Many-Body Perturbation Theory:
(2) Bethe-Salpeter Equation and Optical Excitations

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- Excited states: electrons, holes and excitons
- Equation of motion
- Electron-hole correlation
- Examples

States of a many-electron system

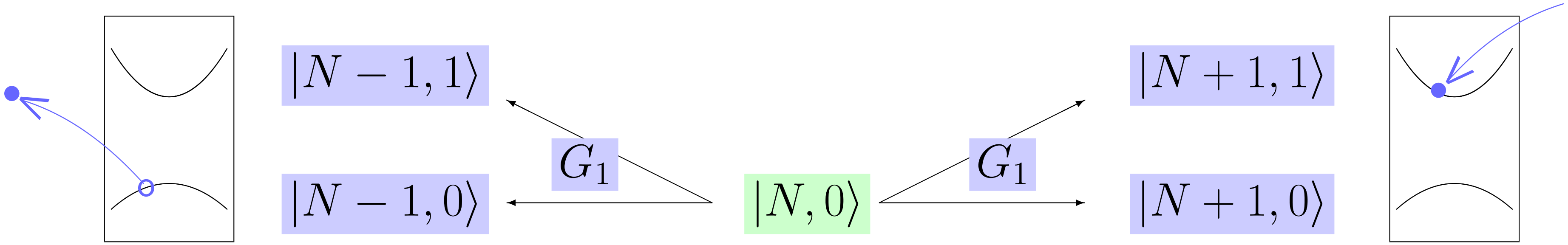
N Electrons

$|N, 0\rangle$

1. Ground state $|N, 0\rangle$: Density-functional theory $\Longrightarrow$ Geometry

States of a many-electron system

$N-1$ Electrons | N Electrons | $N+1$ Electrons



G_1 = Single-particle Green function

1. Ground state $|N,0\rangle$: Density-functional theory $\Longrightarrow$ Geometry

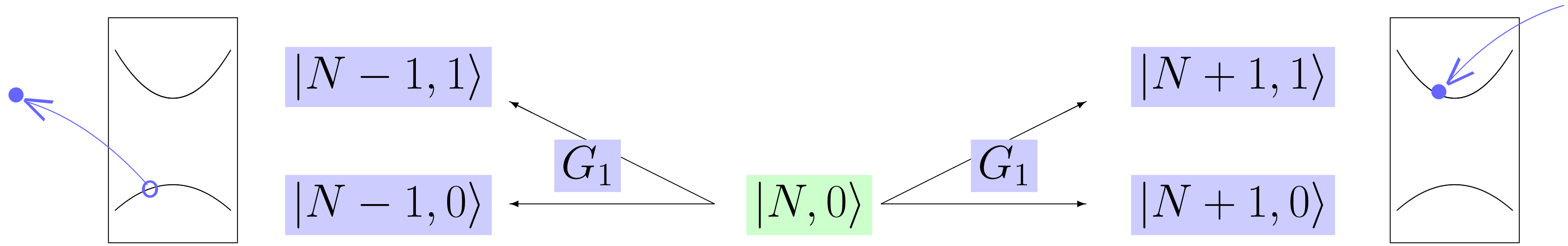
Many-body perturbation theory:

2. $|N,0\rangle \rightarrow |N\pm 1,m\rangle$: $G_1(\mathbf{x}t,\mathbf{x}'t') = -i\,\langle N,0\,|T\,(\psi(\mathbf{x},t)\psi^+(\mathbf{x}',t'))|\,N,0\rangle$

(Propagation of electron or hole between $(\mathbf{x},t)$ and $(\mathbf{x}',t')$)

States of a many-electron system

$N-1$ Electrons N Electrons $N+1$ Electrons



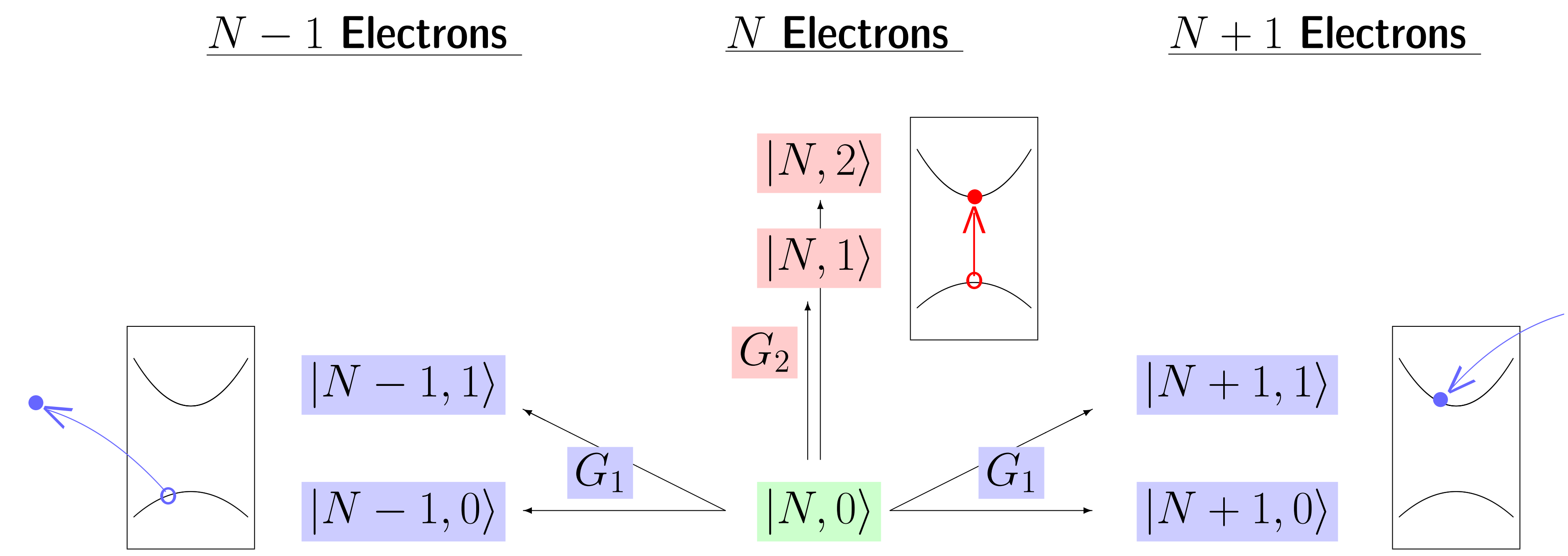
G_1 = Single-particle Green function

1. Ground state $|N,0\rangle$: Density-functional theory $\Longrightarrow$ Geometry

Many-body perturbation theory:

2. $|N,0\rangle \rightarrow |N\pm1,m\rangle$: Dyson equation for G_1 $\Longrightarrow$ Band structure

States of a many-electron system



G_1 = Single-particle Green function $\quad$ G_2 = Two-particle Green function

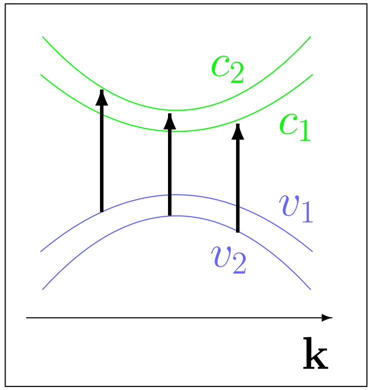
1. Ground state $|N,0\rangle$: Density-functional theory $\Longrightarrow$ Geometry

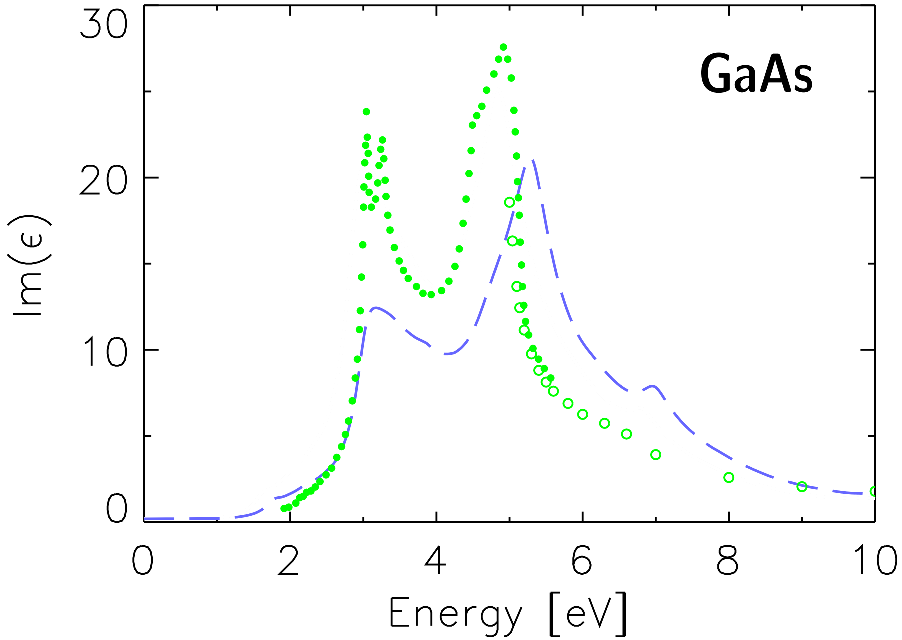
Many-body perturbation theory:

