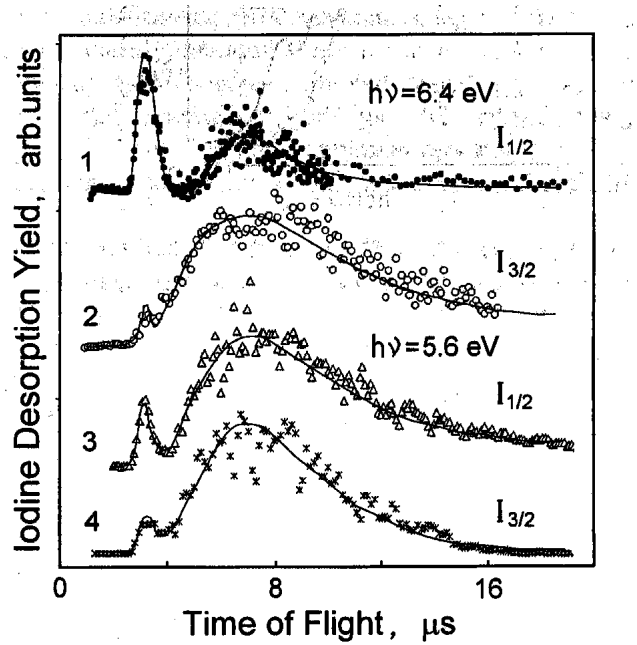
State: DFT ?



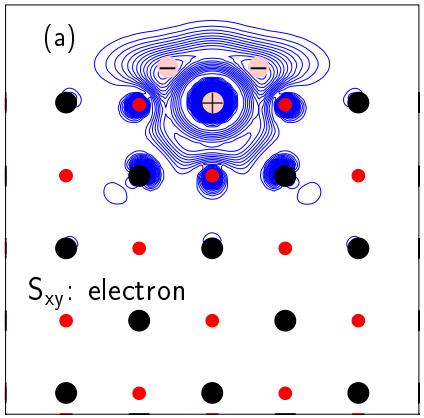
Interplay between Electrons and Structure

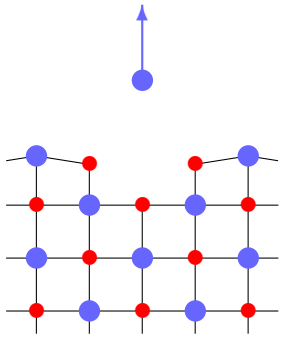


Iodine emission from KI after laser excitation:

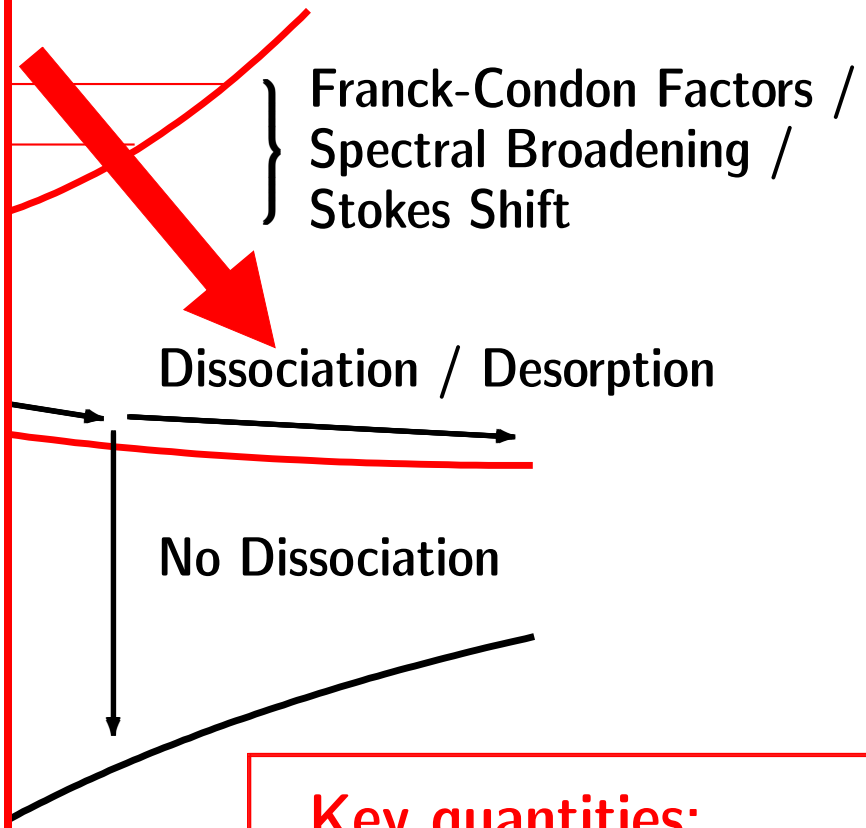


[A. Alexandrov et al., PRL 86, 536 (2001)]





ture



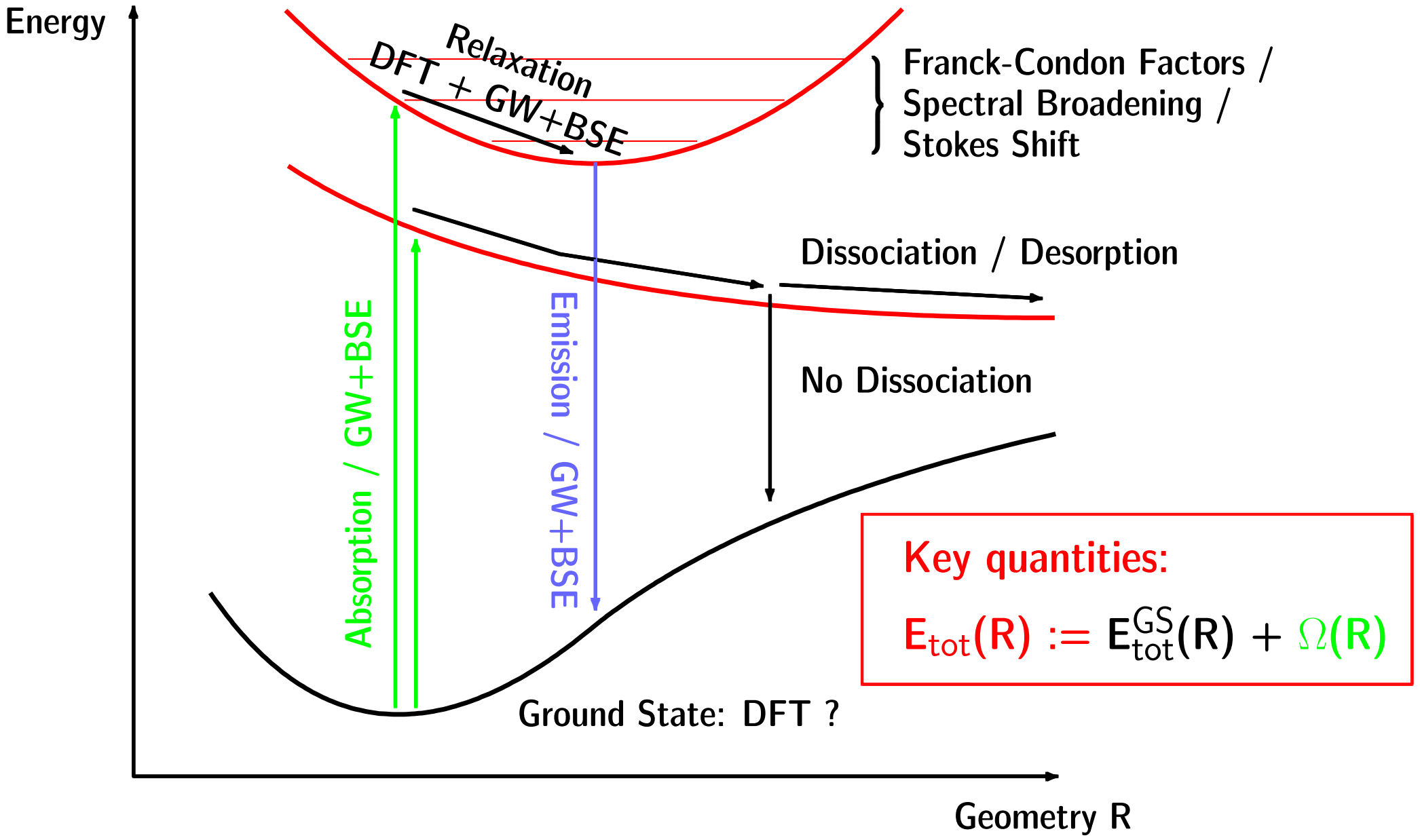
Key quantities:

