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SPRING COLLEGE ON
NUMERICAL METHODS IN ELECTRONIC STRUCTURE THEORY

(7 - 25 May 2001)

"Electronic excitations and response functions in solids and reduced dimensional systems"

presented by:

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Electronic Excitations and Response Functions in Solids and Reduced Dimensional Systems

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Outline

- Introduction

- Excited States and Spectroscopies

  - Quasiparticle excitations and the GW approximation
  - Excitonic effects in optical response and the Bethe-Salpeter equation

- Examples of Applications

  - Semiconductors and insulators
  - Conjugated polymers
  - Surfaces, clusters, and atoms

- Summary

Properties of Solids

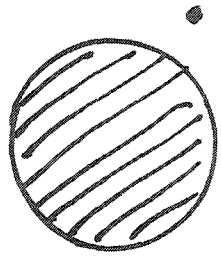
Ground-state Properties:

Cohesive
Structural
Vibrational
Magnetic structure
Phase transformations
...

- Etot [{Ri}]
- Density Functional Theory (LDA, GGA)

Spectroscopic Properties:

Photoemission
Tunneling
...



- N+1 Particle Problem
- Quasiparticle Approach (GW)

Optical

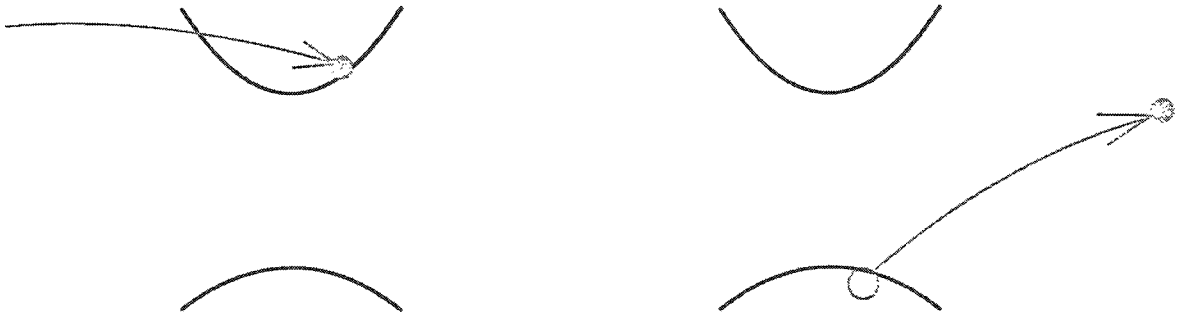
- N+2 Particle Problem
- Electron-hole interaction

- **Quasiparticle band structure:**

  describes individually excited holes and electrons
  (↔ One-particle Green function G_1)

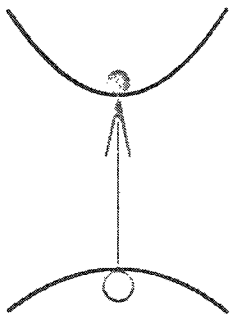
  Quasi-electron: $N \rightarrow N+1$
  (inverse photoemission; tunneling)

  Quasi-hole: $N \rightarrow N-1$
  (photoemission; tunneling)



- **Optical experiment (e.g., absorption):**

  – **Creation of** electron-hole pair: $N \rightarrow N^*$
  – **Electron-hole interaction**
  – Requires a two-particle approach
  on top of the QP band structure



Quasiparticle (QP) band structure calculations

- Density-functional theory:

$$\left\{-\nabla^2 + V_{\text{ext}} + V_{\text{Coul}} + V_{\text{xc}}\right\} \psi_{\mathbf{nk}}^{\text{DFT}} = \varepsilon_{\mathbf{nk}}^{\text{DFT}} \psi_{\mathbf{nk}}^{\text{DFT}}$$

Hohenberg, Kohn, and Sham 1965

- Green-function approach + QP approximation:

$$\left\{-\nabla^2 + V_{\text{ext}} + V_{\text{Coul}} + \Sigma(\varepsilon_{\mathbf{nk}}^{\text{QP}})\right\} \psi_{\mathbf{nk}}^{\text{QP}} = \varepsilon_{\mathbf{nk}}^{\text{QP}} \psi_{\mathbf{nk}}^{\text{QP}}$$

Dyson's Eq.

$\Sigma = iG_1 W$ GW approximation for the self energy

G_1 one-particle Green function

$W = \epsilon^{-1} v$ screened Coulomb interaction

Hedin 1965, Hybertsen and Louie 1985

$$W(\underset{\sim}{r}, \underset{\sim}{r}', \omega) = \int \epsilon^{-1}(\underset{\sim}{r}, \underset{\sim}{r}'', \omega) \frac{e^2}{|\underset{\sim}{r}'' - \underset{\sim}{r}'|} d\underset{\sim}{r}''$$

Quasiparticle Excitations

Kohn-Sham Eigenvalues ≠ QP Energies

Two simple examples:

- Homogeneous Interacting Electron System

  Standard K-S equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{ext} + V_H + \frac{\delta E_{xc}}{\delta \rho(r)}\right]\psi(r) = \varepsilon_{KS}\,\psi(r)$$

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)} = \text{constant} \Rightarrow \text{Free electron dispersion}$$

$(m^* = m_e, \text{etc.})$, ∞ lifetime

Incorrect!

- Generalized K-S eigenvalues not unique

  Different "K-S equations" → new set of eigenvalues

GW Approximation $\Sigma =$ 

$$\Sigma(\vec{r},\vec{r}';E) = \frac{i}{2\pi}\int W(\vec{r},\vec{r}',\omega)G(\vec{r},\vec{r}',E+\omega)e^{i\delta\omega}d\omega$$

with

$$W(\vec{r},\vec{r}',\omega) = \int v(\vec{r},\vec{r}'')\varepsilon^{-1}(\vec{r}'',\vec{r}',\omega)d^3r''$$

$$G(\vec{r},\vec{r}',\omega) = \sum_{n\vec{k}} \frac{\psi_{n\vec{k}}(\vec{r})\psi^{*}_{n\vec{k}}(\vec{r}')}{\omega - E_{n\vec{k}} - i\delta_{n\vec{k}}}$$

Require:

(1) Full dielectric matrix (local fields)

$$\varepsilon^{-1}(\vec{r}',\vec{r},\omega) \text{ or } \varepsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q},\omega)$$

(2) Good starting $\psi_{n\vec{k}}$ and $E_{n\vec{k}}$ to construct the Green's function G.

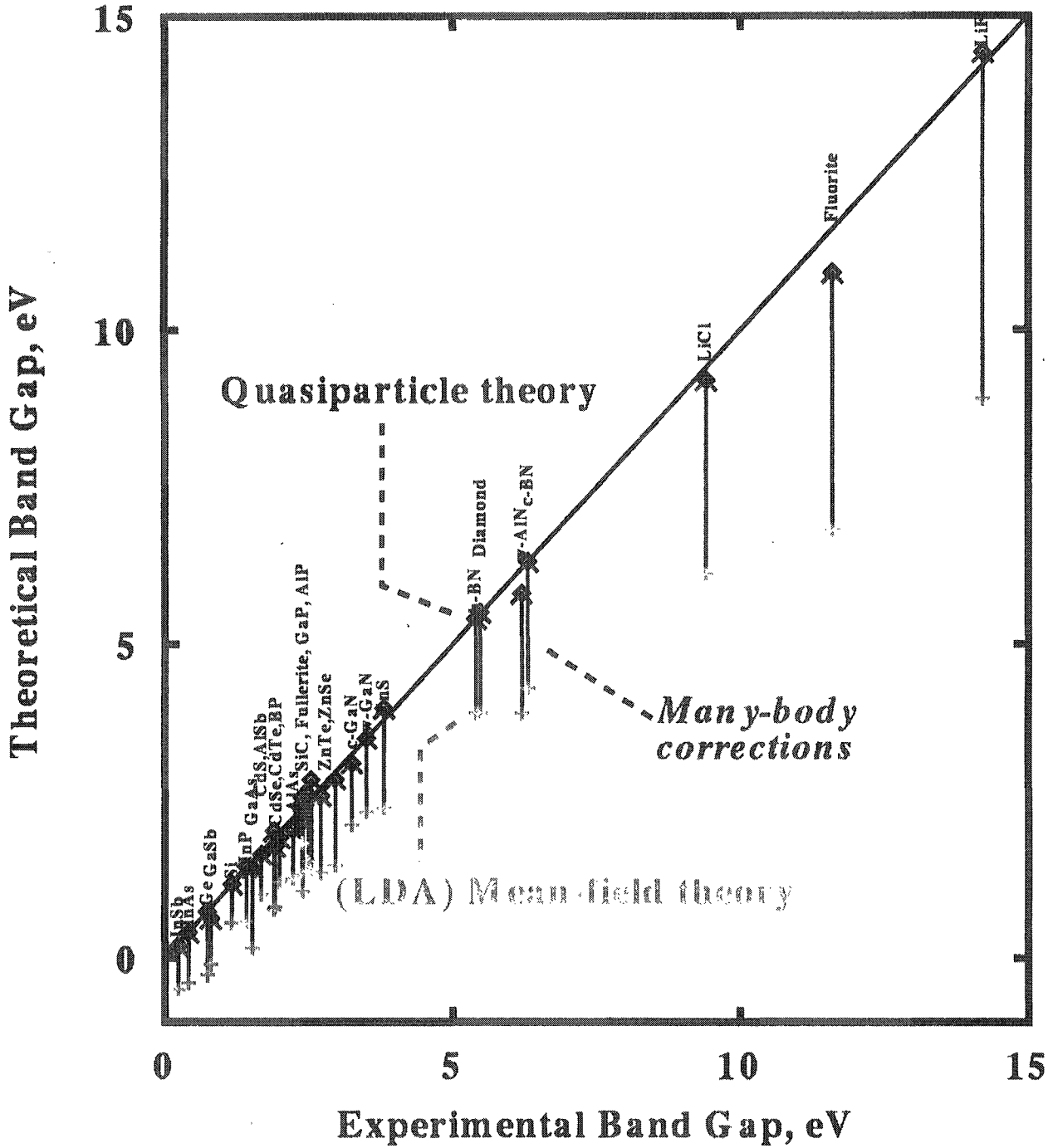
Band Gaps of Semiconductors and Insulators (in eV)

Theory

	LDA	QP	Expt
diamond	3.9	5.6	5.48
Si	0.52	1.16	1.17
Ge	<0	0.73	0.744
LiCl	6.0	9.1	9.4
AlAs	1.18	2.01	2.24
GaAs	0.56	1.42	1.52