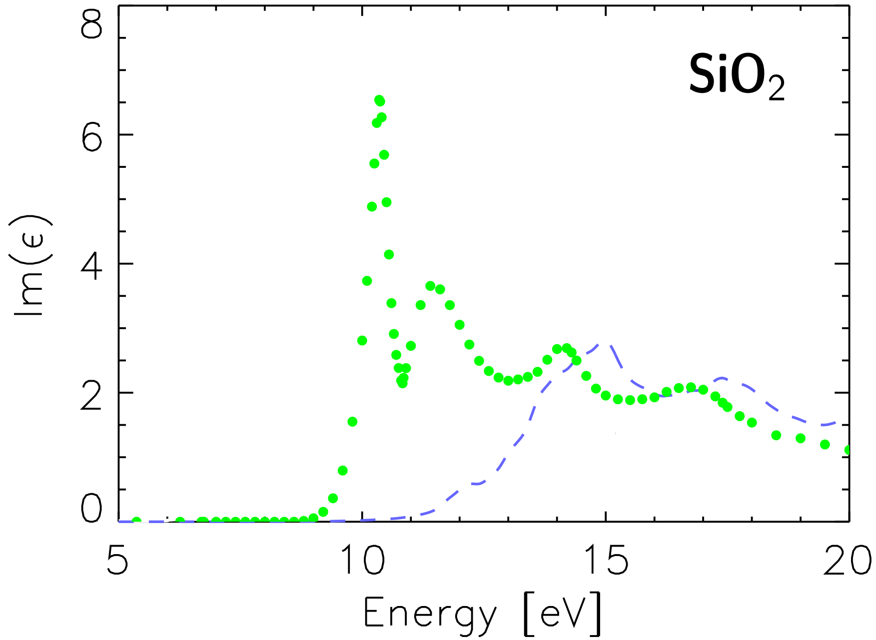
2. $|N,0\rangle \rightarrow |N \pm 1, m\rangle$: Dyson equation for G_1 $\Longrightarrow$ Band structure
3. $|N,0\rangle \rightarrow |N, m\rangle$: G_1 + Bethe-Salpeter Eq. for G_2 $\Longrightarrow$ El.-hole pairs

Bulk crystals: Optical absorption spectrum

- - - Free interband transitions: $\epsilon_2(\omega) \sim \sum_{v c \mathbf{k}} |M_{v c \mathbf{k}}|^2 \delta(\omega - (\varepsilon^{\text{QP}}_{c\mathbf{k}} - \varepsilon^{\text{QP}}_{v\mathbf{k}}))$







● ○ ○ Exp.:
D.E. Aspnes and A.A. Sturge, PRB 27, 985 (1983);
P. Lautenschlager et al., PRB 35, 9174 (1987);
H.R. Philipp, Sol.St.Comm. 4, 73 (1966).

[M. Rohlfing and S.G. Louie, PRL 81, 2312 (1998);
E. Chang, M.R. and S.G. Louie, PRL 85, 2613 (2000).]

The two-particle Green function G_2

[G. Strinati, PRB 29, 5718 (1984); Rivista del Nuovo Cimento 11, 1 (1988).]

$G_2(12;1'2') = -\langle N,0|T(\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(2')\hat{\psi}^\dagger(1'))|N,0\rangle$

Two-particle correlation function: $L(12,1'2') := -G_2(12,1'2') + G_1(11')\cdot G_1(22')$

Equation of motion (Bethe-Salpeter equation: BSE):

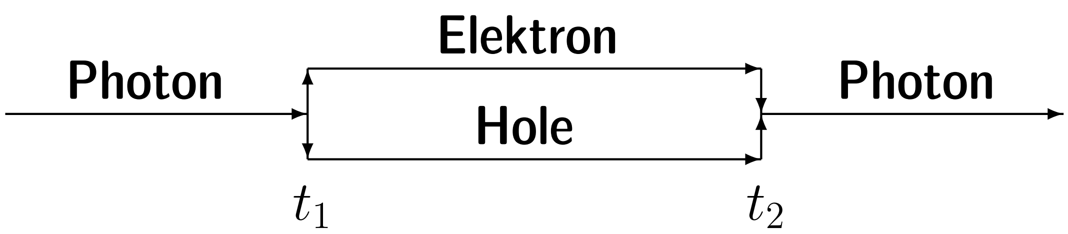
$$L(12;1'2') = L_0(12;1'2') + \int d(3456) L_0(14;1'3)K(35;46)L(62;52')$$

$L_0(12;1'2') \hat{=}$ independent particles $\quad K(35;46)$: Interaction kernel $\Longrightarrow$ Coupling

Depending on the order of the times t_1, t_2, t_1', t_2':

Propagation of two electrons / two holes / electron+hole

Here: t_1=t_1' and t_2=t_2' $\Longrightarrow$ Simultaneous creation of an electron/hole PAIR:



Explicit formulation of the Bethe-Salpeter equation

- Calculate G_1 from the (GW) QP states

$$\Longrightarrow L_0(12,1'2';\omega) = i\sum_{v,c}\left[\frac{\psi_c(\mathbf{x}_1)\psi_v^*(\mathbf{x}_1')\psi_v(\mathbf{x}_2)\psi_c^*(\mathbf{x}_2')}{\omega-(\epsilon_c-\epsilon_v)} - \frac{\psi_v(\mathbf{x}_1)\psi_c^*(\mathbf{x}_1')\psi_c(\mathbf{x}_2)\psi_v^*(\mathbf{x}_2')}{\omega+(\epsilon_c-\epsilon_v)}\right]$$

v = Sum over occupied states $\quad$ c = Sum over empty states

- Similar expansion: $L(12,1'2';\omega) = i\sum_{S}\left[\frac{\chi_S(\mathbf{x}_1,\mathbf{x}_1')\chi_S^*(\mathbf{x}_2',\mathbf{x}_2)}{\omega-\Omega_S} - \frac{\chi_S(\mathbf{x}_2,\mathbf{x}_2')\chi_S^*(\mathbf{x}_1',\mathbf{x}_1)}{\omega+\Omega_S}\right]$

(→ has a structure similar to the QP expansion of G_1)

- Particle-hole amplitudes $\chi_S(\mathbf{x},\mathbf{x}') = -\langle N,0|\psi^\dagger(\mathbf{x}')\psi(\mathbf{x})|N,S\rangle$

$$= \sum_{v}^{\text{occ}}\sum_{c}^{\text{empty}} A_{vc}^S\psi_c(\mathbf{x})\psi_v^*(\mathbf{x}') + B_{vc}^S\psi_v(\mathbf{x})\psi_c^*(\mathbf{x}')$$

- Expansion of χ_S in the QP states (v,c) $\hat{=}$ "Second Quantization":

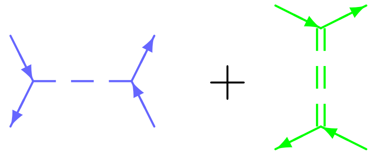
Double transformation from the continuous 3D space into a discrete basis

The electron-hole interaction K^{eh}

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

$[\ 1 \hat{=} (\mathbf{r}_1, \sigma_1, t_1)$ etc.$]$

Assume: $\Sigma = iG_1 W$ **and** $G_1 \dfrac{\delta W}{\delta G_1} \approx 0$



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

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

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

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

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

Bethe-Salpeter equation: (standard) eigenvalue problem

- Equation of motion for $L \Longrightarrow$ Eigenvalue problem

$$
\begin{aligned}
(E_c - E_v)A^S_{vc} + \sum_{v'c'} K^{AA}_{vc,v'c'}(\Omega_S)A^S_{v'c'} \; + \; \sum_{v'c'} K^{AB}_{vc,v'c'}(\Omega_S)B^S_{v'c'} &= \Omega_S A^S_{vc} \\
\sum_{v'c'} K^{BA}_{vc,v'c'}(\Omega_S)A^S_{v'c'} \; + \; (E_c - E_v)B^S_{vc} + \sum_{v'c'} K^{BB}_{vc,v'c'}(\Omega_S)B^S_{v'c'} &= -\Omega_S B^S_{vc}
\end{aligned}
$$

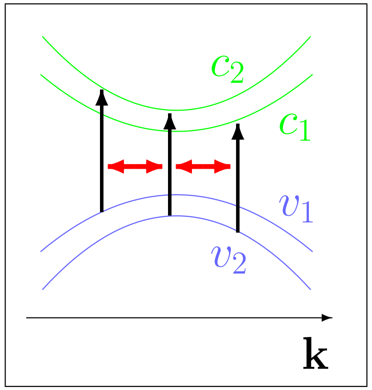
- The electron-hole interaction matrix elements are given by

$$
\begin{aligned}
K^{AA}_{vc,v'c'}(\Omega_S) &= i \int d(3456)\, \psi_v(\mathbf{x}_4)\, \psi^*_c(\mathbf{x}_3)\, K(35,46;\Omega_S)\, \psi^*_{v'}(\mathbf{x}_5)\, \psi_{c'}(\mathbf{x}_6) \\
K^{AB}_{vc,v'c'}(\Omega_S) &= i \int d(3456)\, \psi_v(\mathbf{x}_4)\, \psi^*_c(\mathbf{x}_3)\, K(35,46;\Omega_S)\, \psi^*_{v'}(\mathbf{x}_6)\, \psi_{c'}(\mathbf{x}_5) \\
&\cdots
\end{aligned}
$$