$$E_{tot}(R) := E^{GS}_{tot}(R) + \Omega(R)$$

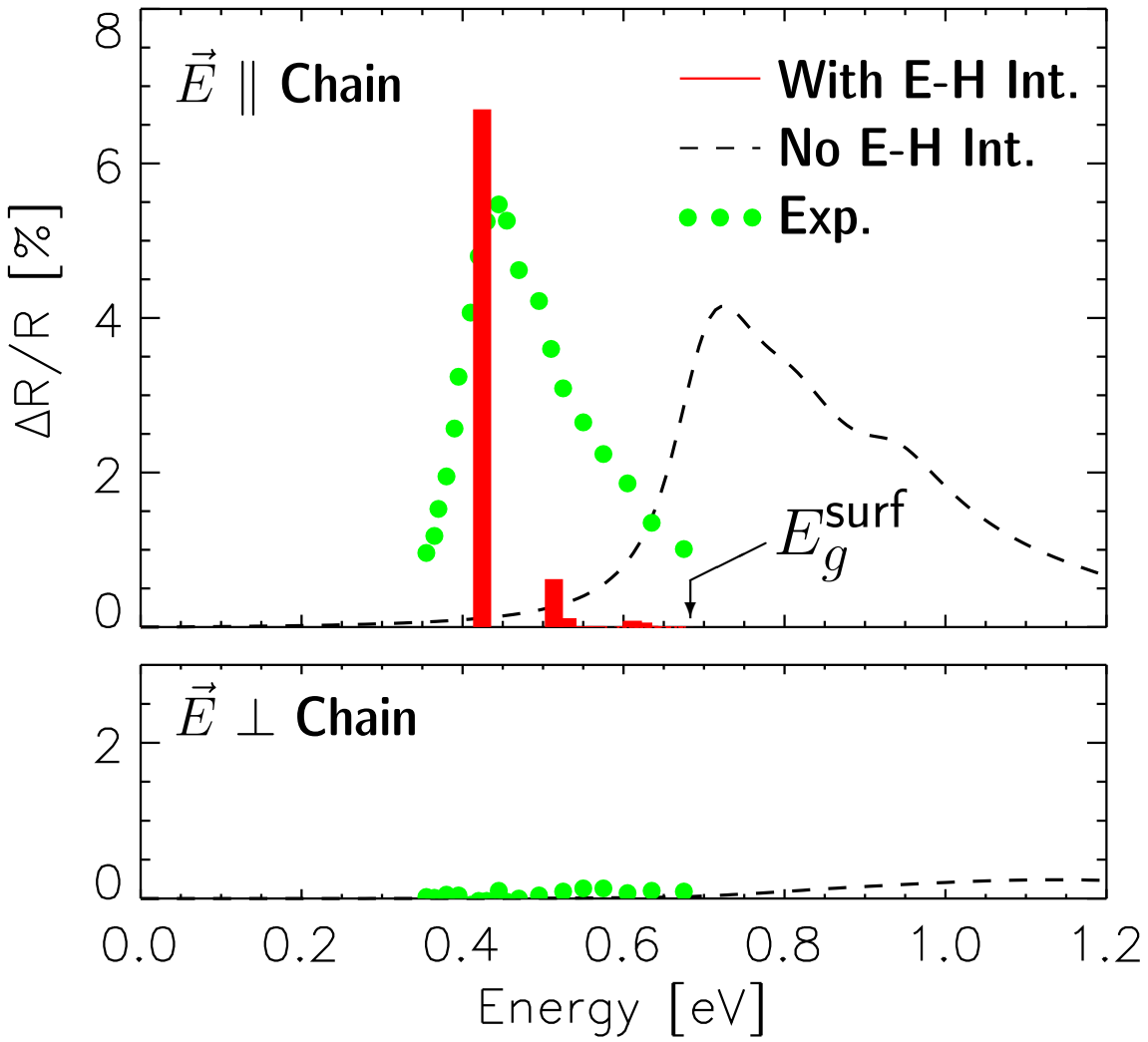
e: DFT ?

Geometry R

Interplay between Electrons and Structure



Si(111)-(2×1): Differential Reflectivity Spectrum (DRS)



Exp.: P. Chiaradia et al., PRL 52, 1145 (1984).

$$\frac{\Delta R}{R}(\omega) = 4\frac{\omega}{c}\frac{\Im(d \cdot \epsilon^{\text{surf}}(\omega))}{\epsilon_b - 1}$$

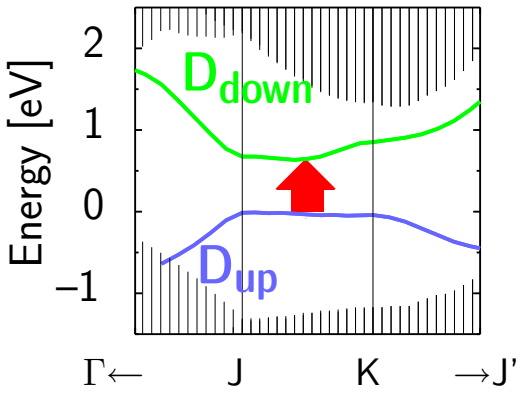
[S. Selci *et al.*, J.V.Sc.Tc. A 5, 327 (1987)]

- Discrete exciton spectrum.
- The optical spectrum is dominated by the lowest exciton at 0.43 eV.
- Binding energy: 0.26 eV ($\gg E_B^{\text{bulk}} = 0.015$ eV).

Si(111)-(2×1): Geometry and electronic structure

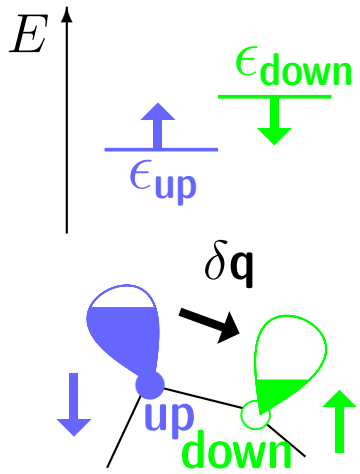
- Full treatment: Coupling to all phonon modes ⟶ very demanding.
- Instead: Coupling to that deformation mode which is created by the exciton itself
  ⟷ Relaxation in the excited state

Band structure:

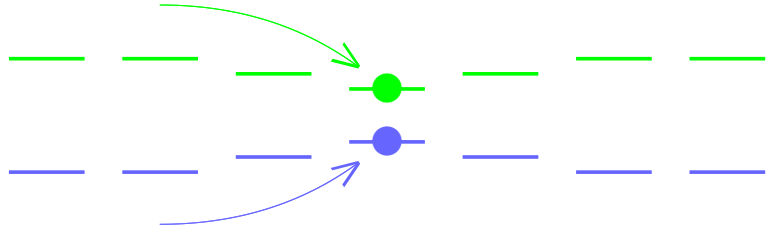


Exciton $\hat{=}$
Change of occupation

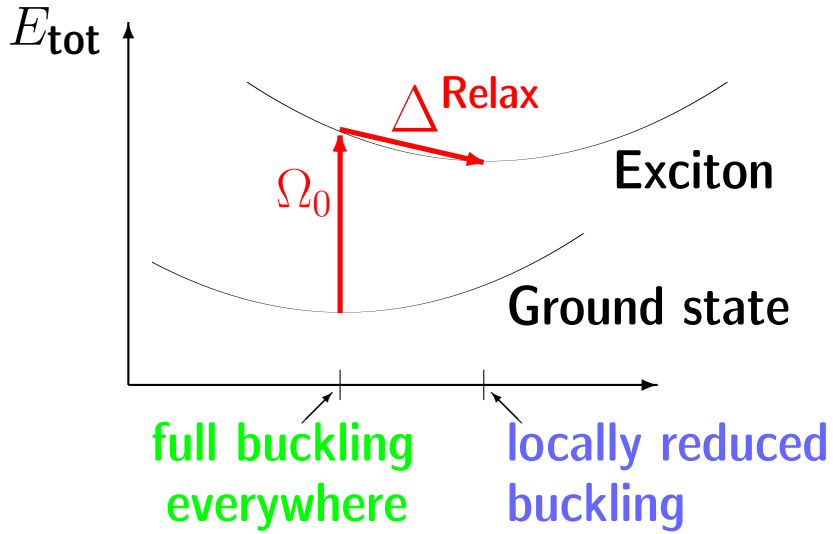
Local change of structure:



Self Trapping of Electron/Hole/Exciton:

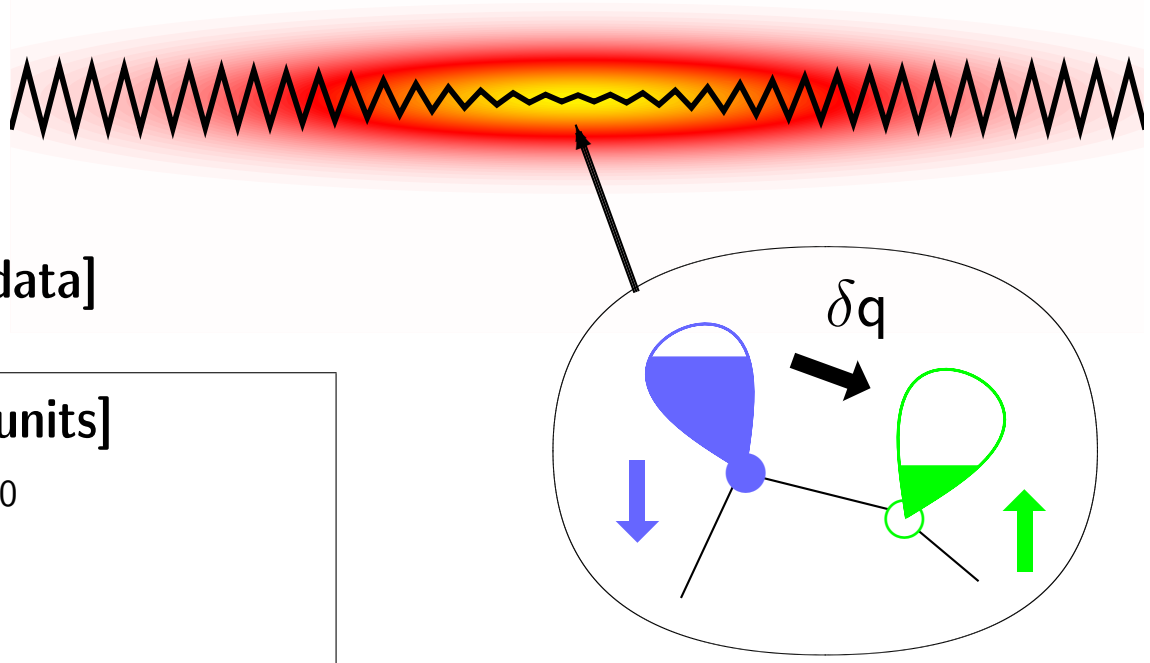


Reduction of Total Energy:

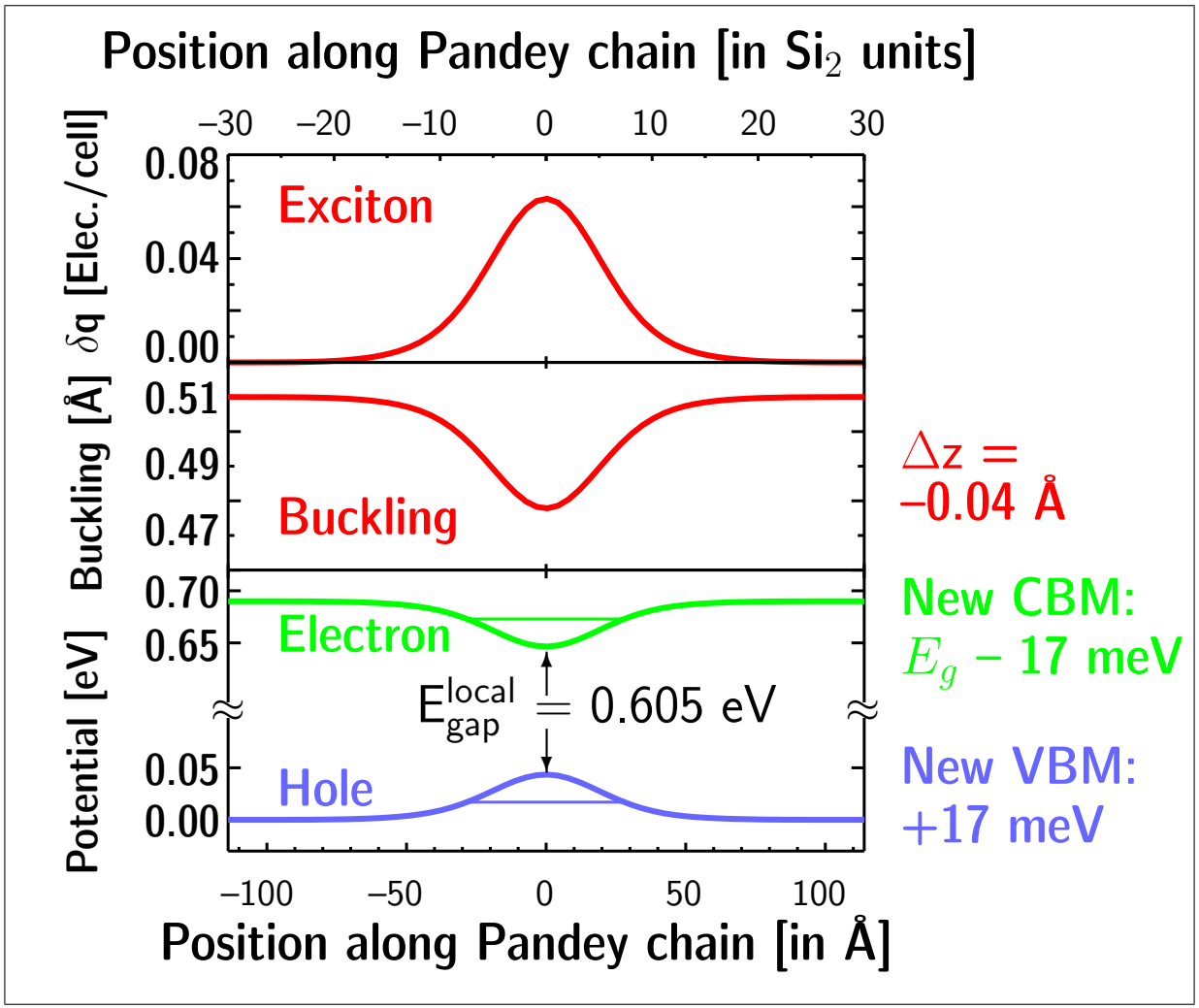


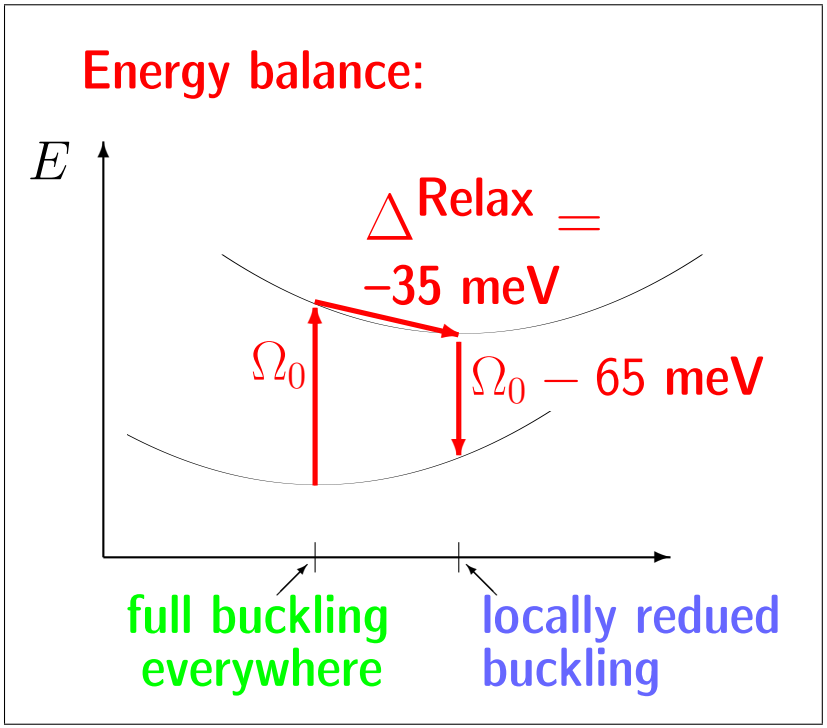
M.R. and J. Pollmann, PRL 88, 176801 (2002).