- First Principles
- Local Fields are important

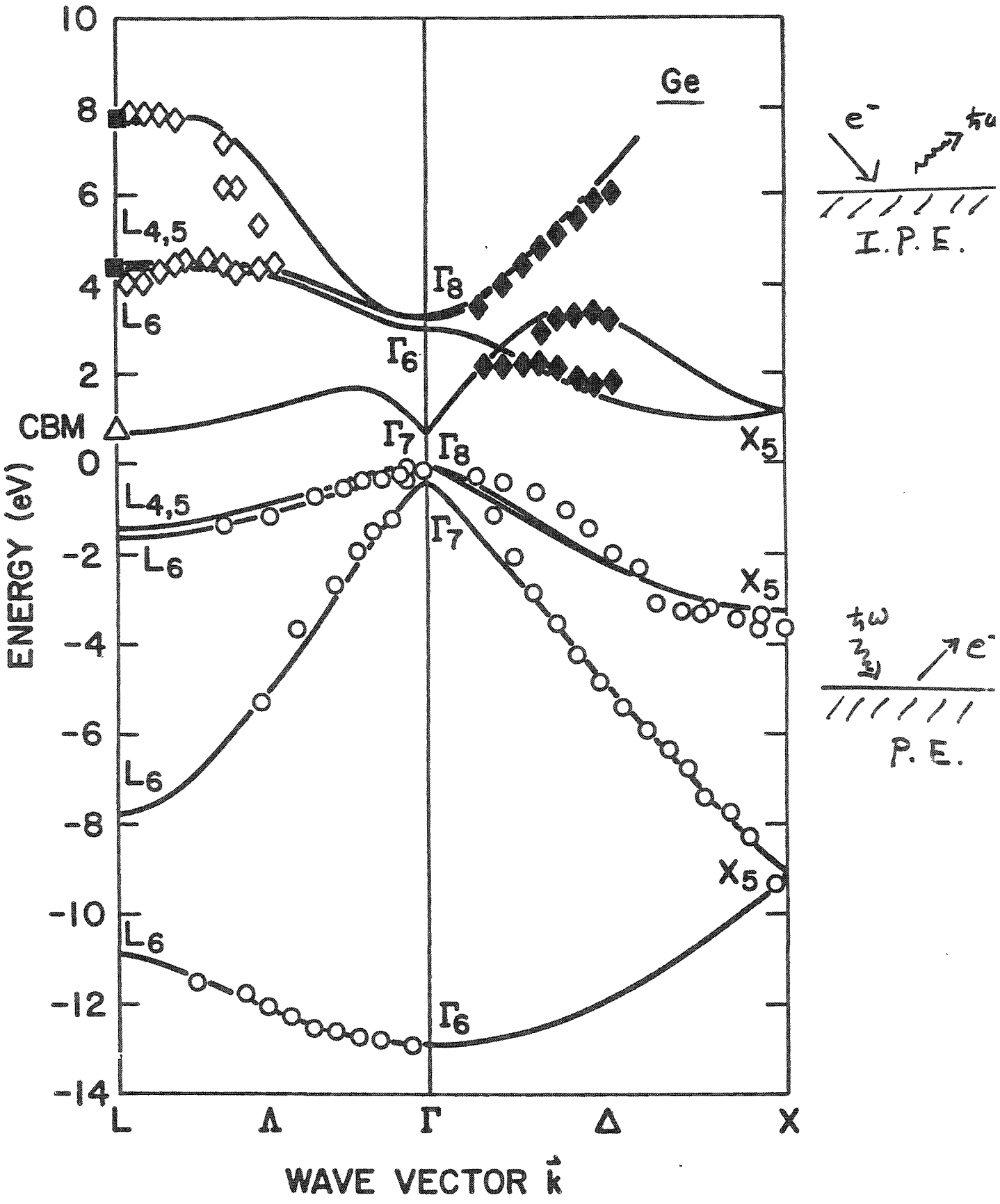
Hybertsen & Louie
Shirley & Louie



$\Sigma = iGW$

Compiled by
E. Shirley

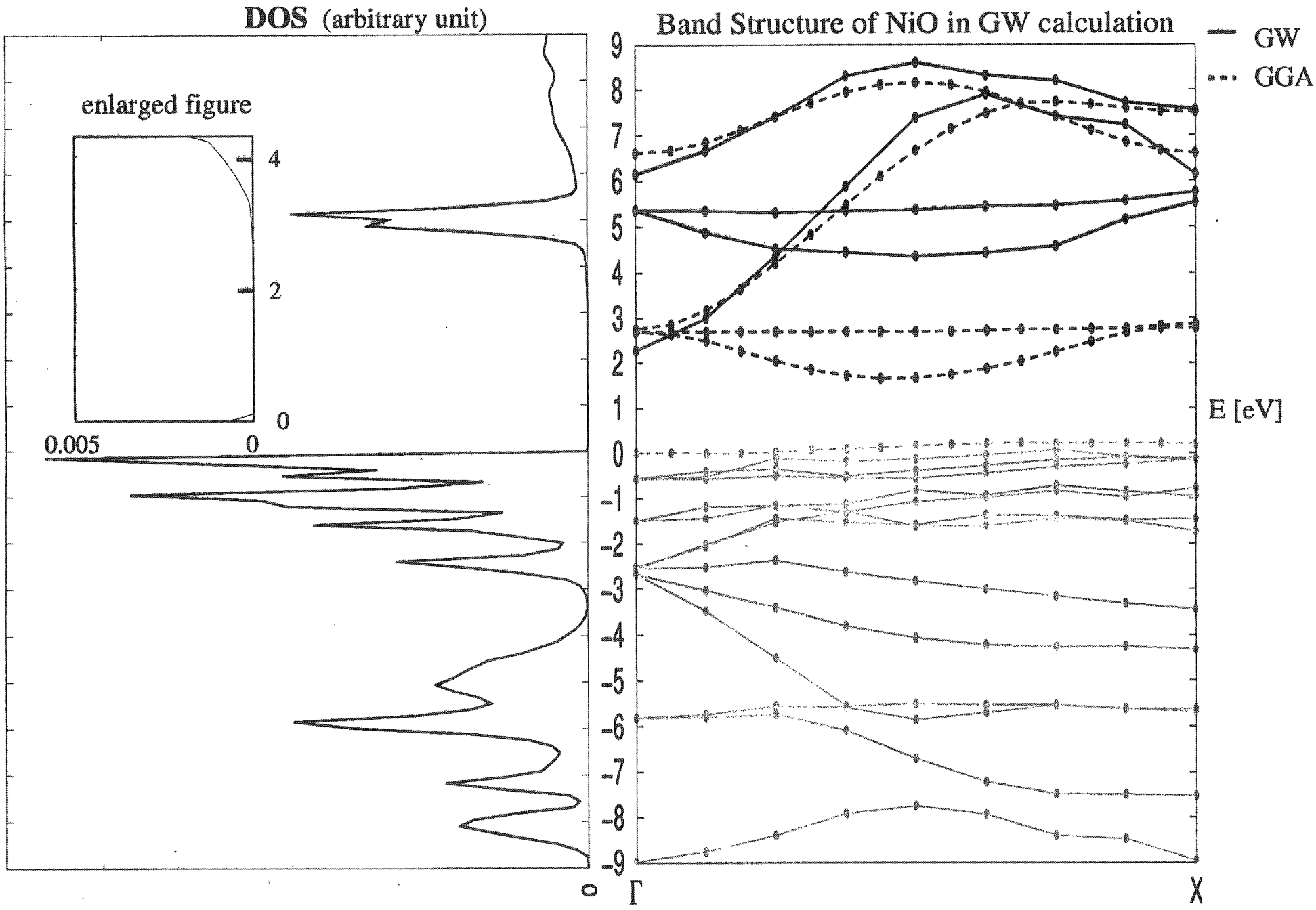
Theory: — (Hybertsen & Louie, 1986)



Expt: ○ Photoemission (Wachs, et al., 1985)

◆ ◆ Inverse Photoem. (Himpsel, 1986, 1?

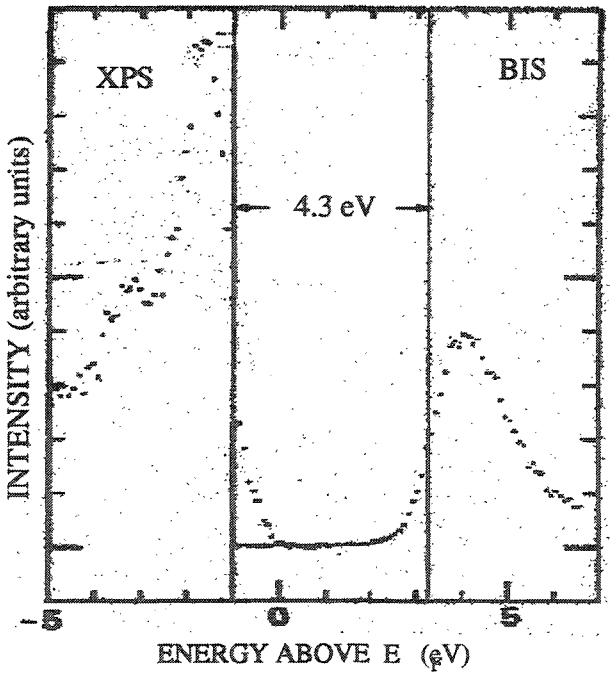
Band Structure and DOS in GW calculation



Compare with Experiment

XPS and BIS spectra

(Sawatzky and Allen 1984)



band gap = 4.3 eV,

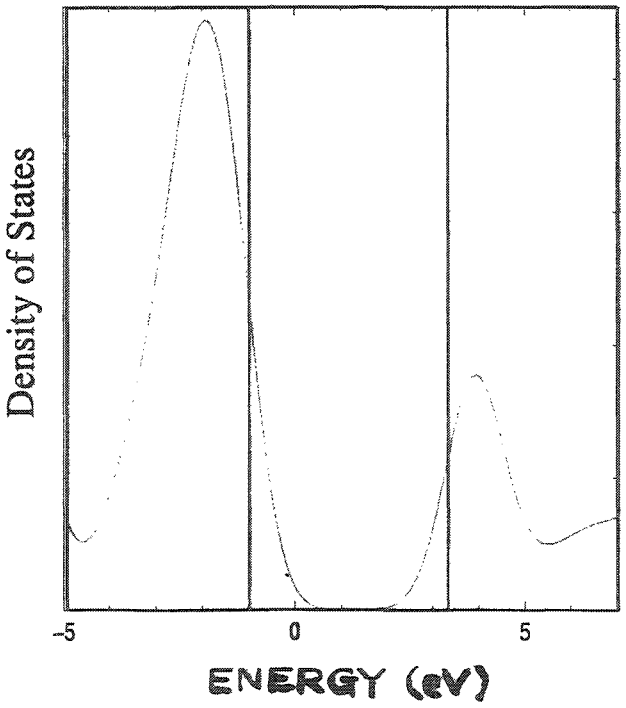
ΔE_{peak} = 5.8 eV

Density of States

computed by *GW* method

gaussian broadening 0.6 eV

(the experimental resolution)