- "Tamm-Dankoff approx.": The off-diagonal blocks K^{AB} and K^{BA} are small $\Longrightarrow$ Neglect them:

$$
(E_c - E_v)A^S_{vc} + \sum_{v'c'} K^{AA}_{vc,v'c'}(\Omega_S)A^S_{v'c'} = \Omega_S A^S_{vc} \quad , \quad \text{i.e.} \quad |N,S\rangle = \sum_{v,c} A^S_{vc}\, \hat{a}^\dagger_v\, \hat{b}^\dagger_c\, |N,0\rangle
$$

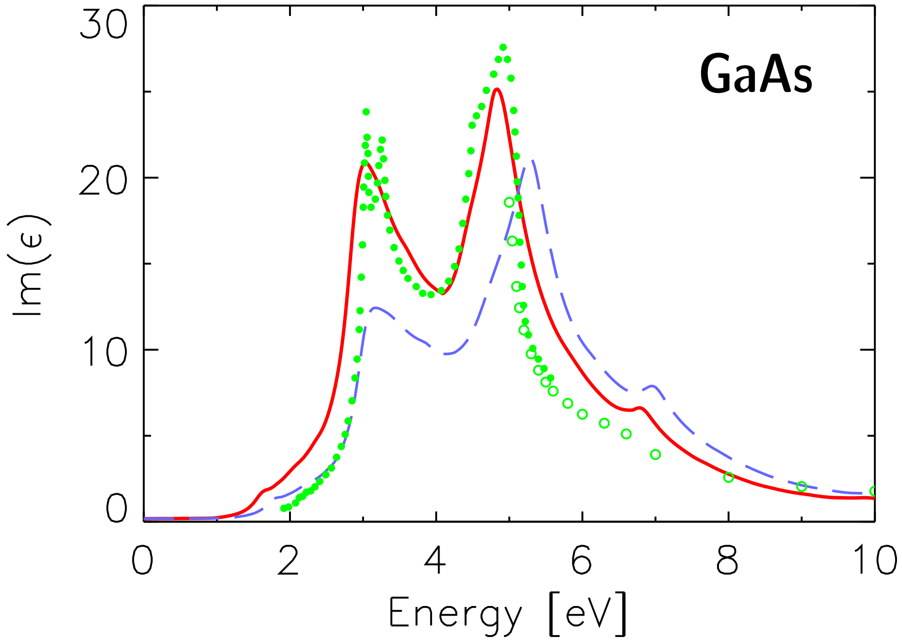
Bulk crystals: Optical absorption spectrum

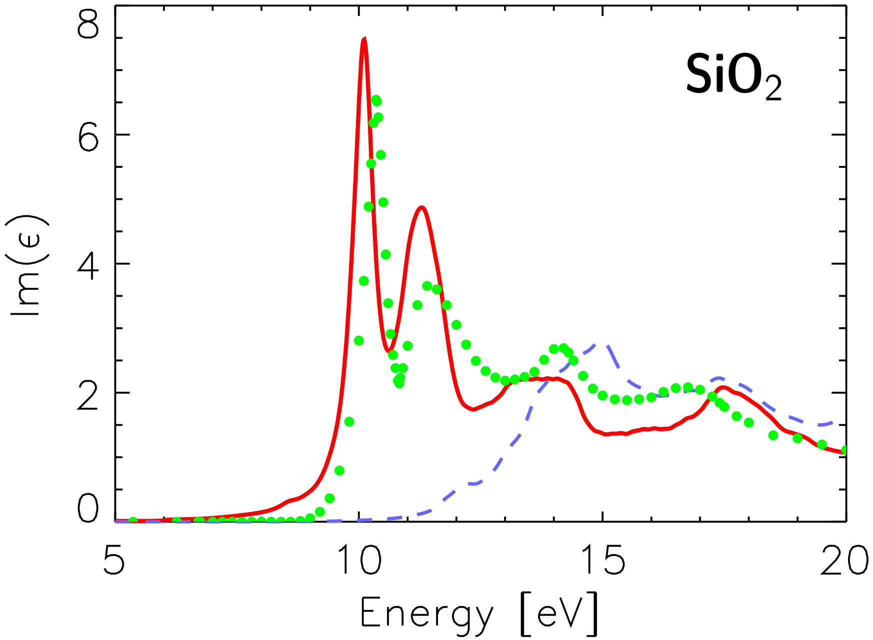


- - - Free interband transitions: $\epsilon_2(\omega) \sim \sum_{vc\mathbf{k}} |M_{vc\mathbf{k}}|^2 \delta(\omega - (\varepsilon_{c\mathbf{k}}^{\mathrm{QP}} - \varepsilon_{v\mathbf{k}}^{\mathrm{QP}}))$

—— With electron-hole interaction: coupled excitations $|S\rangle$

$$\epsilon_2(\omega) \sim \sum_S |M_S|^2 \, \delta(\omega - \Omega_S)$$





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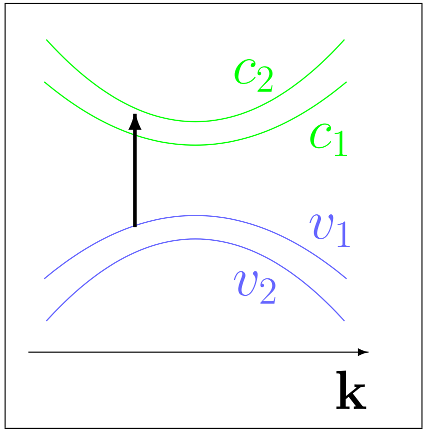
Effect of the electron-hole interaction

- **Without interaction:**

$$(\varepsilon^{\text{QP}}_{c\mathbf{k}+\mathbf{Q}} - \varepsilon^{\text{QP}}_{v\mathbf{k}})\, A^S_{vc\mathbf{k}} = \Omega_S\, A^S_{vc\mathbf{k}}$$

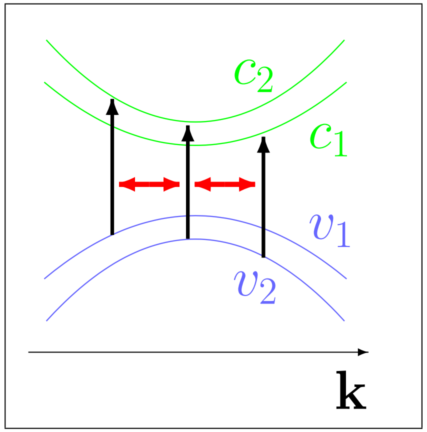
$\Longrightarrow$ Free interband transitions; $\quad \Omega_S = (\varepsilon^{\text{QP}}_{c\mathbf{k}+\mathbf{Q}} - \varepsilon^{\text{QP}}_{v\mathbf{k}})$



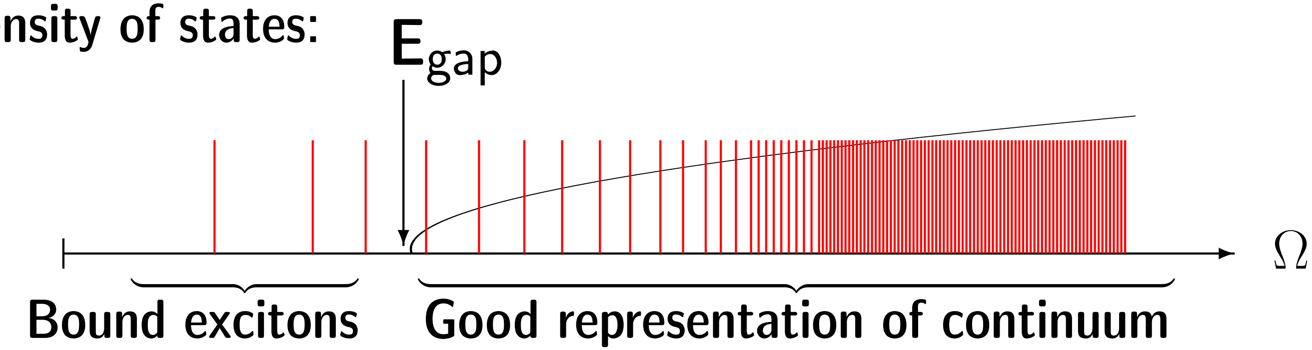
- **With interaction:**

$$(\varepsilon^{\text{QP}}_{c\mathbf{k}+\mathbf{Q}} - \varepsilon^{\text{QP}}_{v\mathbf{k}})\, A^S_{vc\mathbf{k}} + \sum_{v'c'\mathbf{k}'} \langle vc\mathbf{k}|K^{eh}|v'c'\mathbf{k}'\rangle\, A^S_{v'c'\mathbf{k}'} = \Omega_S\, A^S_{vc\mathbf{k}}$$

All electron-hole excitation energies



$\Longrightarrow$ Density of states:



Effect of the electron-hole interaction on the optical spectrum:

- **Free interband transitions / nointeraction:**

$$\epsilon_2(\omega) = \frac{4\pi e^2}{\omega^2} \sum_{vc\mathbf{k}} |M_{vc\mathbf{k}}|^2 \, \delta(\omega - (\varepsilon^{QP}_{c\mathbf{k}} - \varepsilon^{QP}_{v\mathbf{k}}))$$

$M_{vc\mathbf{k}} = \vec{\lambda} \cdot \langle v\mathbf{k}|\vec{V}|c\mathbf{k}\rangle$