Si(111)-(1×1): Self-Trapping of the Surface Exciton

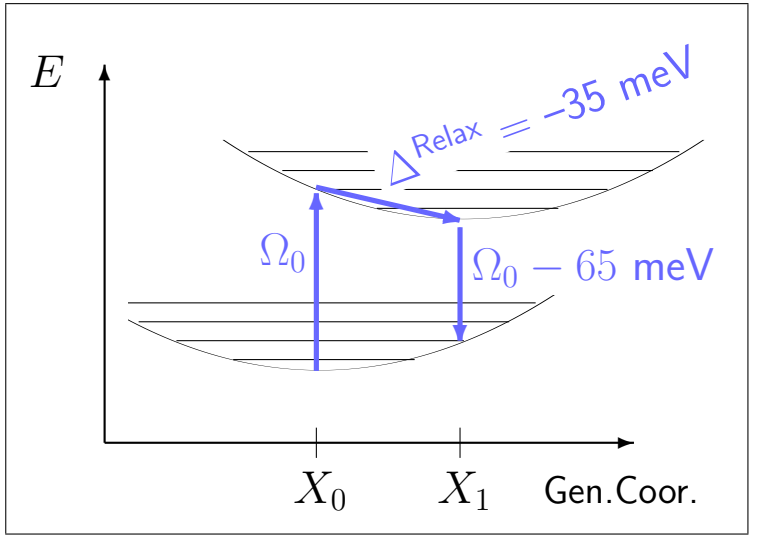


[tight-binding study, based on ab-initio data]



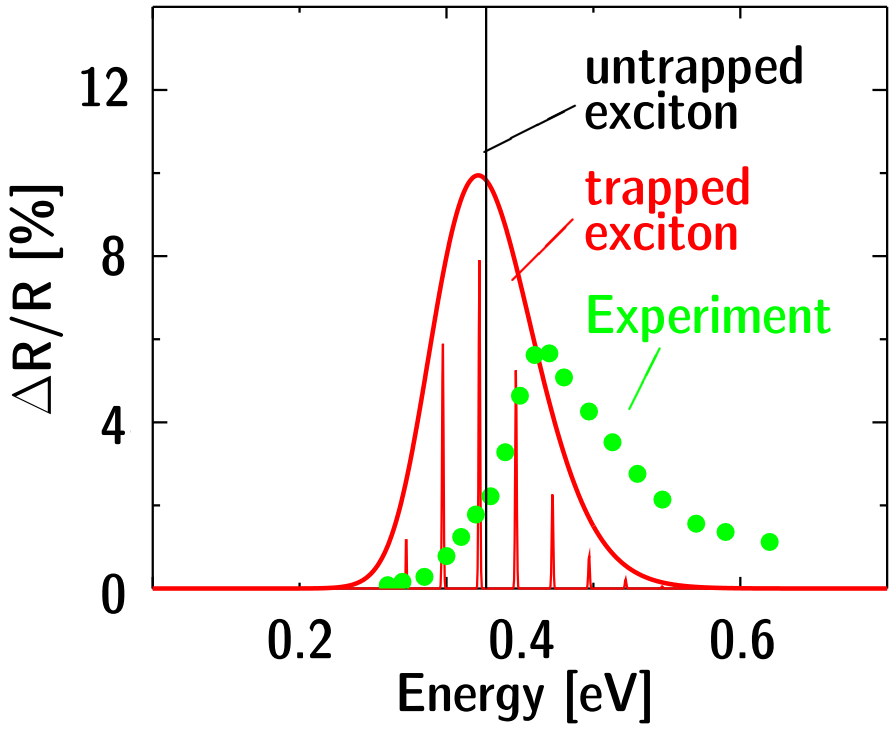


Si(111)-(2×1) Surface Exciton: DRS Line Width

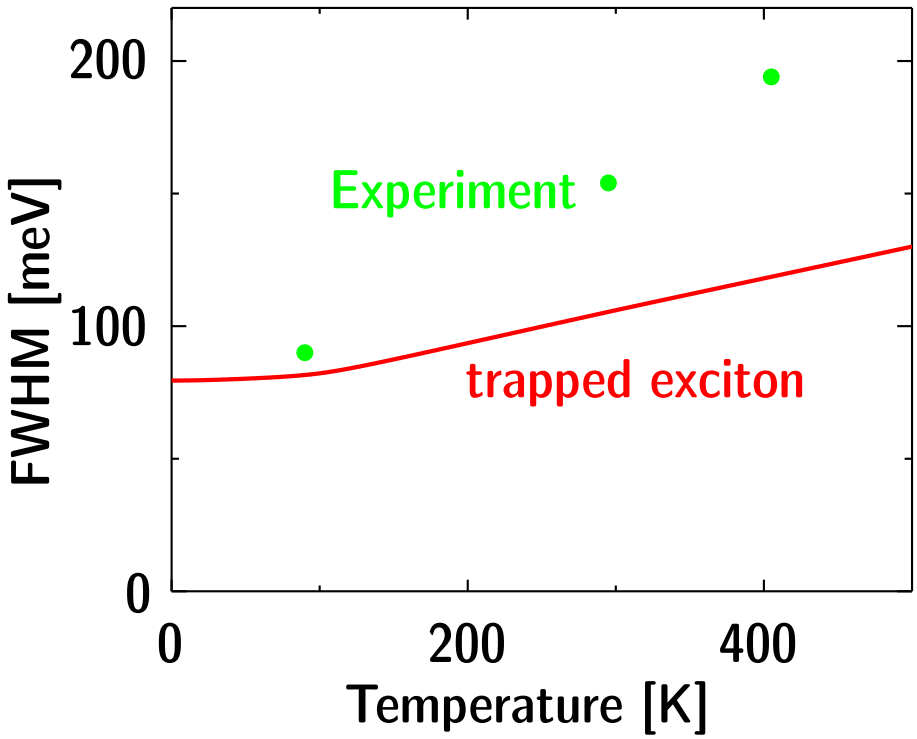


- Vibrational sublevels ($\sim$ 25 meV)
  Franck-Condon factors / temperature dependent
  $\Longrightarrow$ Line broadening
- plus: inhomogeneous broadening / further modes
  $\Longrightarrow$ Vibronic lines cannot be resolved.

DRS Spectrum [T=90K]:



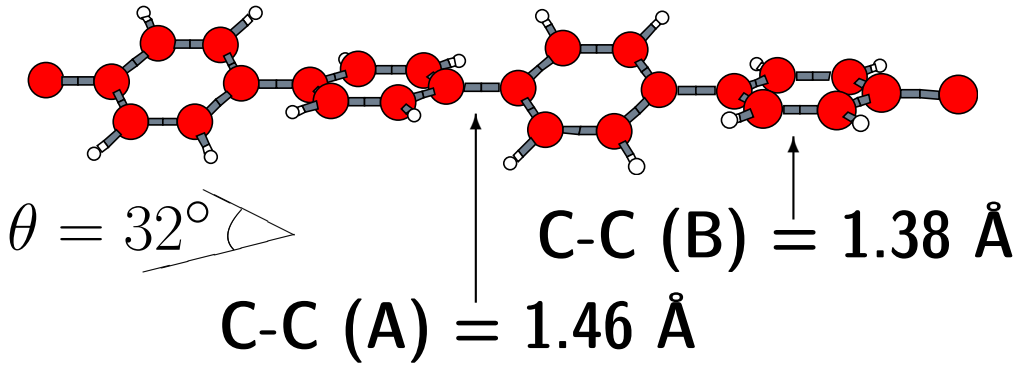
Spectral Width:



- Exp.: Ciccacci et al., PRL 56, 2411 (1986).

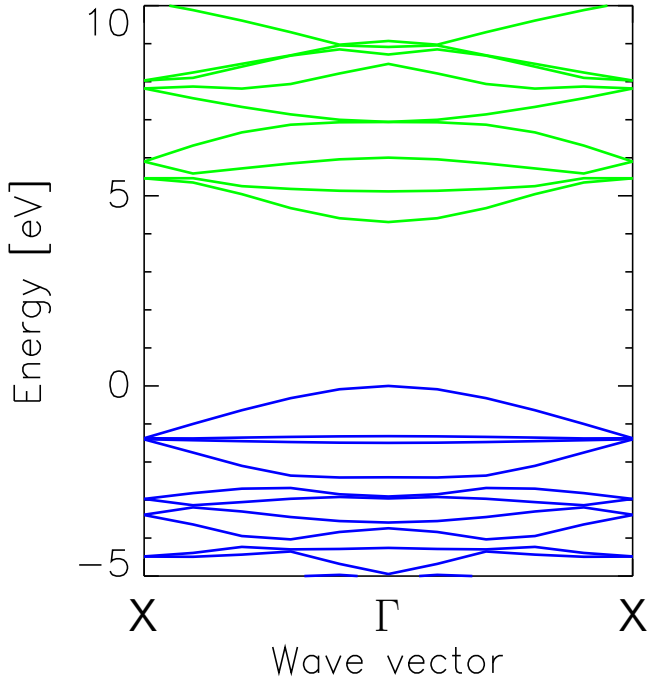
A conjugated polymer: PPP / Poly-(Para-Phenylene) $(C_6H_4)_n$

[E. Artacho, M. Rohlfing, M. Côté, P.D. Haynes, R.J. Needs, C. Molteni, PRL 93, 116401 (2004).]