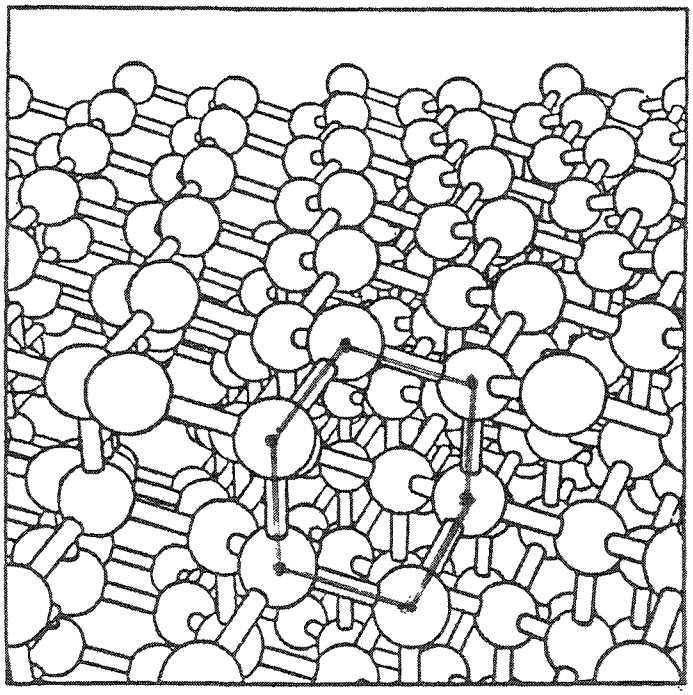


computed E_{d-d}^{gap} = 4.2 eV

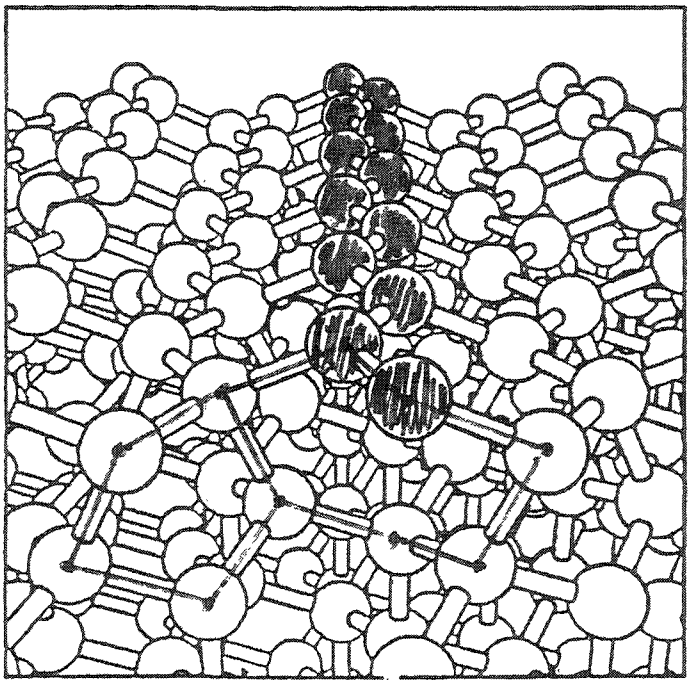
$\Delta E_{\text{peak}} \approx$ 5.8 eV

Si(111) Surface

(a) Ideal 1×1



(b) Reconstructed 2×1



- Well-separated chains
- 1D-like surface band
- Peierls buckling

Pandey π-bonded chain geometry (1981)

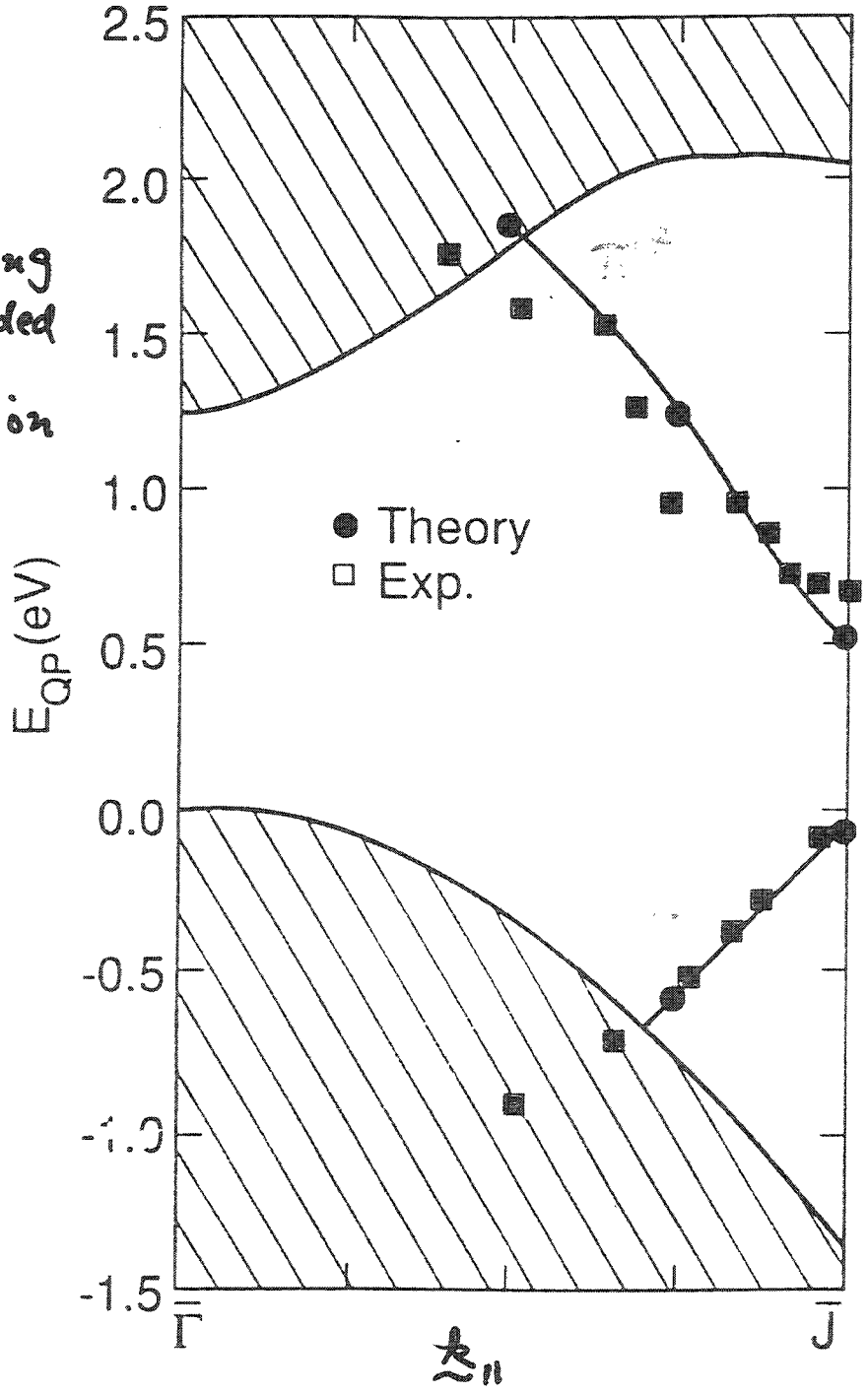
Surface State Band Gap
Si(111) 2×1

DFT-LDA	Experiment
0.27 eV	(a) 0.75 ± .1 eV
	(b) 0.47 eV
	(c) 0.45 eV
	(d) ~0.60 eV

(a) Photoemission + Inverse photoemission (Uhrberg etal.; Perfetti, et al.)
(b) Differential reflectivity (Ciccaci et al.)
(c) Photo-thermal deflection (Olmstead and Amer)
(d) Scanning tunneling spectroscopy (Feenstra) - reanalyze

	DFT-LDA	Experiment
Bulk Si	0.5 eV	1.17 eV

Si(111) 2×1 Surface



$k_{\parallel}$ along π-bonded chain direction

Theory
E_g = 0.65 eV

Photoemission
E_g = 0.7 ± 0.1 eV

STS
E_g = 0.6 eV

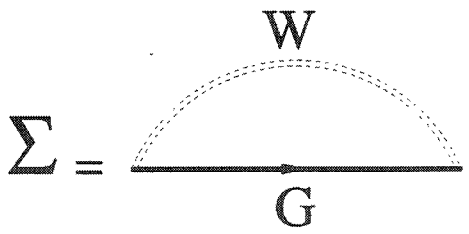
Optical
E_g = 0.45 eV

■ Photoemission data
■ Inverse photoemission data
— Theory

Northrup, Hybertsen & Louie

Lifetime τ for a quasiparticle:

$$\tau_{n\mathbf{k}}^{-1} = 2\langle n\mathbf{k}|Im\Sigma(E_{n\mathbf{k}})|n\mathbf{k}\rangle$$



$$G_{n\mathbf{k}}(\omega) = \frac{1}{\omega - E_{n\mathbf{k}} + i\delta} \qquad W = \epsilon^{-1} v$$

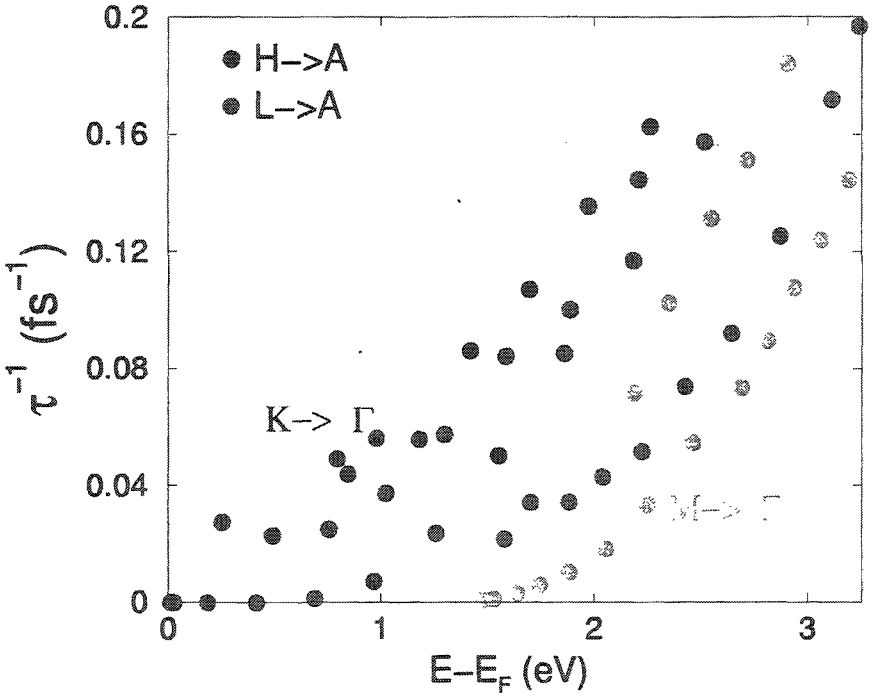
- full frequency-dependent dielectric matrix $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ calculated within RPA