$\vec{\lambda}$ **Polarisation of the light**

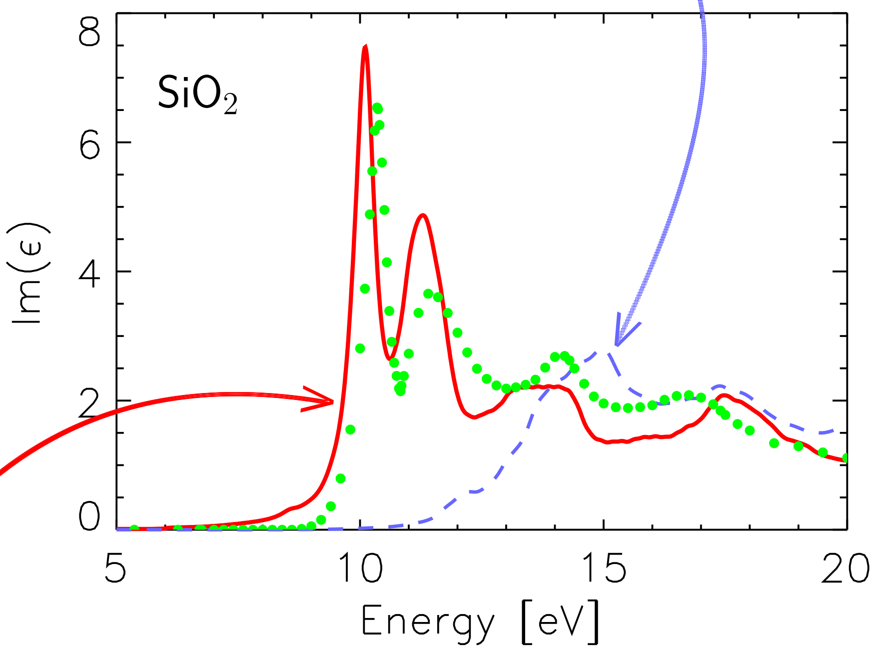
$\vec{V}$ **Velocity operator**

- **Coupled excitations / $(\Delta\varepsilon + K^{eh})A_S = \Omega_S A_S$:**

$$\epsilon_2(\omega) = \frac{4\pi e^2}{\omega^2} \sum_{S} |M_S|^2 \, \delta(\omega - \Omega_S)$$

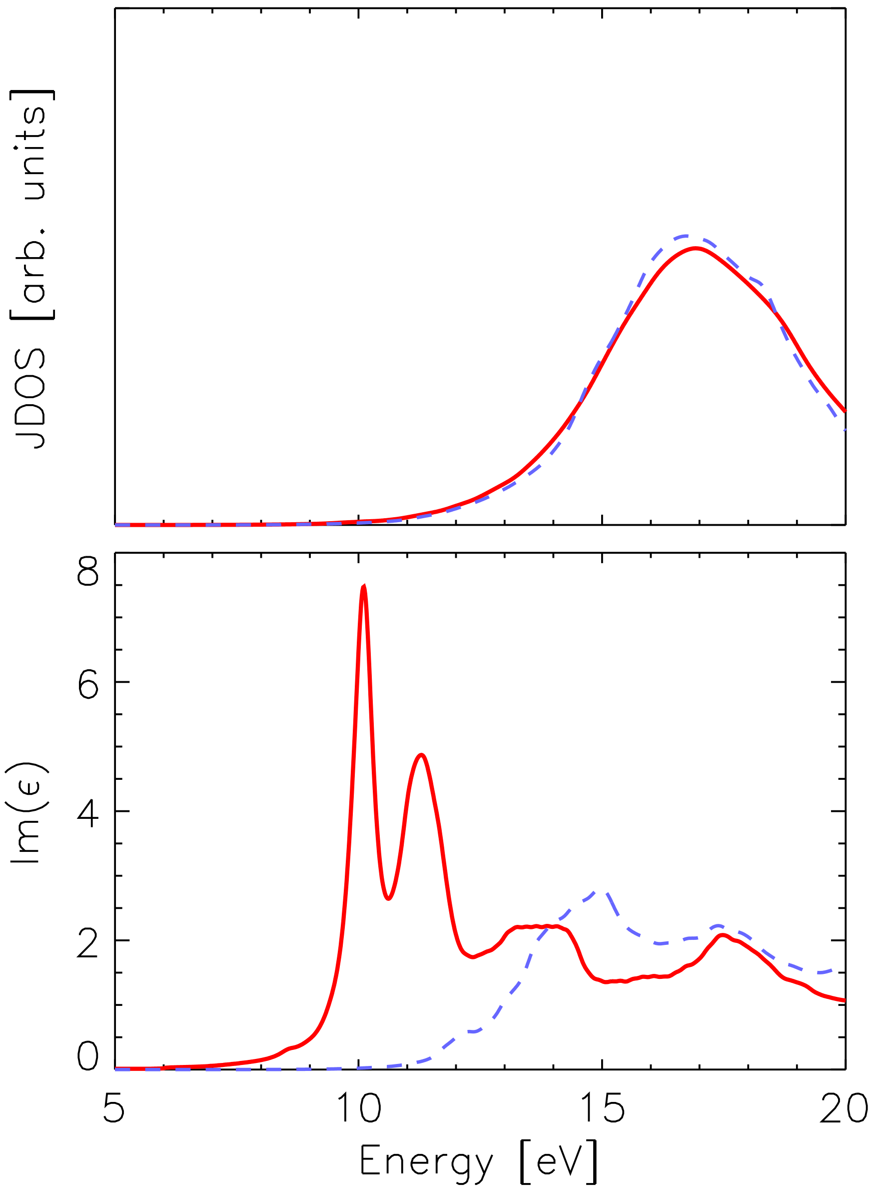
$M_S = \vec{\lambda} \cdot \langle 0|\vec{V}|S\rangle = \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} \, M_{vc\mathbf{k}}$

Coherent superposition $M_{vc\mathbf{k}} \rightarrow M_S$;
phase sensitive $\longrightarrow$ constructive / destructive!



● ○ ○ **Exp.:**
H.R. Philipp, Sol.St.Comm. 4, 73 (1966).

SiO_2: $\epsilon_2(\omega) \longleftrightarrow$ JDOS



- - - Without interaction:
Free interband transitions $|vc\mathbf{k}\rangle$

—— With interaction:
Coupled Excitations $|S\rangle$

- The density of states is only weakly modified by K^{eh}.
- The modifications in the SPECTRUM result from INTERFERENCE:

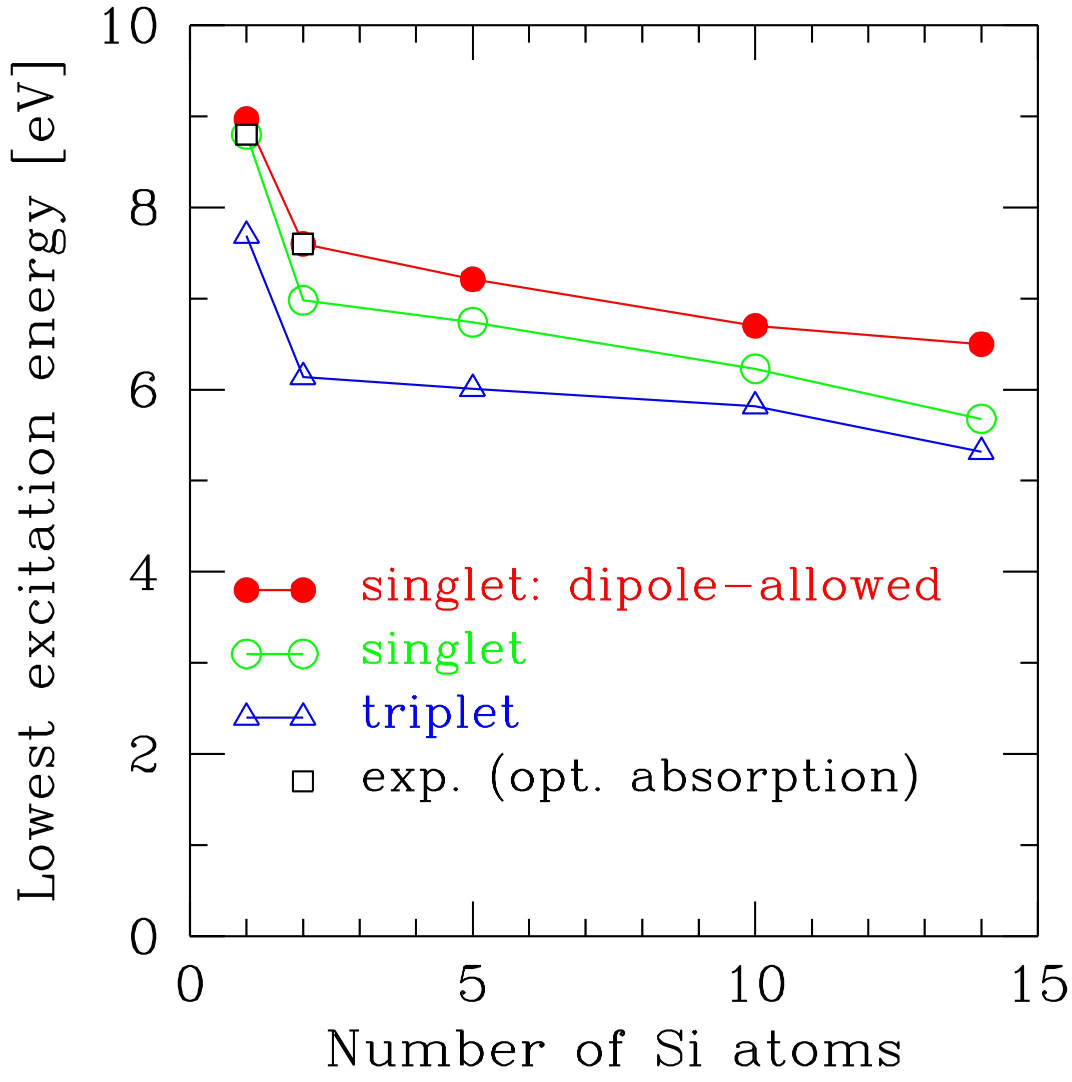
$$M_S = \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} M_{vc\mathbf{k}}$$

Excitation energies of atoms and molecules

[eV]	Spin singlet BSE	Spin singlet Exp.[a]	Spin triplet BSE	Spin triplet Exp.[a]
He	20.75	20.615	19.81	19.818
Ne	16.95	16.848	16.71	16.668
Ar	11.99	11.827	11.76	11.631
CO	7.9	8.03	5.5	6.01
HCl	7.5	8.1	6.9	
CH_4	8.6	8.52	8.2	
C_2H_4	7.0	7.11	3.7	4.36

[a]Exp.: Landolt-Börnstein, Vol. I-1 (1950);
G. Herzberg, *Molecular Spectra* (1966);
L. Serrano-Andres *et al.*, JCP 98, 3151 (1993).