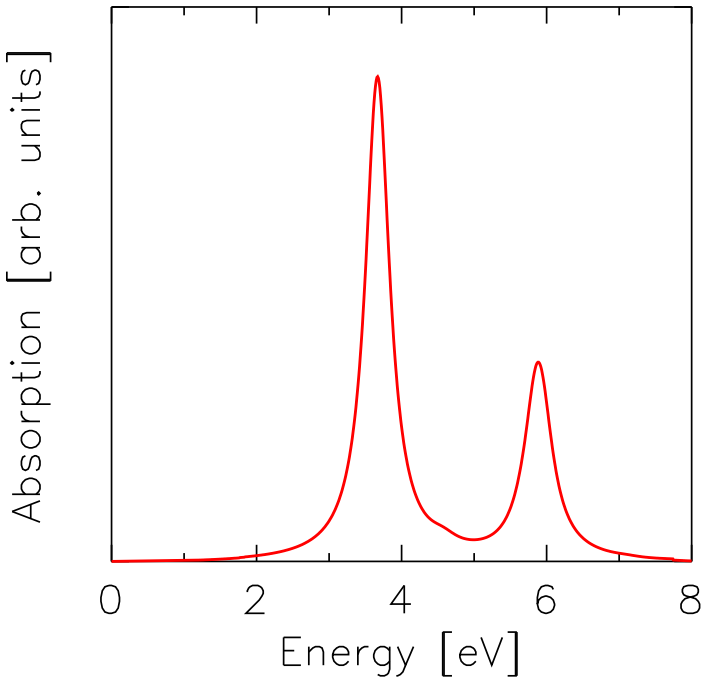


- Small H-H distance (1.9 Å)
  $\Longrightarrow$ Repulsion / Twisting
- Delocalized π-electron system
- Semiconducting band structure
- Exciton at 3.6 eV

Band structure:

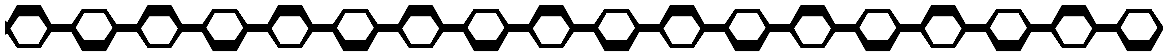


Optical Spectrum:

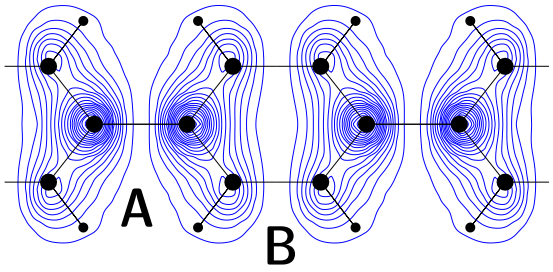


Structure of PPP

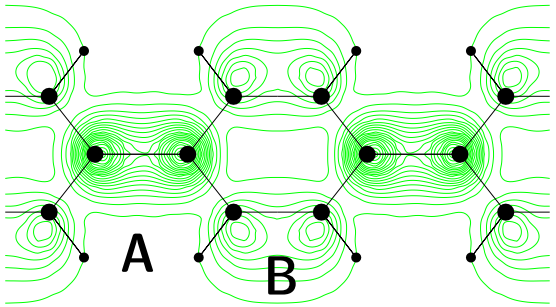
Ground-state geometry:



HOMO / VBM (at Γ):



LUMO / CBM (at Γ):



HOMO$\rightarrow$LUMO transition: favours planar, π-like "A" bond

$\Longrightarrow$ Exciton causes "planarization" of the polymer and shortening of "A" bond

Excited-state geometry:

Exciton wave function:

PPP: Exciton self trapping / relaxation in the excited state

Locally (in one unit cell): DFT + MBPT

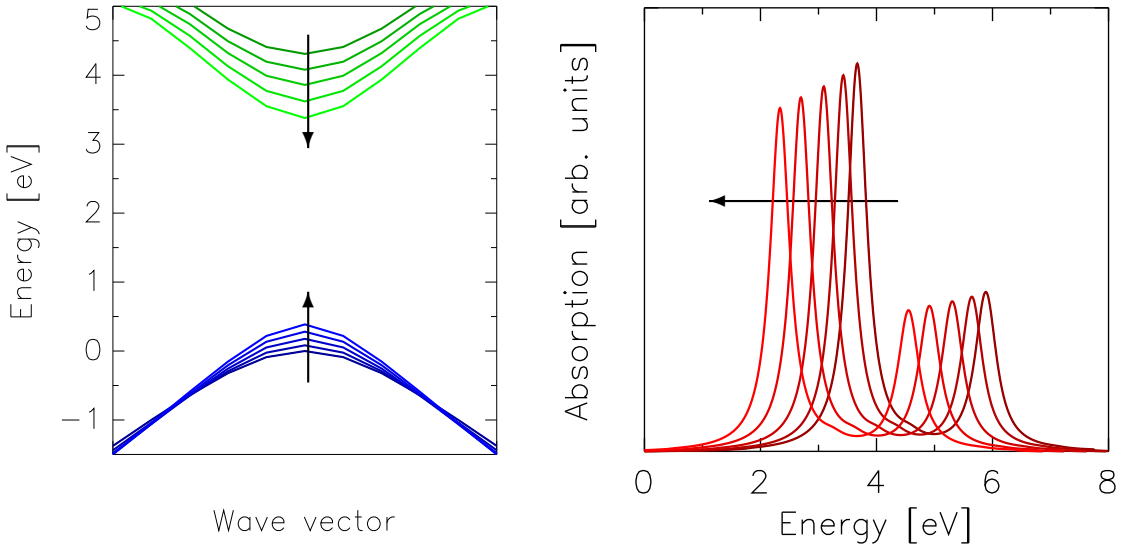
Excited state has a different

band occupation / charge distribution

$\Longrightarrow$ Structural relaxation

$\Longrightarrow$ gap is lowered /

excitation energy becomes smaller:



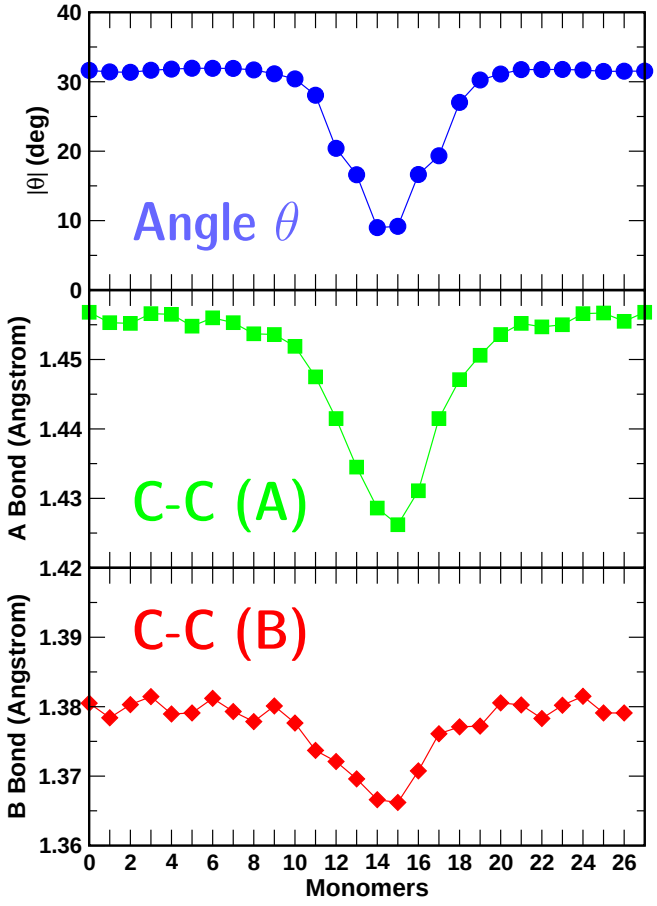
[Relaxation mode from self-trapped exciton; see right-hand side]

$\Longrightarrow$ This drives the relaxation !