References:

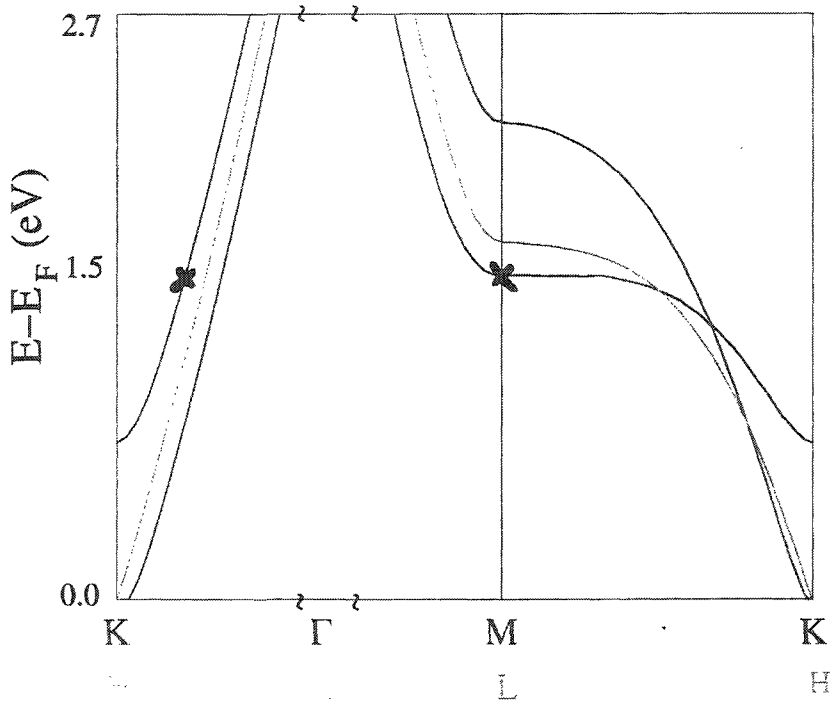
M.S. Hybertsen and S.G. Louie, PRB **34** (1986) 5390

P.M. Echenique et al., Chem Phys. **251** (2000) 1

QP lifetimes in graphite along several directions

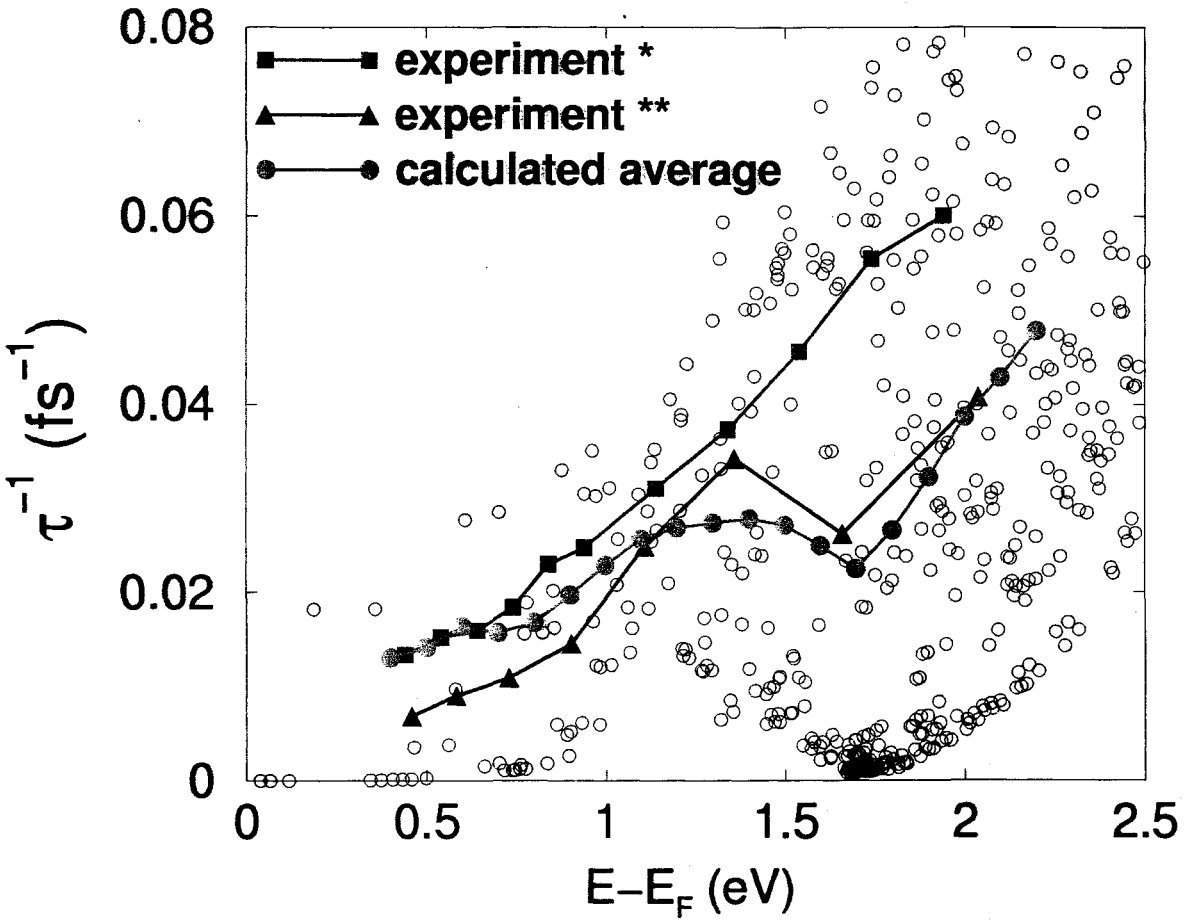


Graphite AB stacking



Calculated average lifetime

- $\tau^{-1}(E)$ calculated by averaging $\tau^{-1}_{n\mathbf{k}}$ over all states having energy E.
- QP energies updated from DFT-LDA to GW.

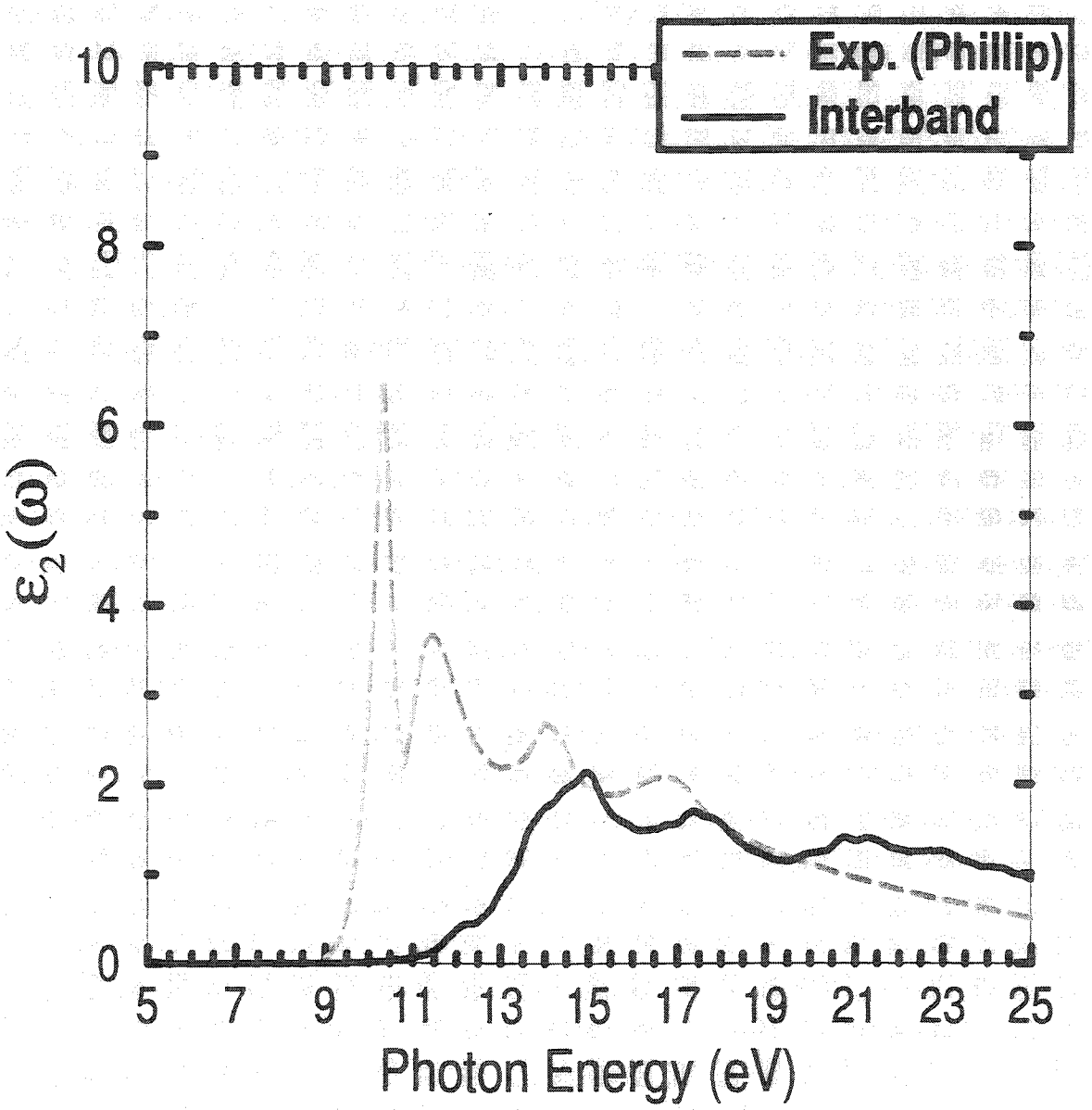


- Energy dependence cannot be fit with simple power law $(E - E_F)^n$.
- Measured inverse lifetime can depend appreciably on the experimental setup.