Si_mH_n Cluster:



Exp.: U. Itoh et al., J.Chem.Phys. 85, 4867 (1986).

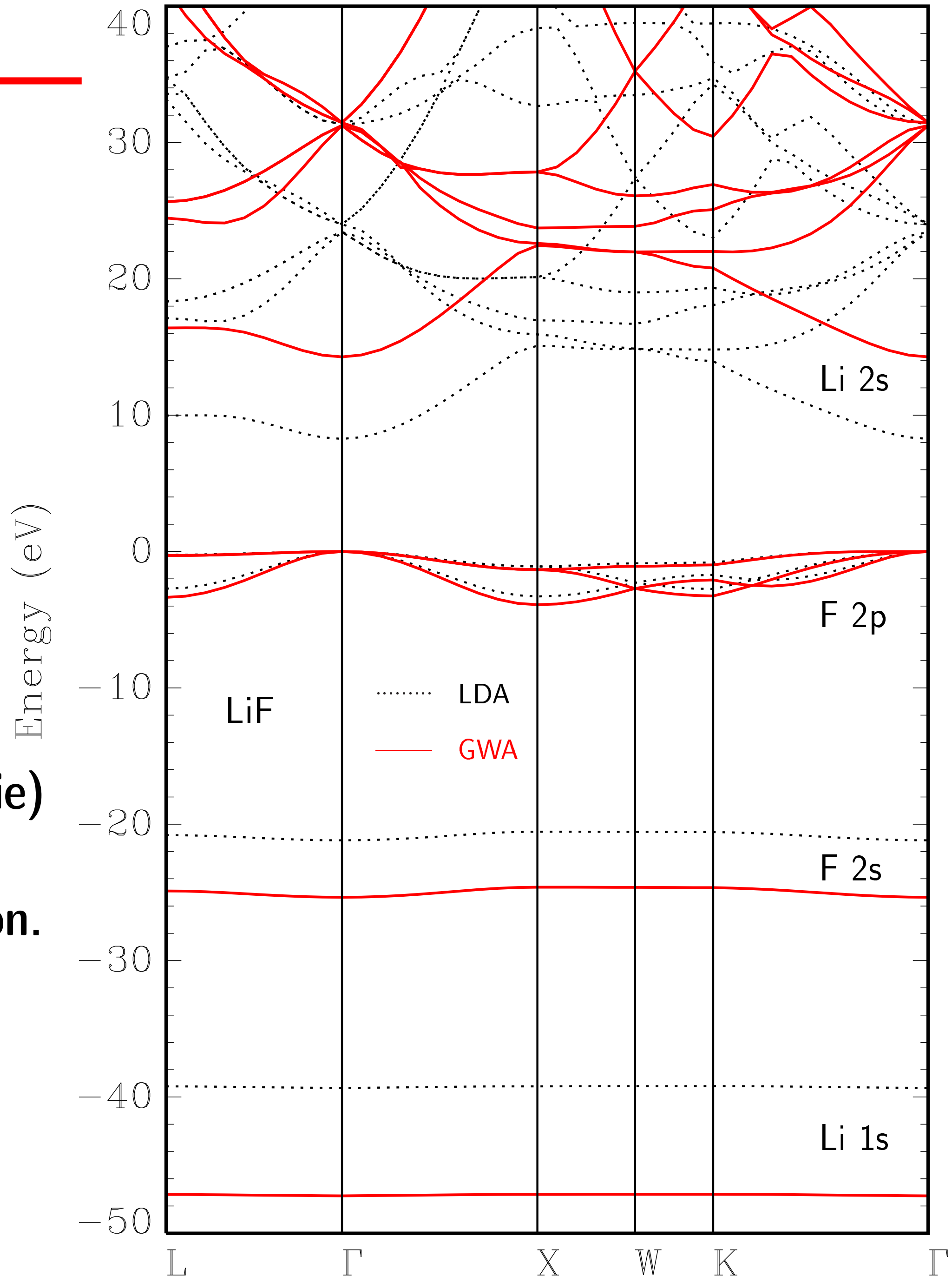
LiF: Bulk Band Structure

- Dielectric constant: $\epsilon_\infty^{\text{RPA}} = 1.8$

- Some band-structure energies:

[eV]	LDA	Δ^{QP}	QP	Exp.[1]
Li $1s$	–39.3	–7.9	–47.2	–49.8
F $2s$	–20.8	–4.2	–25.0	–23.9
F $2p$	-2.7..0	–0.6..0	–3.3..0	
"Li $2s$"	8.3...	+6.0...	14.3...	14.4...
E_{gap}	8.3	+6.0	14.3	14.4...

- A dielectric model function (Hybertsen/Louie) yields the same band structure near the gap
  $\Longrightarrow$ We use this model function from now on.



Exp.: L.I. Johansson and S.B.M. Hagström,
Physica Scripta 14, 55 (1976);
D.M. Roessler and W.C. Walker,
J.Opt.Soc.Am. 57, 835 (1967).

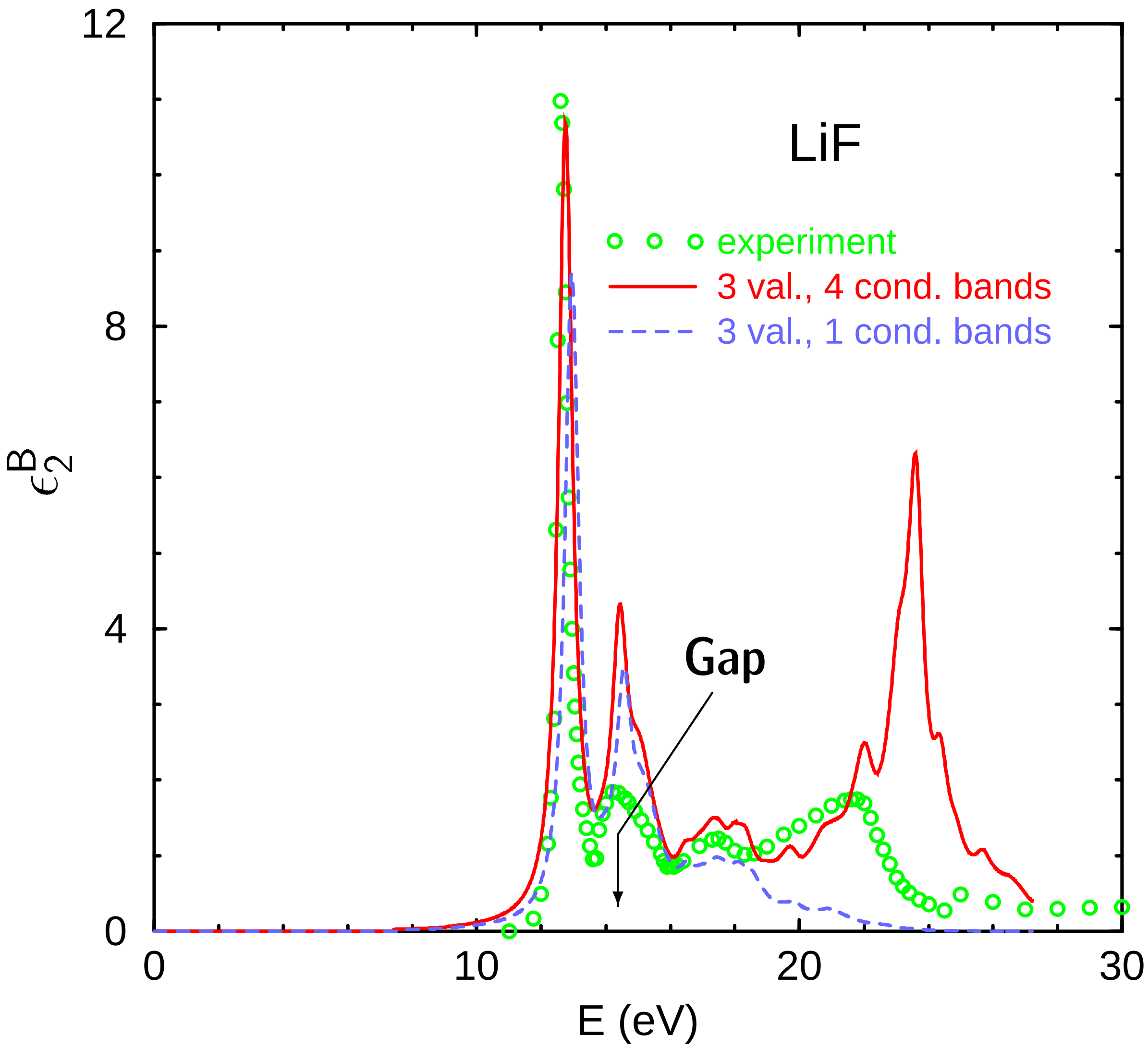
LiF: Bulk Absorption Spectrum

- Exciton at 12.8 eV
  (1.5 eV below E_{gap}=14.3 eV)

- Matrix size of $H^{e,h}$:

	F $2p \rightarrow$ "Li $2s+p$"	F $2p \rightarrow$ "Li $2s$"
Bulk (256 k)	3 x 4 x 256 = 3072	3 x 1 x 256 = 768
6-L Slab (64 $k_{\|}$)	18 x 24 x 64 = 27648	18 x 6 x 64 = 6912

- F $2p \rightarrow$ "Li $2s$":
  Good representation of the exciton
  AND convenient matrix size.