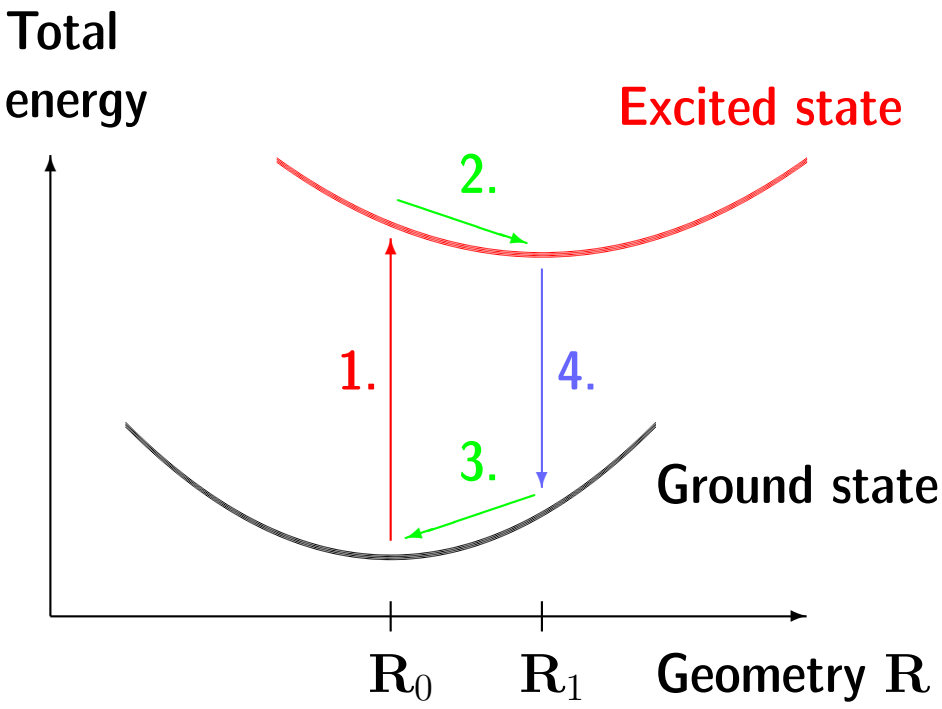
Globally (entire polymer): constrained DFT

Self-trapped exciton

[balence between kin. energy of the exciton and relaxation energy]

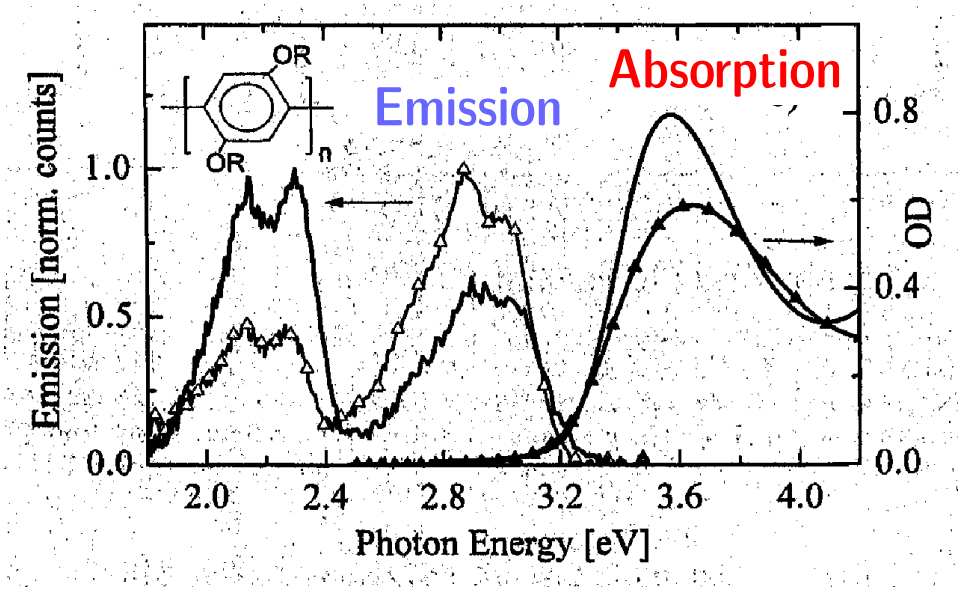


PPP: Relaxation / Stokes Shift



Experiment:

[D. Hertel et al., Adv.Mat. 13, 65 (2001)]

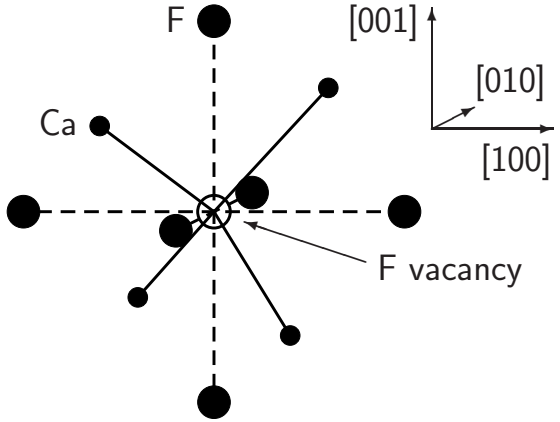


1. Optical absorption: $\Omega = 3.5$ eV (MBPT)
2. Relaxation in the excited state: $\triangle$E $= 0.2$ eV (constrained DFT)
3. "Lattice energy" in the ground state: $\triangle$E' $= 0.2$ eV (DFT)

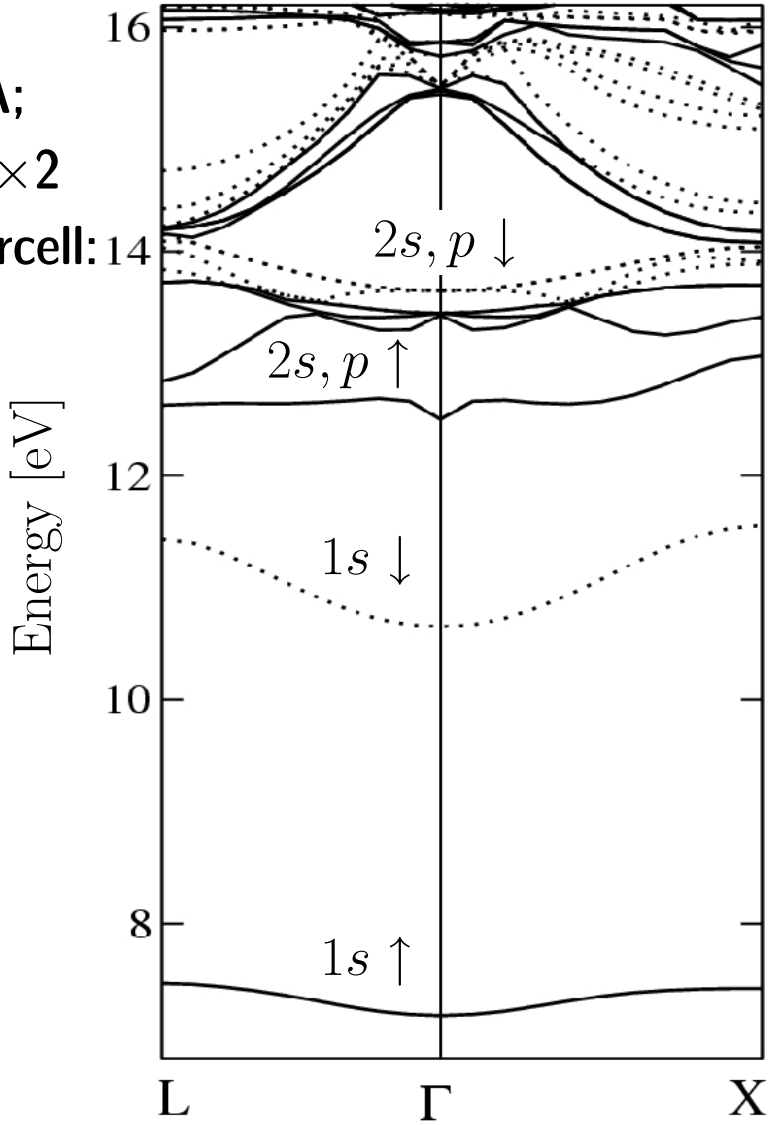
$\Longrightarrow$ Emission (4.): $\Omega' = 3.1$ eV ; Stokes shift $= 0.4$ eV

Point defects — Example: F Center in CaF_2

[Y. Ma and M.R., Phys. Rev. B 77, 115118 (2008).]



GWA;
2×2×2
supercell:



- F center in CaF_2: Missing F atom
- Charge neutral $\Longleftrightarrow$
  Vacancy hosts one unpaired electron
- Spin-polarized GW/BSE approach
- Deep defect level $1s \uparrow$
- "$2s$", "$2p$": Strong hybridisation with bulk bands

Cf. Surh, Chacham, Louie, PRB 51, 7464 (1995); Tiago, Chelikowsky, PRB 73, 2053 (2006);
Rohlfing, Louie, PRB 51, 2312 (1998): bulk LiF; Ma, Rohlfing, PRB 75, 205114 (2007): bulk CaF_2

Point defects — Example: F Center in CaF_2 (1)

[Y. Ma and M.R., Phys. Rev. B 77, 115118 (2008).]