* S. Xu et al., PRL **76** (1996) 483

** T. Hertel et al., in preparation

Optical Absorption of SiO_2



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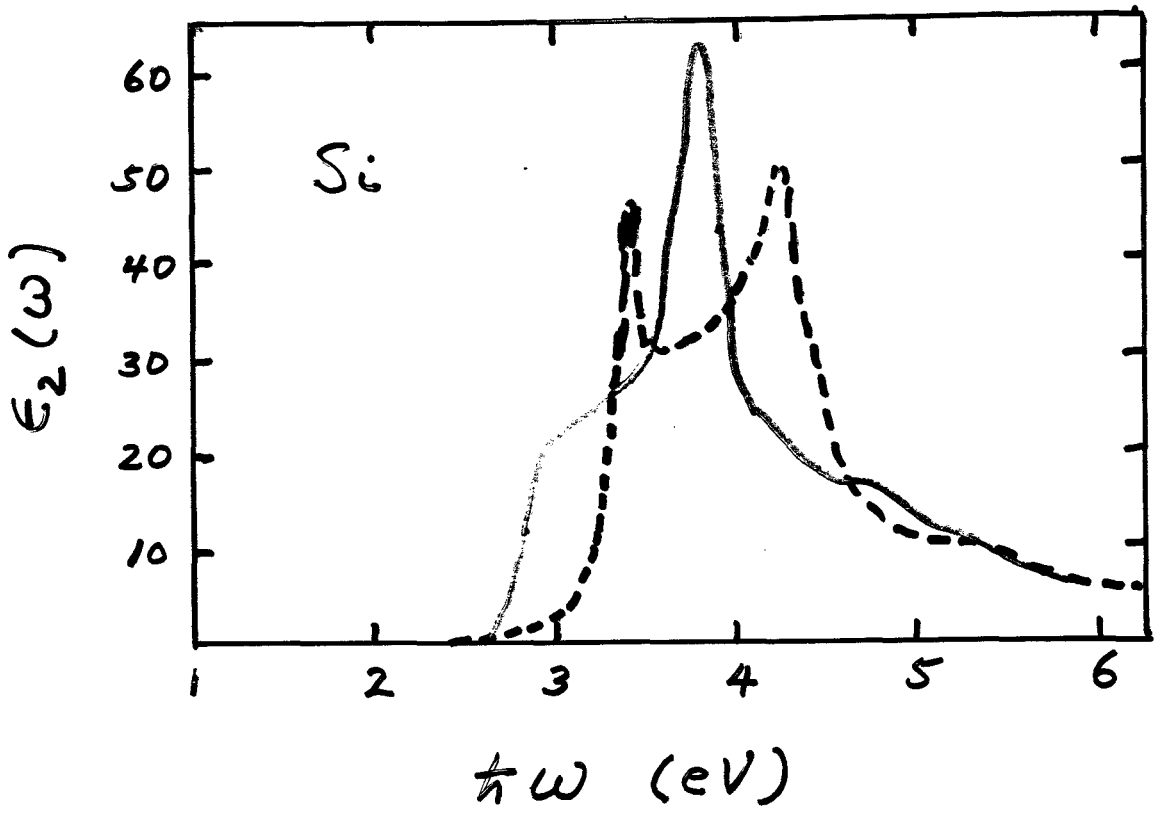
Time Dependent Density Functional Theory

TDLDA



---- EXPT

—— TDLDA (Kootstra, de Boeij, Snijders, 2000)

Optical Absorption Cross Section

Solve the Bethe-Salpeter equation for the two-particle Green's function G_2 $\Rightarrow$ electron-hole excitations:

- excitation energy Ω_S of $|N,S\rangle$

$$\Omega_S = E_{N,S} - E_{N,O}$$

$$|N,S\rangle = \sum_{m,n} A_S(m,n)\, a_m^+ b_n^+ |N,O\rangle$$

- Bethe-Salpeter equation for electron-hole amplitude

$$\chi_S(\underline{r},\underline{r}') = \sum_{nm} A_S(m,n)\, \phi_m(\underline{r})\phi_n^*(\underline{r}')$$

- dipole transition matrix element

$$\langle \vec{p}_{op} \rangle_S = \langle N,S|\vec{p}_{op}|N,0\rangle$$

$$= \sum_{nm} A_S(m,n) \langle \phi_n|\vec{p}|\phi_m\rangle$$

- absorption cross section

$$f(E) \sim \sum_S \left|\langle \vec{p}_{op} \rangle_S\right|^2 \delta(E - \Omega_S)$$

References:

G. Strinati, Phys. Rev. B **29**, 5718 (1984)

M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **80**, 3320 (1998)

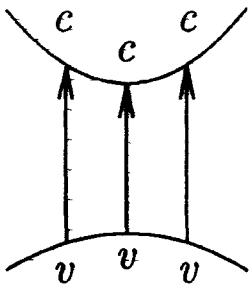
M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **81**, 2312 (1998)

S. Albrecht, L. Reining, R. Del Sole, and G. Onida, Phys. Rev. Lett. **80**, 4510 (1998)

L. X. Benedict, E. L. Shirley, and R. B. Bohn, Phys. Rev. Lett. **80**, 4514 (1998)

Theoretical Framework

- Coupled electron-hole excitations:



$$|S\rangle = \sum_{v}^{\text{elec}} \sum_{c}^{\text{hole}} A^{S}_{vc}\, \hat{a}^{\dagger}_{v}\, \hat{b}^{\dagger}_{c}\, |0\rangle$$

$|0\rangle$ ground state of many-electron system

$\hat{a}^{\dagger}_{v}$, $\hat{b}^{\dagger}_{c}$ creates quasi-hole, -electron

A^{S}_{vc} coupling coefficients

- The Bethe-Salpeter Equation for the two-particle Green's function G_2 yields:

$$(\varepsilon^{\text{QP}}_{c} - \varepsilon^{\text{QP}}_{v}) A^{S}_{vc} + \sum_{v'c'} \langle vc|K^{eh}|v'c'\rangle A^{S}_{v'c'} = \Omega^{S} A^{S}_{vc}$$

G. Strinati, Phys. Rev. B 29, 5718 (1984).

$\varepsilon^{\text{QP}}_{c}$, $\varepsilon^{\text{QP}}_{v}$ single-quasiparticle energies

K^{eh} electron-hole interaction

$\Longrightarrow$ Ω^{S} excitation energies

- $\Longrightarrow$ Optical absorption spectrum: $\epsilon_2(\omega)$

Computational Details

$W(\underline{r},\underline{r}',\omega)$
$= \int \epsilon^{-1}(\underline{r},\underline{r}',\omega)\, v(\underline{r}''-\underline{r}'$
$d\underline{r}''$

- GW quasiparticle calculation ($\Sigma = iG_1W$; $W \hat{=}$RPA)

  $\Longrightarrow \psi_n(\mathbf{r})$ **quasiparticle wavefunctions**

  $\varepsilon_n^{\mathsf{QP}}$ **quasiparticle energies**

- Electron-hole interaction kernel:

$$K^{eh} = \frac{\delta V_{\mathsf{Coul}}}{\delta G_1} + \frac{\delta \Sigma}{\delta G_1}$$

$\frac{\delta V_{\mathsf{Coul}}}{\delta G_1} \searrow v$; $\frac{\delta \Sigma}{\delta G_1} \searrow W$ + ..

$$\langle vc|K^{eh}|v'c'\rangle = \int d^3r d^3r'\, \psi_c^*(\mathbf{r})\psi_v(\mathbf{r})\, v(\mathbf{r},\mathbf{r}')\, \psi_{c'}(\mathbf{r}')\psi_{v'}^*(\mathbf{r}')$$

exchange term

$$- \int d^3r d^3r'\, \psi_c^*(\mathbf{r})\psi_{c'}(\mathbf{r})\, W^{[\Omega S]}(\mathbf{r},\mathbf{r}')\, \psi_v(\mathbf{r}')\psi_{v'}^*(\mathbf{r}')$$

screened direct term

Optical spectrum:

- Free transitions $v\mathbf{k} \longrightarrow c\mathbf{k}$:

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

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

$\vec{\lambda}$ polarization vector of the light

$\vec{V}$ velocity operator

- Coupled transitions $|S\rangle$:

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

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

- $\epsilon_2 \longrightarrow \epsilon_1, n, k, R, T, A, \ldots$

Nonlocal Potentials, Electromagnetic Fields and Gauge Invariance

Nonlocal pseudopotential formalism:

$$H^\circ = \frac{\vec{p}^2}{2m} + V(\vec{r}) + V_{NL}(\vec{r},\vec{r}')$$

With E-M perturbations:

$$\vec{p} \rightarrow \vec{p} - \frac{q}{c}\vec{A}$$

$$V_{NL} \rightarrow \left[e^{\frac{iq}{c}\int_{\vec{r}'}^{\vec{r}} \vec{A}\cdot d\vec{\ell}}\right] V_{NL}(\vec{r},\vec{r}')$$

straight-line path integral

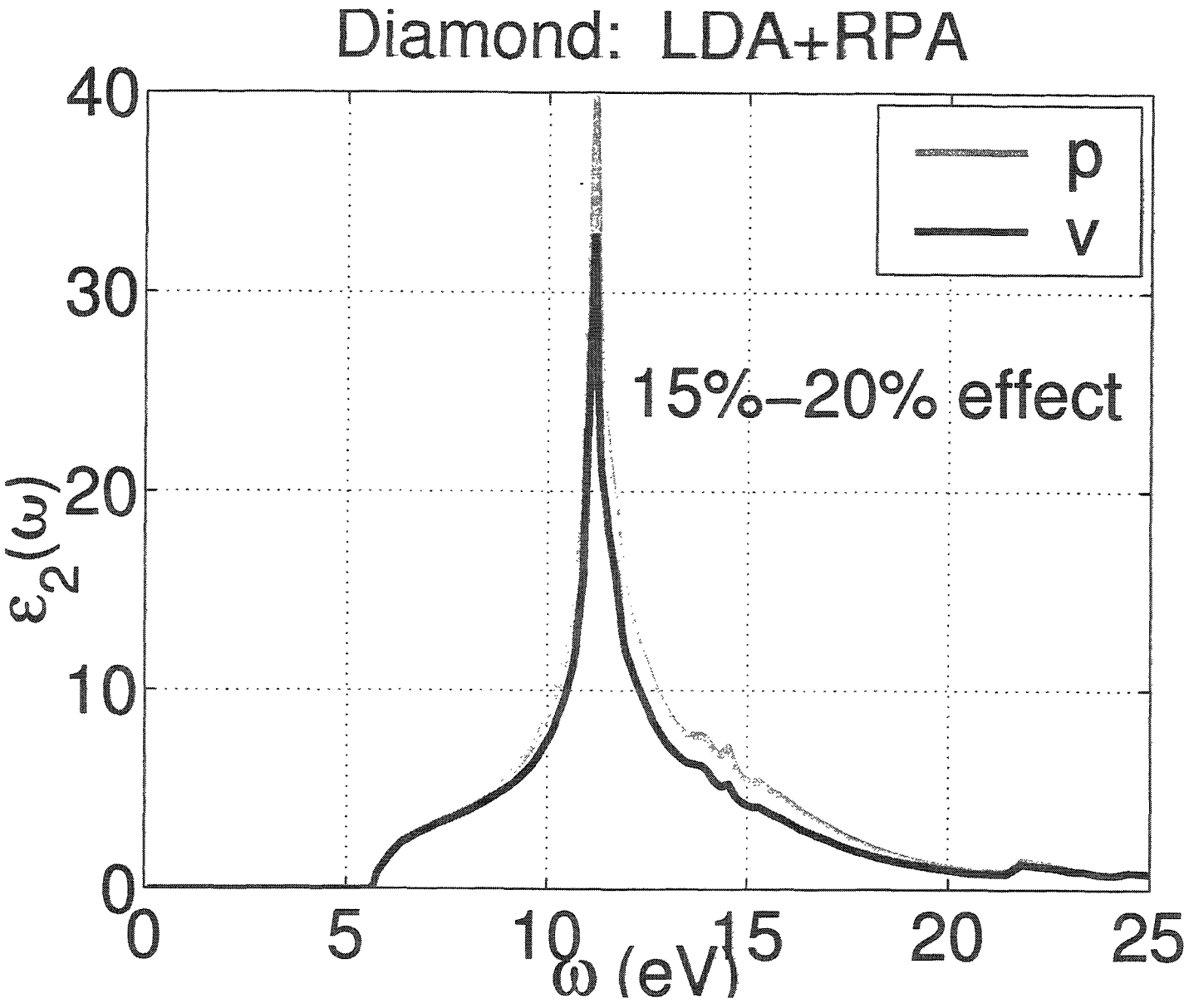
Choose $\vec{\nabla}\cdot\vec{A} = 0$: $\quad H = H^\circ + H_{int}$

$$H_{int} = -\frac{q}{mc}\vec{A}\cdot\vec{p} + \frac{q^2}{2mc^2}\vec{A}^2 + \left[e^{\frac{iq}{c}\int_{\vec{r}'}^{\vec{r}} \vec{A}\cdot d\vec{\ell}} - 1\right] V_{NL}(\vec{r},\vec{r}')$$