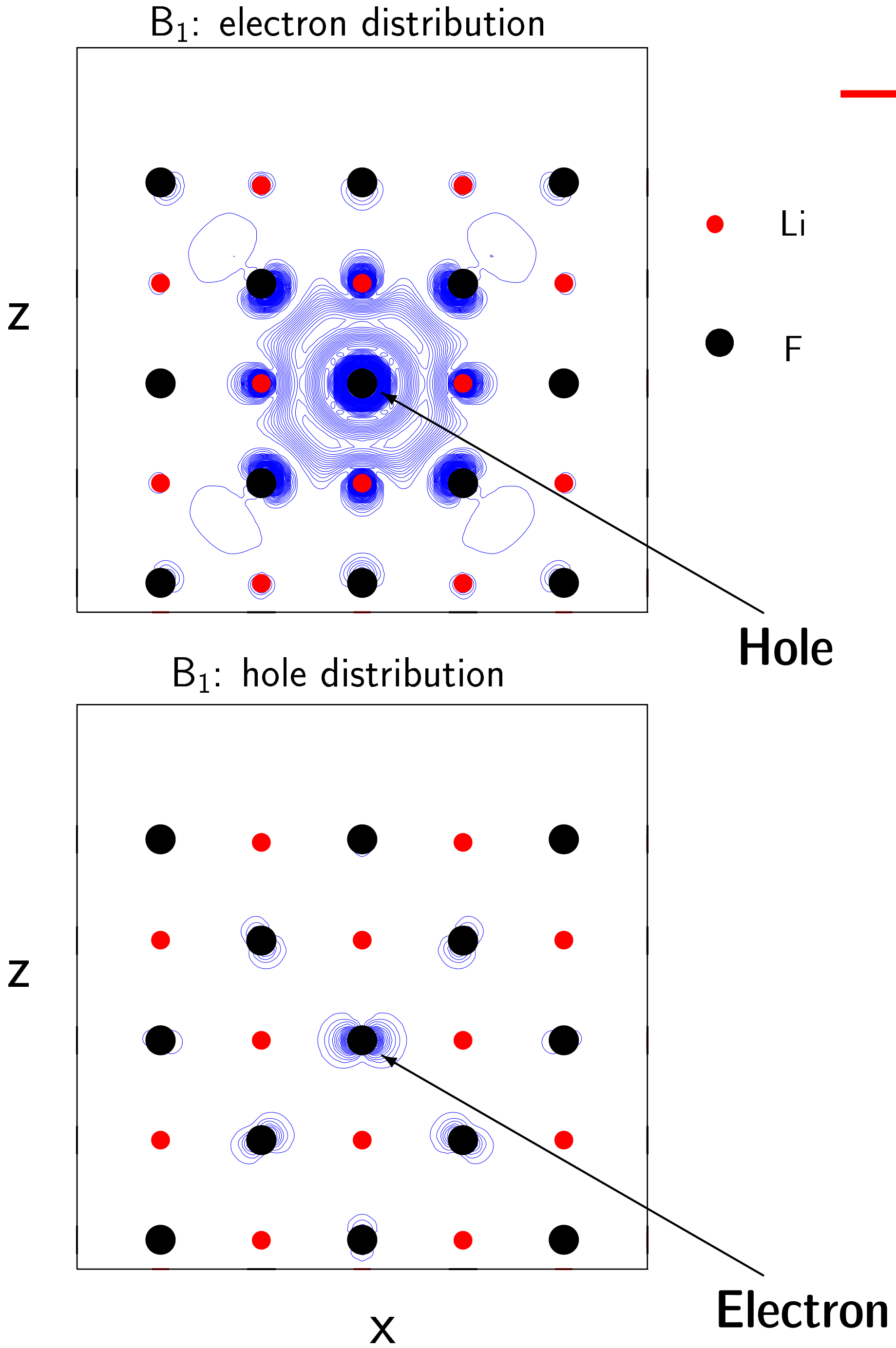
LiF Exciton: Electron-Hole Correlation

Exciton wave function (2-particle correlation function):

$$\chi_S(\mathbf{r_h}, \mathbf{r_e}) \;=\; \sum_{\mathbf{k}} \sum_{v}^{hole} \sum_{c}^{elec} A^S_{vc\mathbf{k}} \psi^*_{v\mathbf{k}}(\mathbf{r_h}) \psi_{c\mathbf{k+Q}}(\mathbf{r_e})$$

$\mathbf{r_h}$ **fixed** $\Longrightarrow \chi_S(., \mathbf{r_e})$ **= Distribution of the electron**

$\mathbf{r_e}$ **fixed** $\Longrightarrow \chi_S(\mathbf{r_h}, .)$ **= Distribution of the hole**

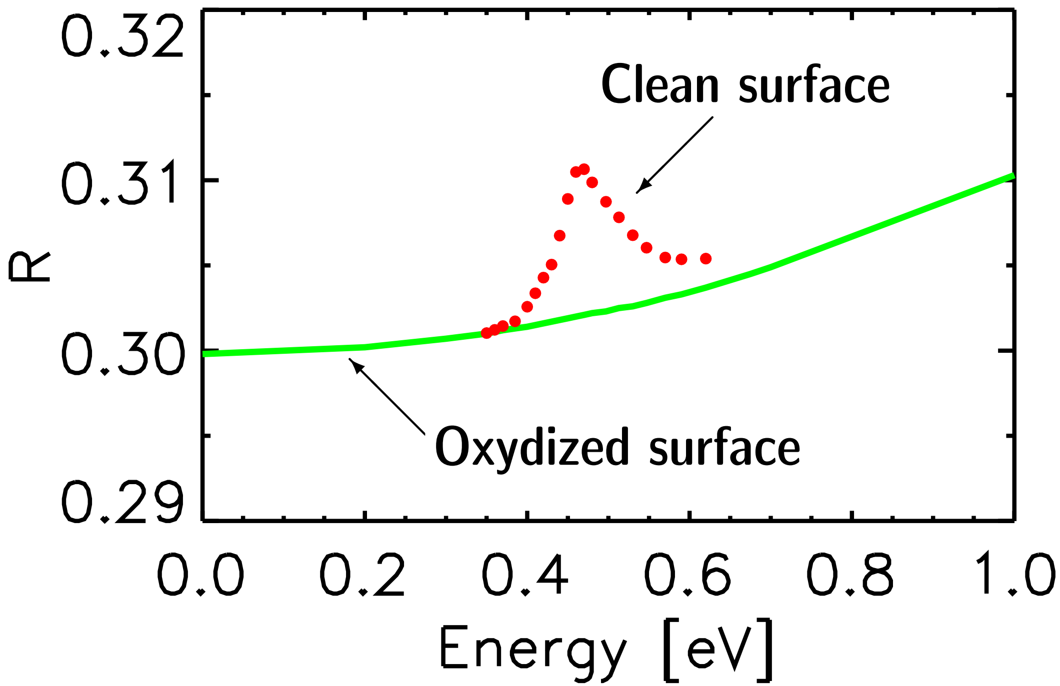


Si(111)-(2×1): Surface Exciton

Experiment (Internal Reflection; DRS):
G. Chiarotti,, PRB 4, 3398 (1971);
P. Chiaradia et al., PRL 52, 1145 (1984);
F. Ciccaci et al., PRL 56, 2411 (1986).

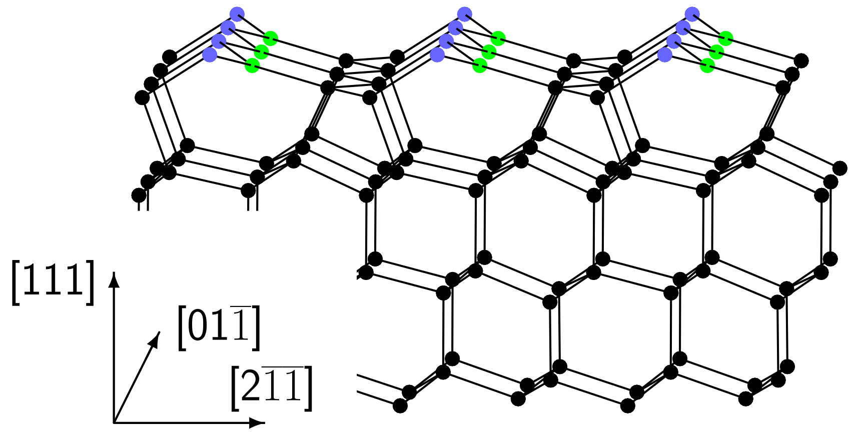
Theory: J.E. Northrup et al., PRL 66, 500 (1991);
L. Reining and R. Del Sole, PRL 67, 3816 (1991);
M. Rohlfing and S.G. Louie, PRL 83, 856 (1999).
M. Rohlfing and J. Pollmann, PRL 88, 176801 (2002).