Transition $1s\uparrow \rightarrow$ "$2p$"$\uparrow$:

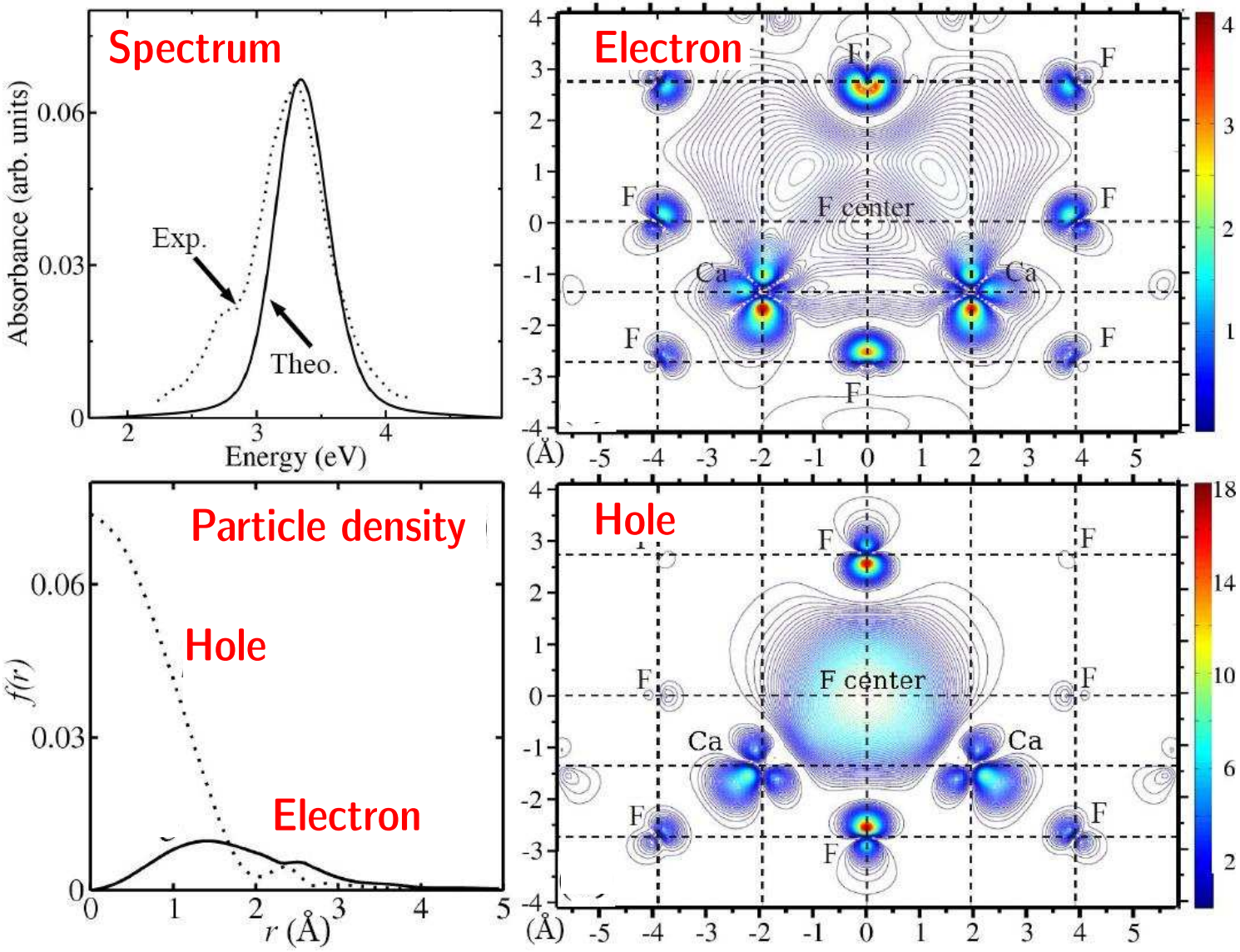
Excitation energy 3.3 eV

Electron localization by attraction to the hole

$\rho(r)$ around vecancy:
repels Ca^{2+}, attracts F^-.

$\Longrightarrow$ Lattice deformation
$\sim$ 0.2 Å
Line width $\sim$ 0.5 eV
Stokes shift $\sim$ 1.5 eV

[Constrained DFT
+ GW/BSE]



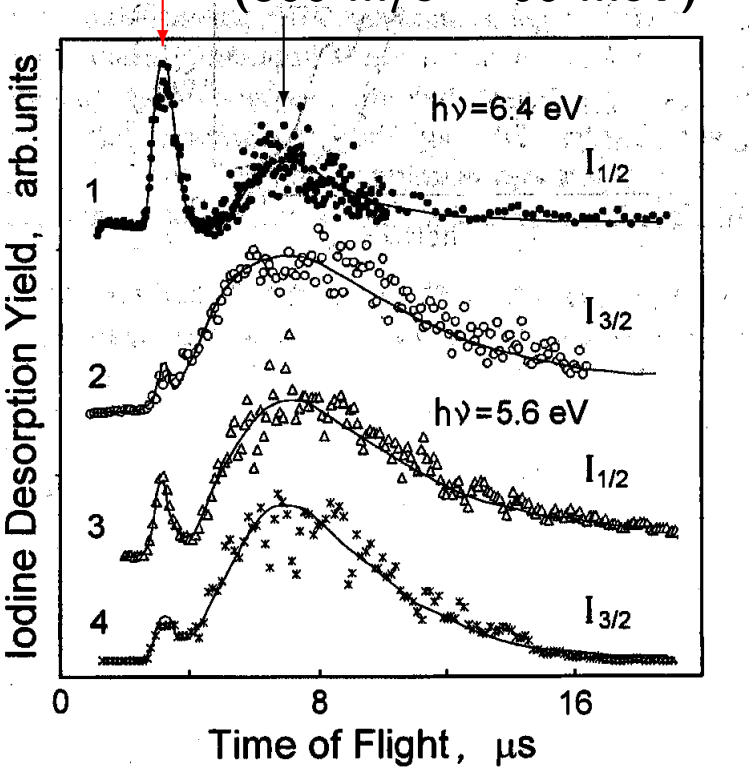
Exp.: Arends, PSS 7, 805 (1964); Patterson, Fuller, PRL 18, 1123 (1967)

Desorption of Iodine Atoms from Optically Excited KI

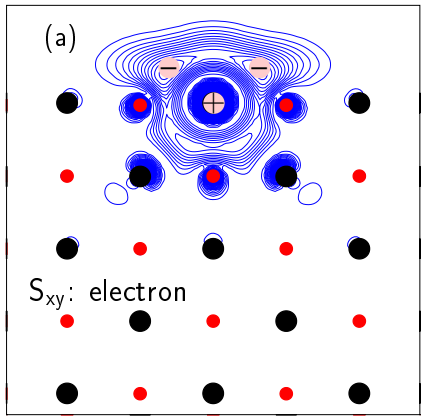
Iodine emission from KI after laser excitation:
[A. Alexandrov et al., PRL 86, 536 (2001)]

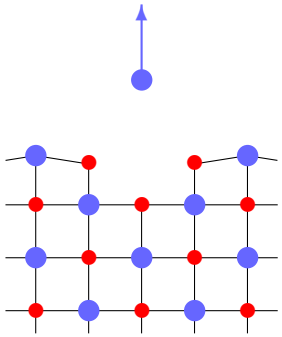
Faster than thermal velocity:
700 m/s $\hat{=}$ 320 meV

Thermal velocity
(300 m/s $\hat{=}$ 60 meV)

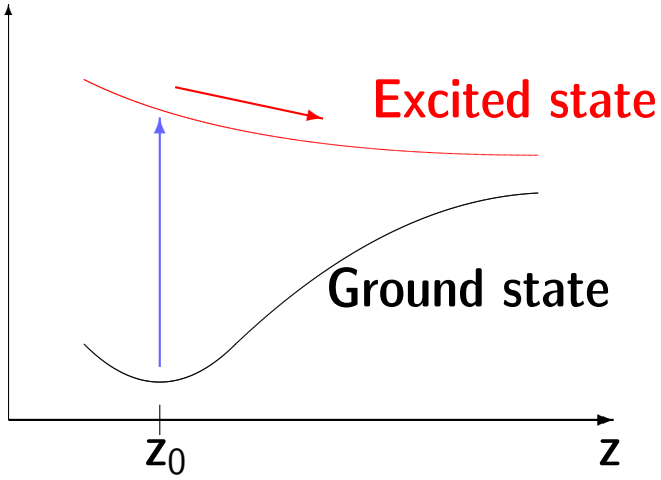


Possible mechanism:



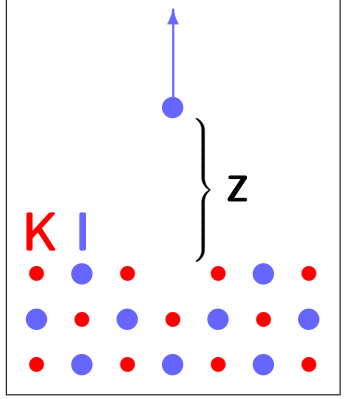


Total Energy:

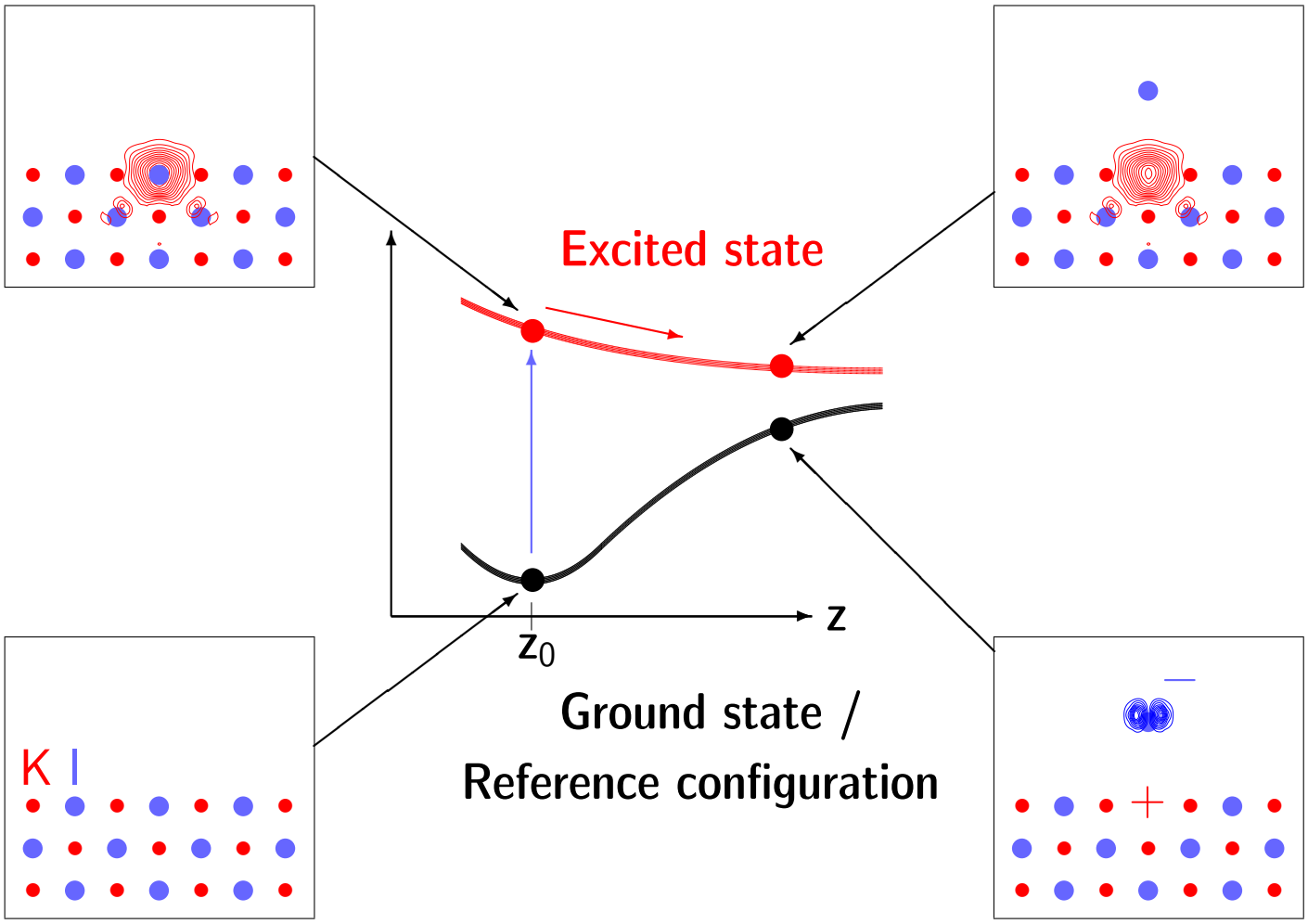


Desorption of Iodine atoms from optically excited KI

Desorption path:

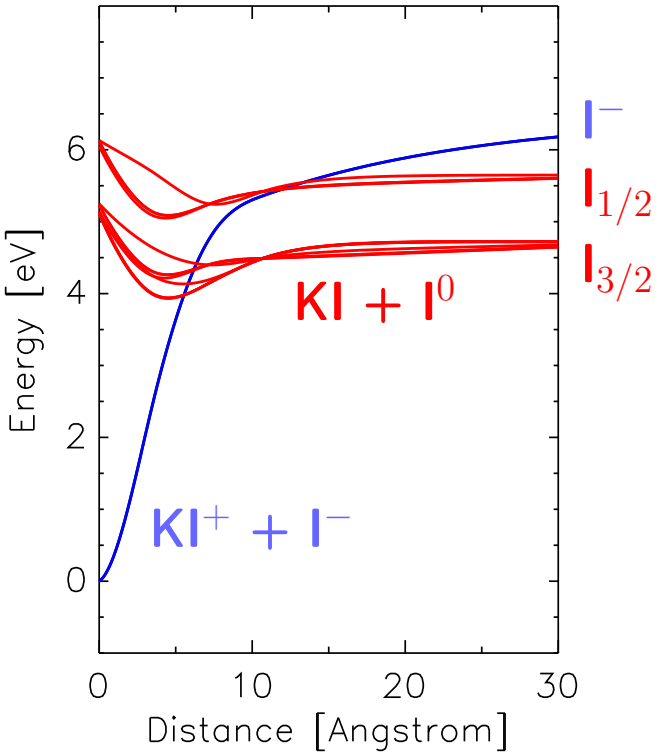


Total energy, depending on the height of the iodine atom:

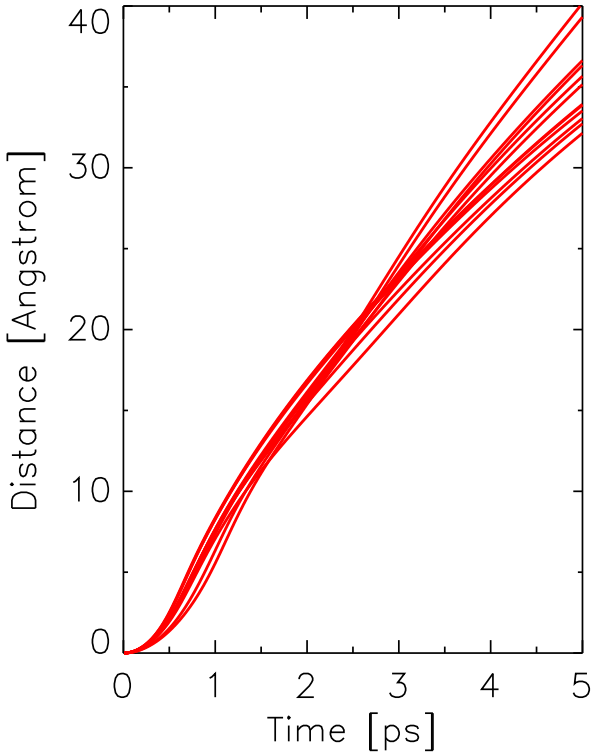


Desorption of Iodine atoms from optically excited KI

Calculated total energy, including LS interaction:



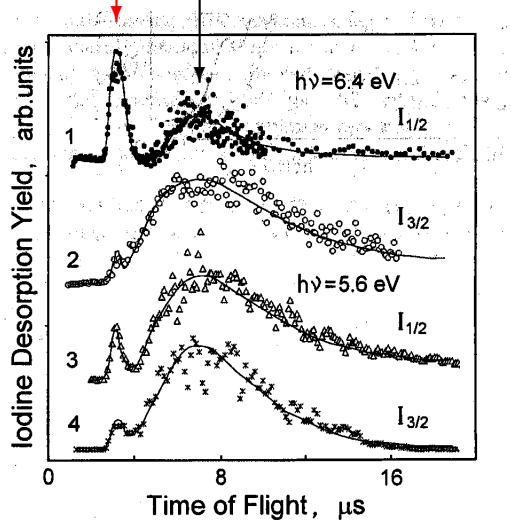
Particle dynamics in the excited states:



Time-of-flight data [A. Alexandrov et al., PRL 86, 536 (2001).]

Faster than thermal

Thermal velocity



[3 p orbitals (p_x, p_y, p_z),
4 spin conf's (1 sing., 3 trip.)
$\Longrightarrow$ 12 excited states]

- Desorption of neutral Iodine, within $\sim$ 1 ps
- Spin memory: $1/2 \rightarrow 1/2$, $3/2 \rightarrow 3/2$
- Kinetic energy = 300-400 meV, velocity = 700-800 m/s

[C. Carbogno, A. Groß, and M. Rohlfing, Applied Physics A 88, 579 (2007).]

Interplay between Electrons and Structure