For a slowly varying, small $\vec{A}$ (to 2nd order in $\vec{A}$):

$$H_{int} \approx -\frac{q}{c}\vec{A}(\vec{r})\cdot\vec{V} + \frac{q^2}{2c^2}\left[\frac{A^2(\vec{r})}{m} - [(\vec{r}-\vec{r}')\cdot\vec{A}]^2 V_{NL}(\vec{r},\vec{r}')\right]$$

where $\quad \vec{V} = [\vec{r}, H^\circ]/i\hbar = \frac{\vec{p}}{m} + [\vec{r}, V_{NL}]/i\hbar$


Diamond: LDA+RPA
p
v
15%–20% effect
$\varepsilon_2(\omega)$
ω (eV)
0
10
20
30
40
0
5
10
15
20
25

Atomic Magnetic Susceptibility

$$\chi = -\left.\frac{\partial^2 E}{\partial B^2}\right|_{B=0} \qquad \vec{B} = \vec{\nabla}\times\vec{A}$$

$$H_A = \underbrace{H_0 - \frac{q}{mc}\vec{A}\cdot\vec{P} + \frac{q^2}{2mc^2}\vec{A}^2}_{H_1} + \underbrace{\frac{iq}{c}\int_{\vec{r}'}^{\vec{r}} \vec{A}\cdot d\vec{x}\, V_{NL}(\vec{r},\vec{r}'}_{H_2}$$

$$\underbrace{-\frac{1}{2}\left[\frac{q}{c}\int_{\vec{r}'}^{\vec{r}} \vec{A}\cdot d\vec{x}\right]^2 V_{NL}(\vec{r},\vec{r}')}_{H_3} + O(\vec{A}^3)$$

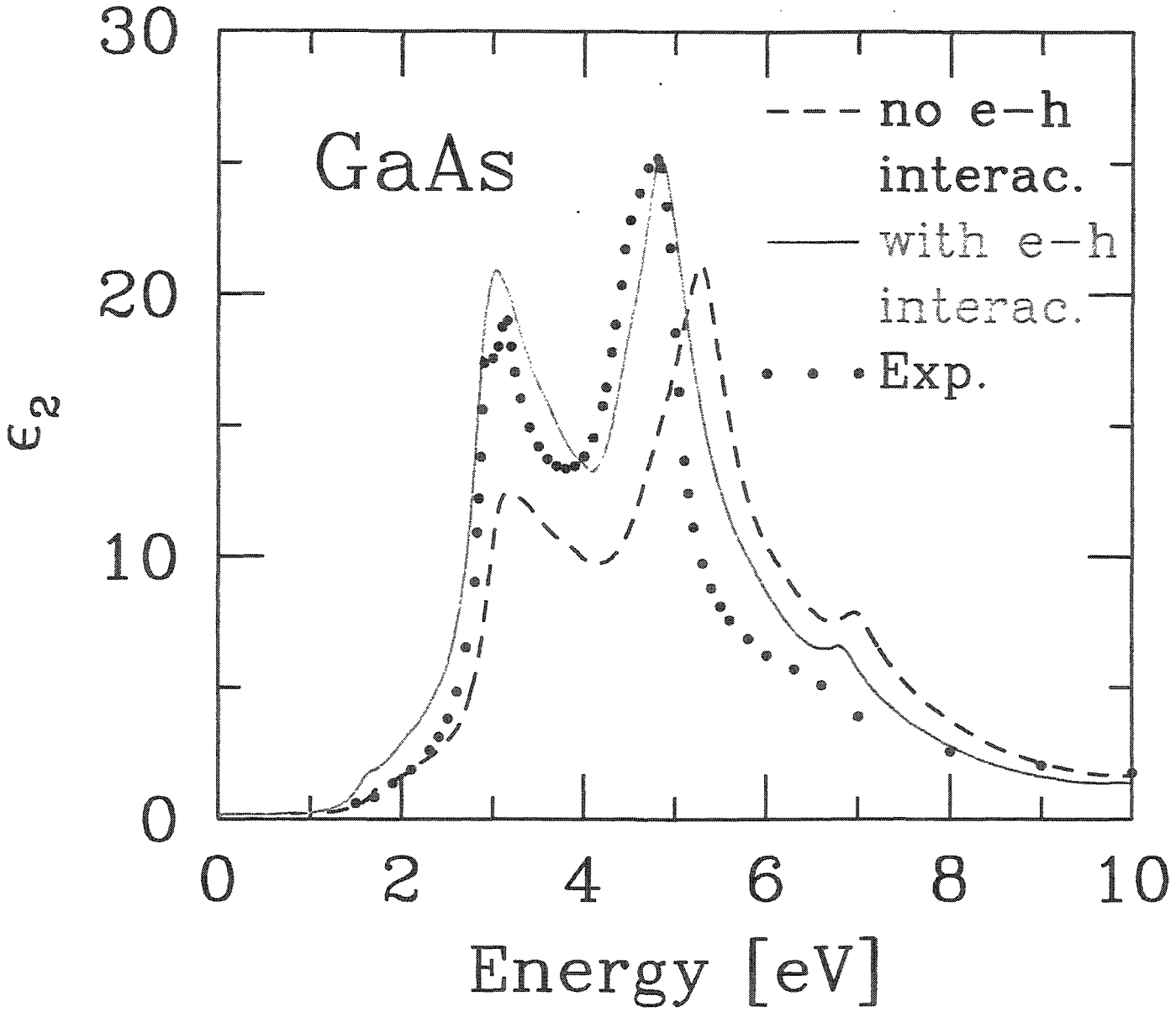
Neon: $-\chi$ (cm^3/mole)

Gauge: $\vec{A} = -(0, 0, x+X_0)B$ $\qquad \vec{\nabla}\times\vec{A} = B\hat{y}$

X_0 (a.u.)	H_1	$H_1 + H_2$	$H_1+H_2+H_3$	All Electron
0	7.84	7.74	7.75	7.75
2	-9.71	7.34	7.75	
4	-62.37	6.15	7.75	

Expt : 7.2

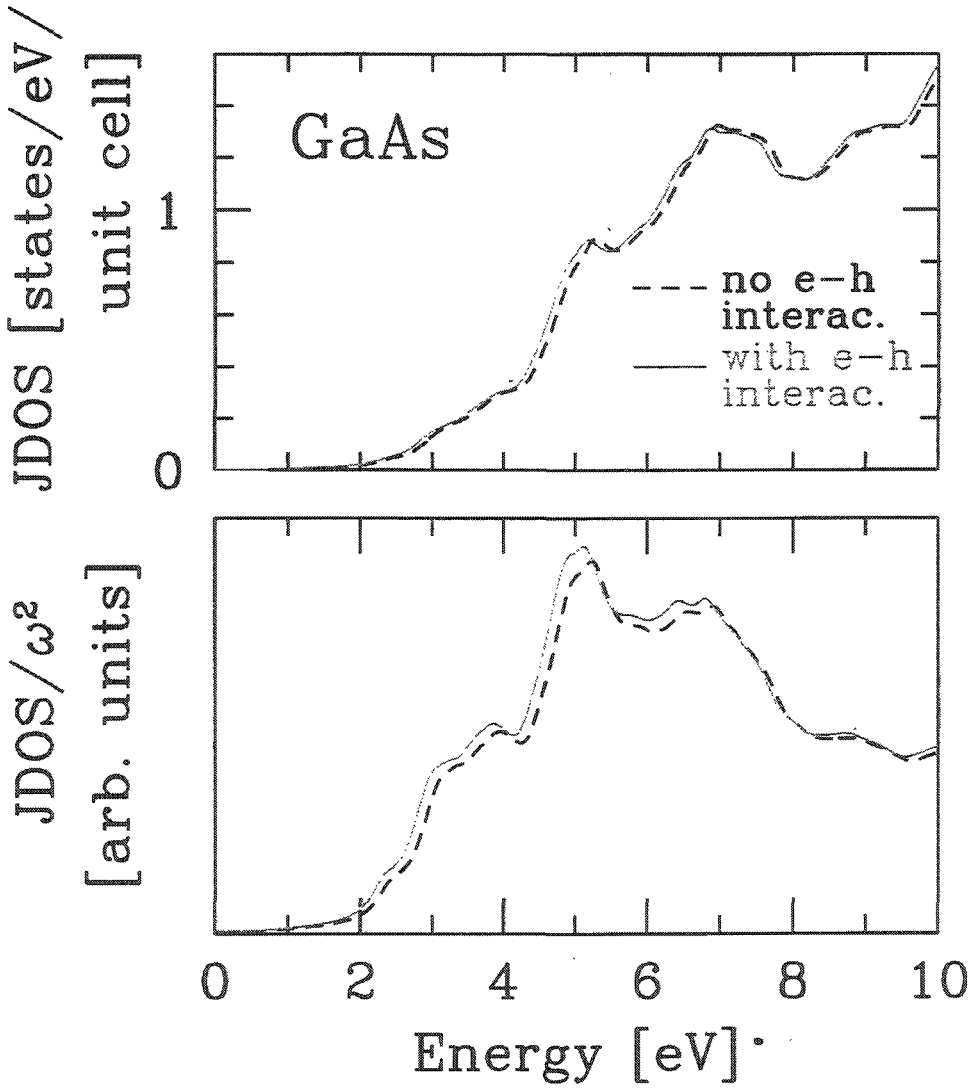
Optical Absorption Spectrum of GaAs



Calculation: 3 occupied, 6 empty bands

Exp.: Aspnes and Sturge, Phys. Rev. B 27, 985 (1983).