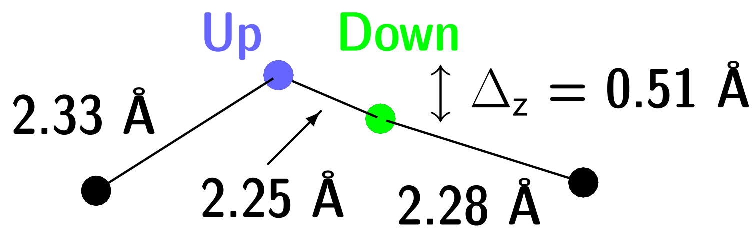
Reflectivity (exp.):



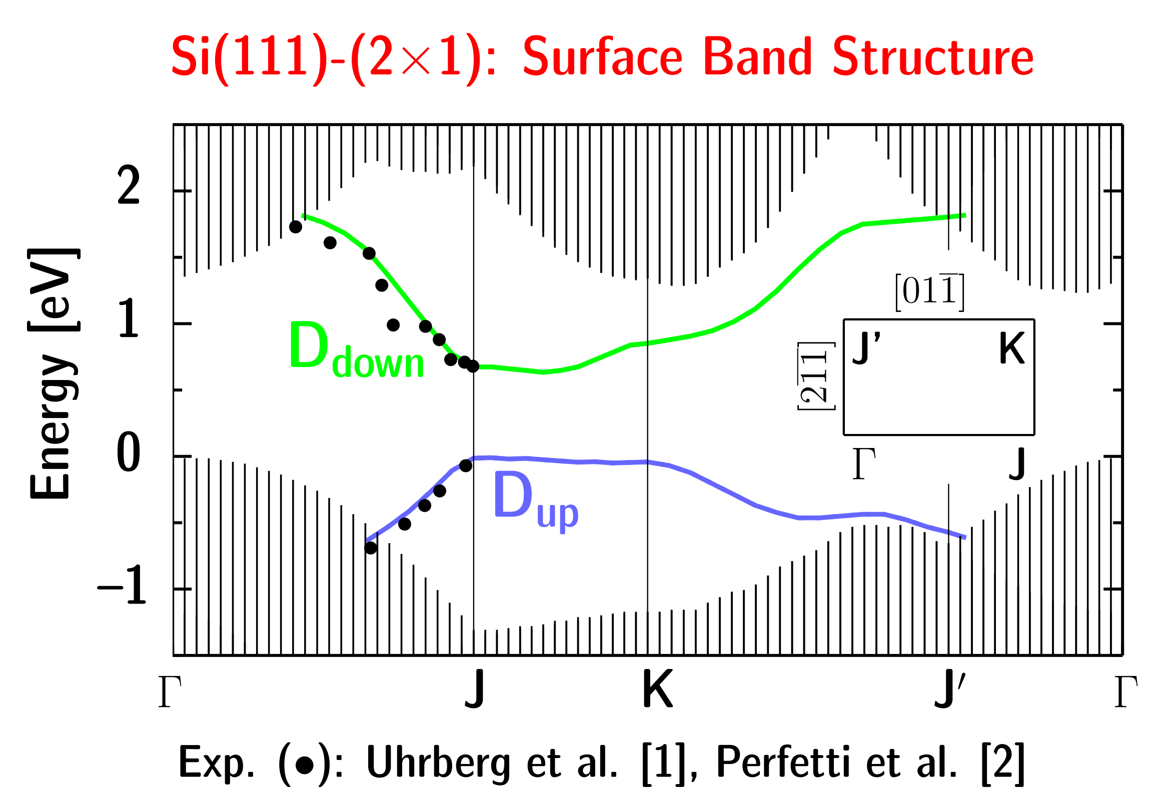
$\Longrightarrow$ Surface Exciton at 0.45 eV

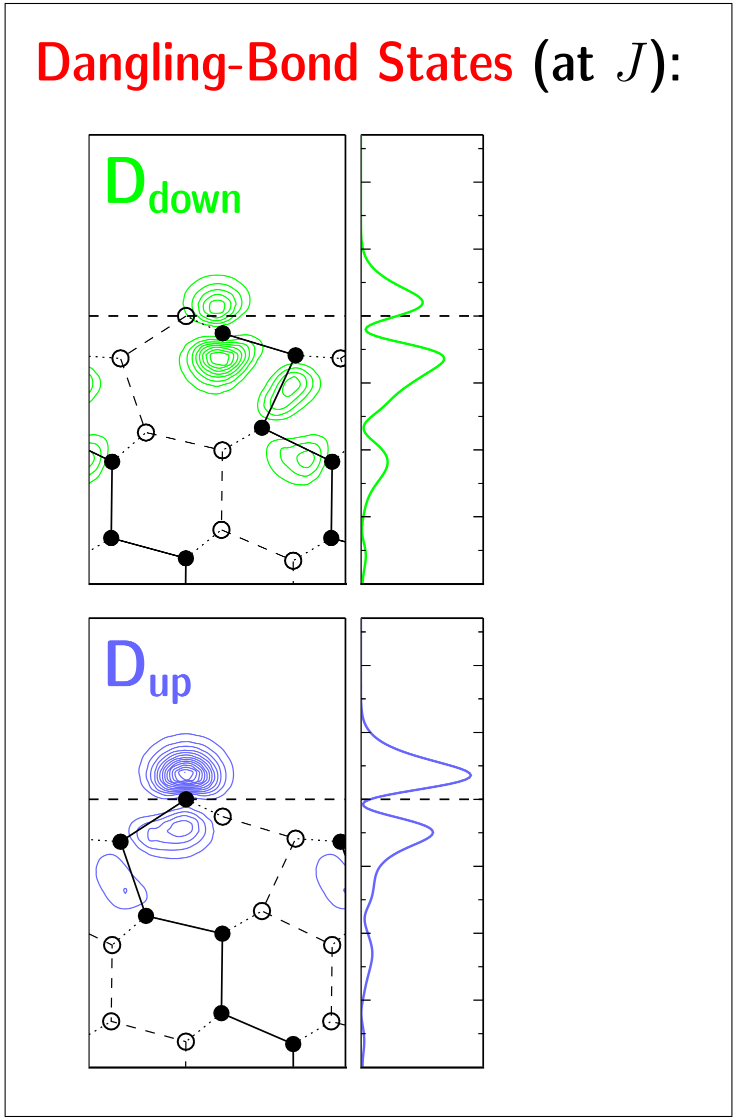
Structure of the surface: Pandey chains





Si(111)-(2×1): Surface Band Structure





Surface Gap [eV]:		
This work	0.69	[GWA]
ARPES+ARIPES	0.75	[1, 2]
ARPES (n-Si)	0.5	[3]
STM	0.6	[4]

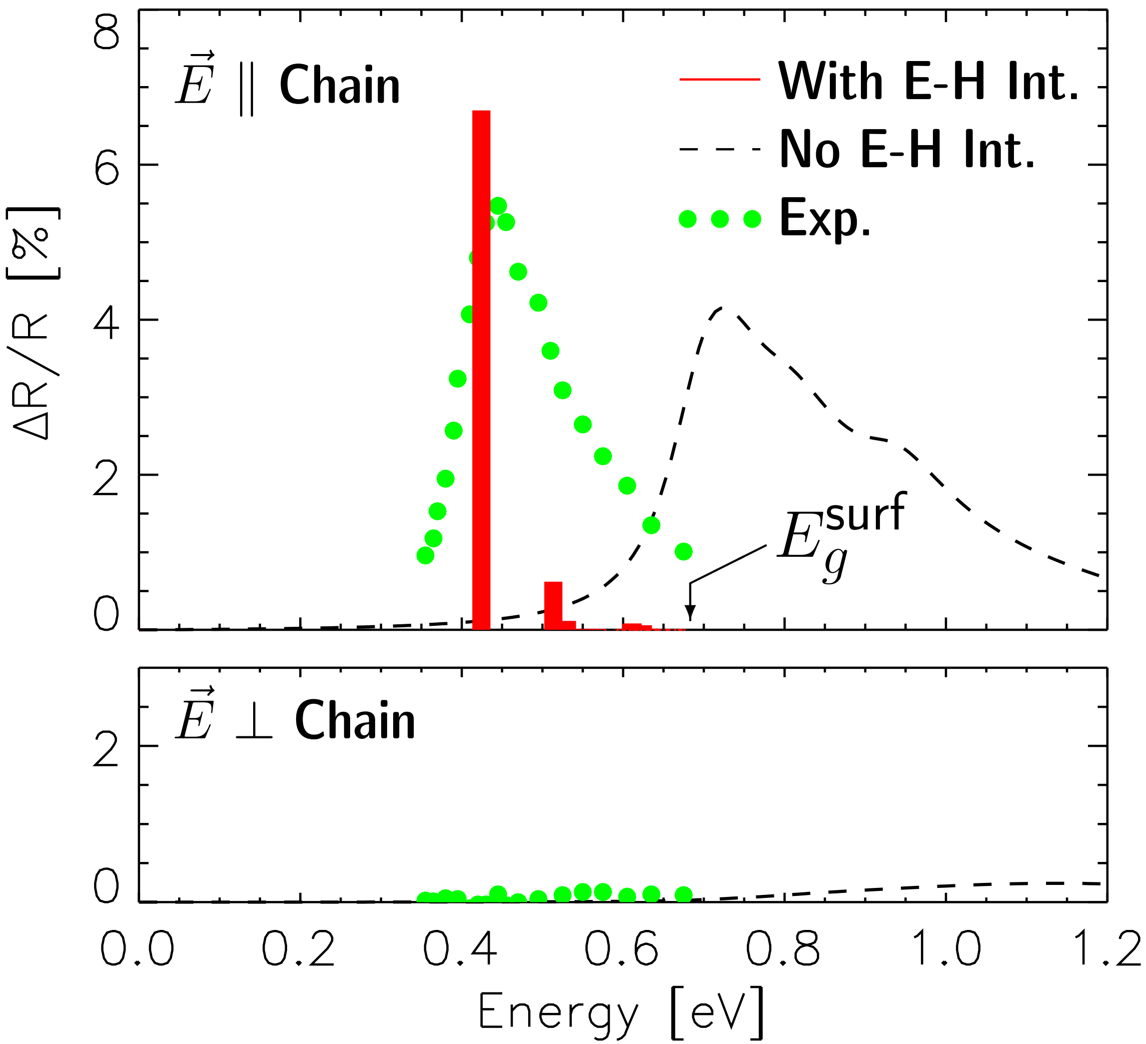
[1] R.I.G. Uhrberg et al. [PRL 48, 1032 (1982)]