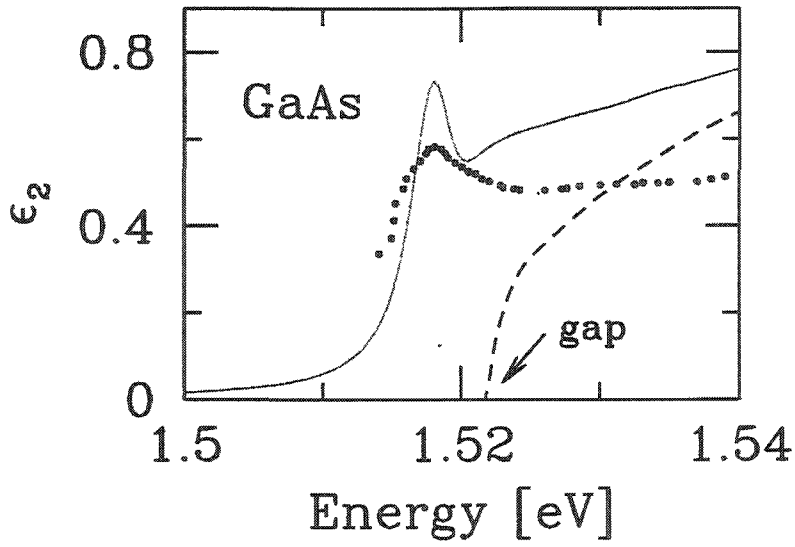
GaAs: the joined density-of-states (JDOS)



Effects of the electron-hole interaction:

- Only marginal changes in the JDOS
- Coherent (constructive, destructive) coupling of the dipole moments

Optical Absorption Spectrum of GaAs at E_g

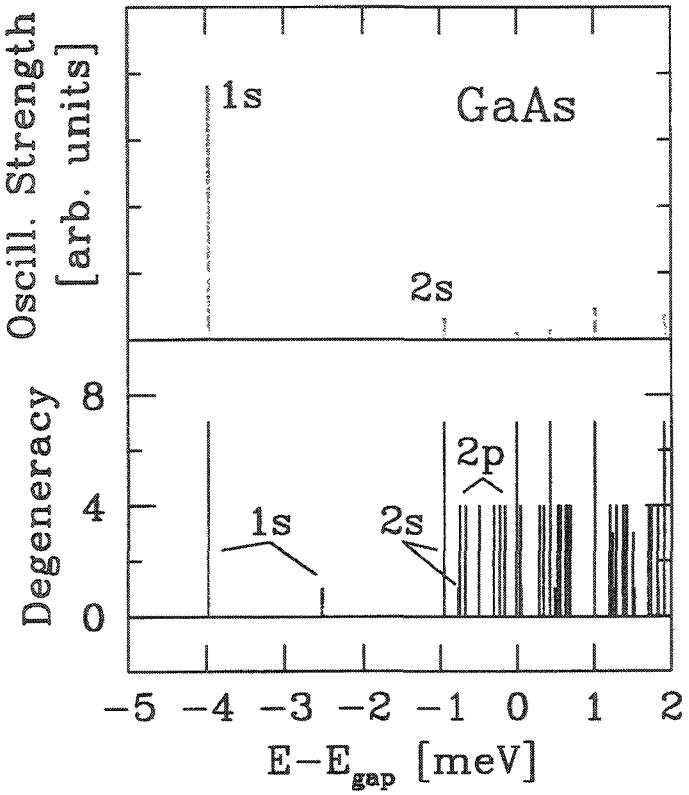


- - - no e-h interac.

—— with e-h interac.

• • • Exp.

Exciton spectrum:



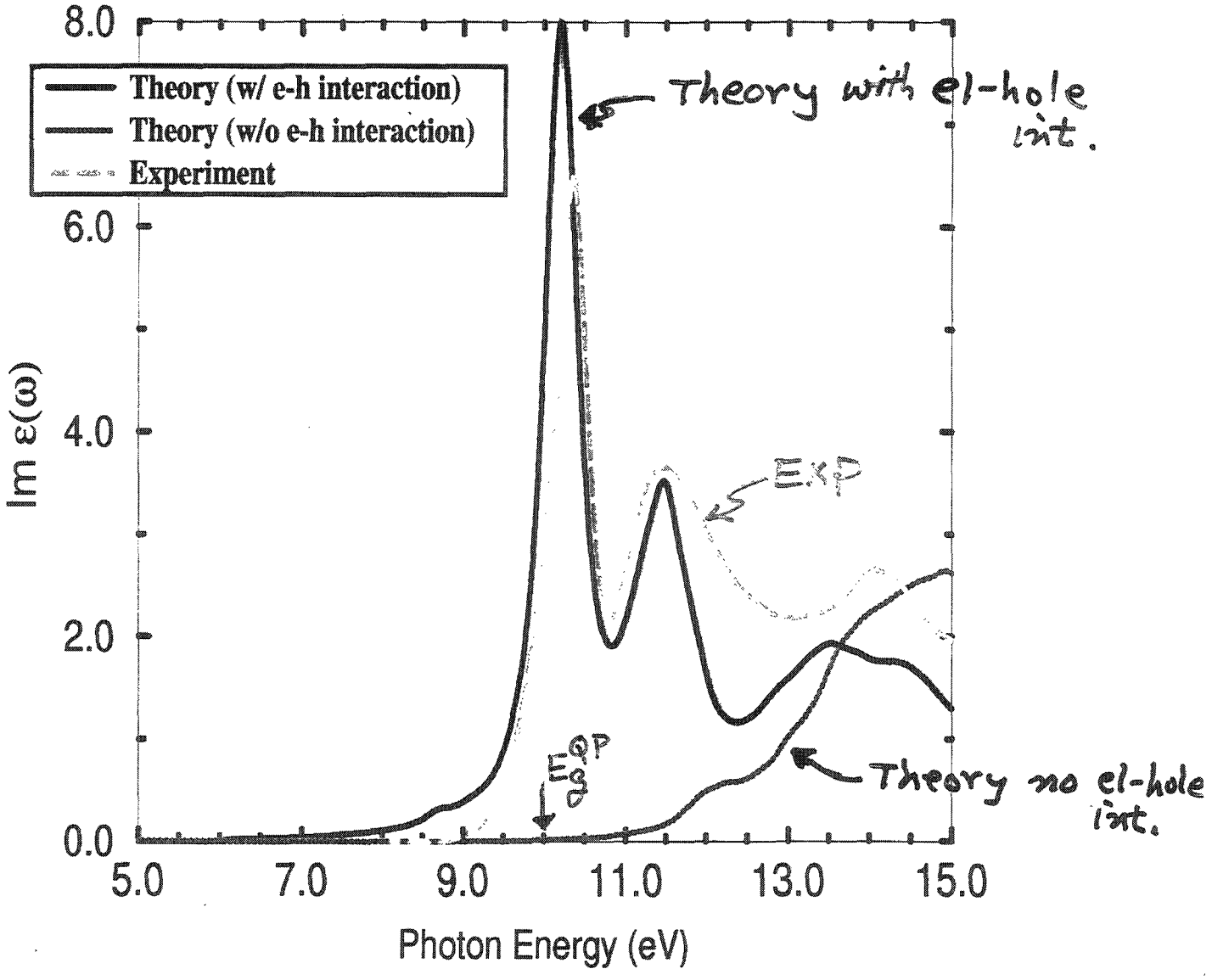
Binding energies:

	Theory [meV]	Exp. [meV]
E_{1s}	4.0	4.2
E_{2s}	0.9	1.0
E_{2p}	0.2—0.7	0—1

Includes LS interaction; 1000 out of 100M k-points.

Exp.: M. D. Sturge, Phys. Rev. **127**, 768 (1962)

Optical Spectrum of SiO_2



peaks ⟷ resonant exciton states

3

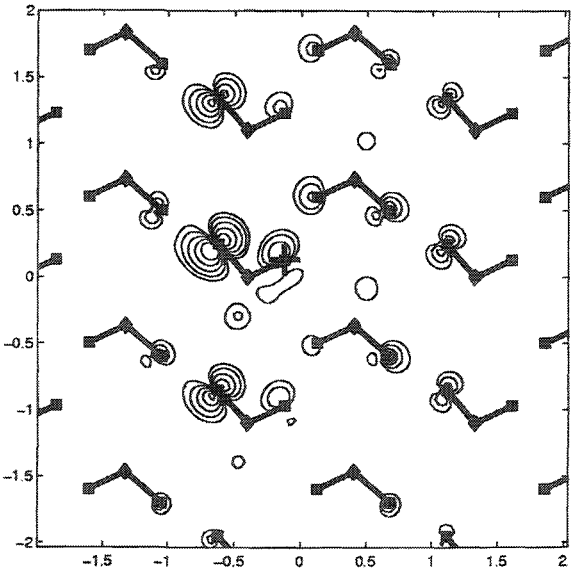
SiO_2

$$\Psi(\vec{r}_h, \vec{r}_e) = \sum_{cv\vec{k}} A_{vc\vec{k}}\, \phi^*_{v\vec{k}}(\vec{r}_h)\, \phi_{c\vec{k}}(\vec{r}_e)$$

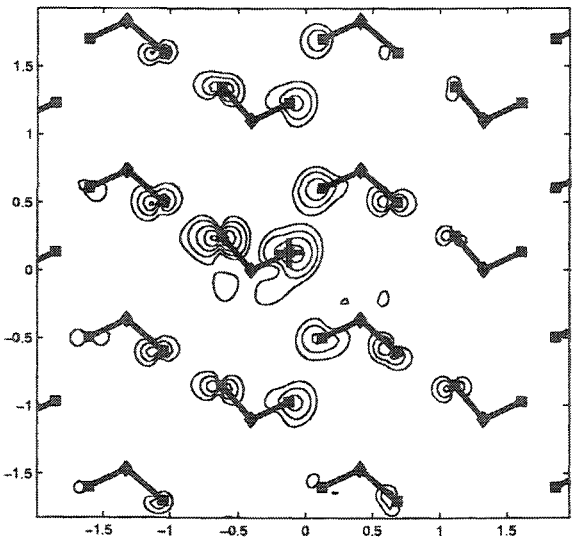
$$f(r_h) = |\Psi(r_h, r_e = +)|^2$$

$(1\bar{1}00)$- - plane

Dark Exciton (8.4 eV)