[2] P. Perfetti et al. [PRB 36, 6160 (1987)]; A. Cricenti et al. [PRB 41, 12908 (1990)]

[3] P. Martensson et al. [PRB 32, 6959 (1985)]

[4] R.M. Feenstra et al. [PRL 56, 608 (1986); PRL 57, 2579 (1986).]

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



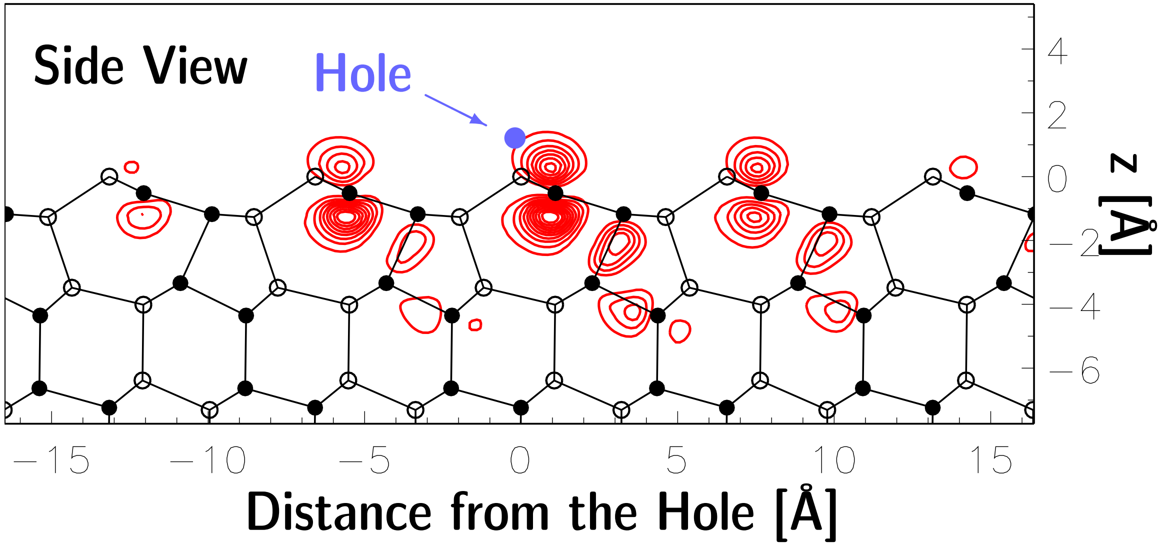
Exp.: P. Chiaradia et al., PRL 52, 1145 (1984).

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

[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).

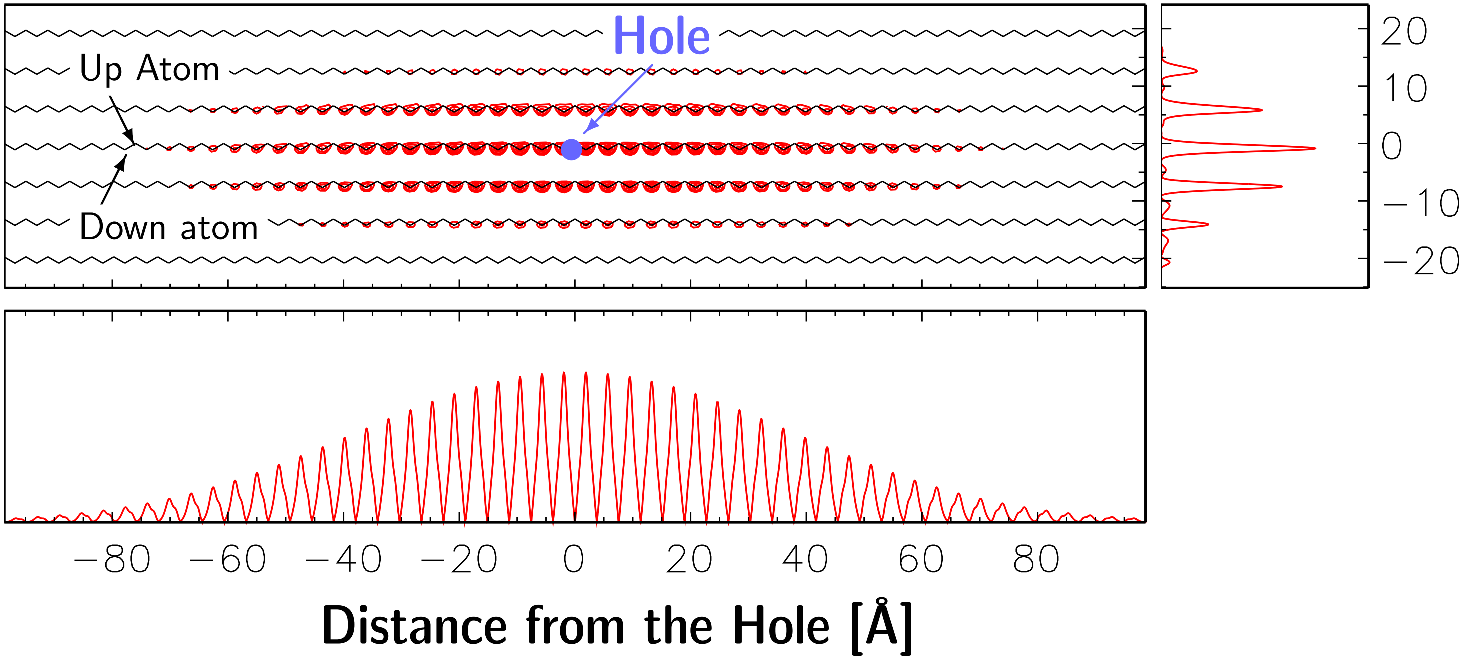
Exciton Wave Function: Electron Distribution Relative to the Hole



$$\chi^S(\mathbf{r}_\mathrm{h}, \mathbf{r}_\mathrm{e}) = \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} \, \psi^*_{v\mathbf{k}}(\mathbf{r}_\mathrm{h}) \, \psi_{c\mathbf{k}+\mathbf{Q}}(\mathbf{r}_\mathrm{e})$$

[$\mathbf{r}_\mathrm{h}$ = coordinates of Hole, $\mathbf{r}_\mathrm{e}$=Electron]

Top View:



Mean distance

Electron—Hole:

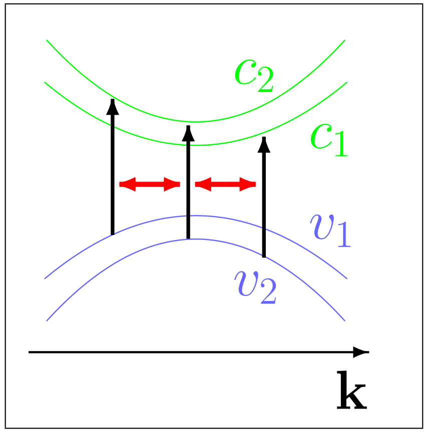
– along chain: 40 Å

(∼ Wannier Exciton)

– perpendicular: 8 Å

(∼ Frenkel Exciton)

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

- **Bethe-Salpeter equation for G_2 or, resp., $|S\rangle$:**

$$(E^{\text{QP}}_{c\mathbf{k}+\mathbf{Q}} - E^{\text{QP}}_{v\mathbf{k}}) \, A^S_{vc\mathbf{k}} + \sum_{v'c'\mathbf{k}'} \langle vc\mathbf{k}|K^{eh}|v'c'\mathbf{k}'\rangle \, A^S_{v'c'\mathbf{k}'} = \Omega_S \, A^S_{vc\mathbf{k}}$$

$E^{\text{QP}}_{v\mathbf{k}}$, $E^{\text{QP}}_{c\mathbf{k}+\mathbf{Q}}$ 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
$\Longrightarrow$ Correlation in the interaction

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