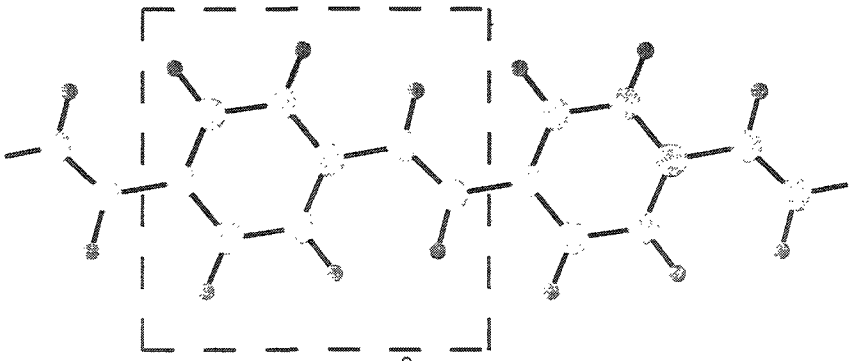
First Bright Exciton (10.1 eV)



2

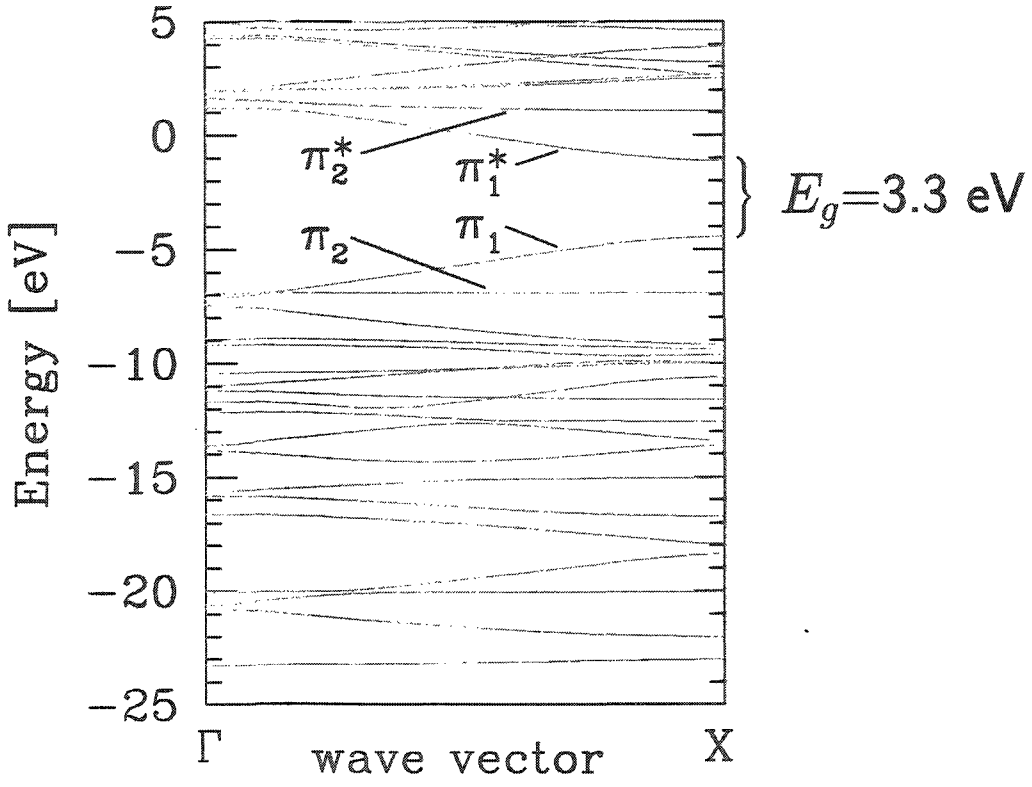
Poly-Phenylene-Vinylene (PPV)

- Most important conducting polymer:
  - LED's, Optoelectronics
  - Photovoltaics



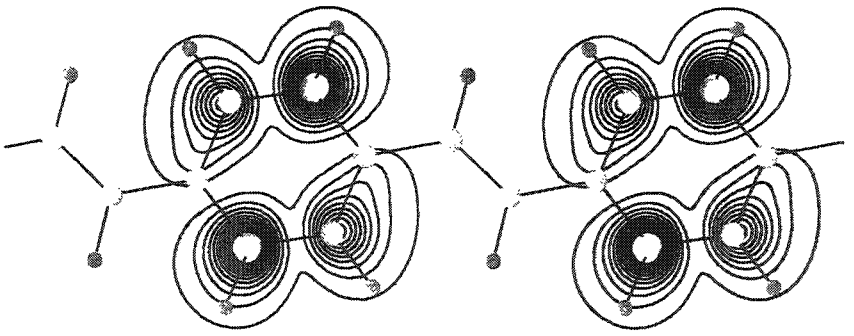
a_0=6.63 Å

QP band structure:

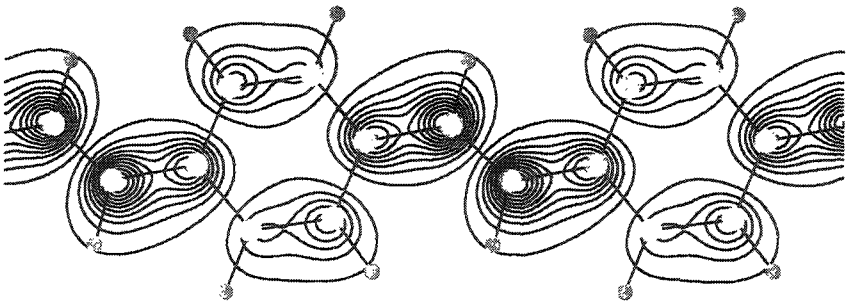


One-particle Wave functions in PPV

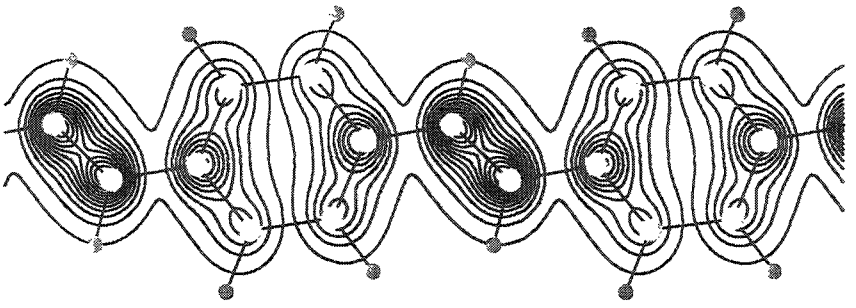
CBM+1 (π_2^*)
(empty)



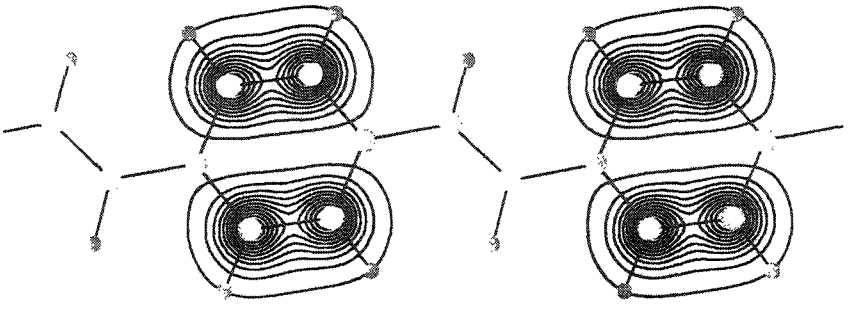
CBM (π_1^*)
(empty)



VBM (π_1)
(occ.)

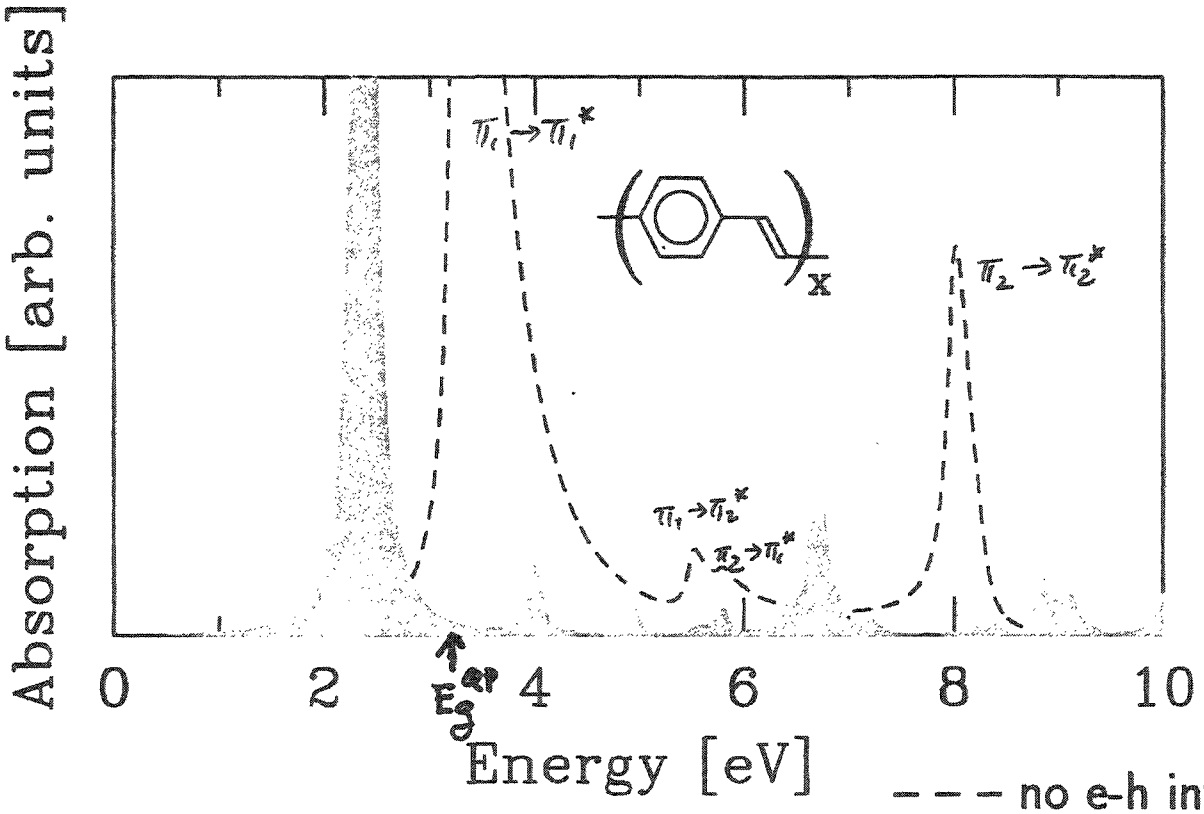


VBM–1 (π_2)
(occ.)



calculated at the X point; 0.6 Å above atomic plane

Absorption spectrum of PPV



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Previous model studies:

Gartstein, Rice & Conwell ('95)

Chandross & Mazumdar ('97)

Mukamel, et al ('97)

⋮

	Theory [eV]	Exp. [eV]
E_1	2.4	2.5
E_2	4.0	3.7
E_3	4.9	4.8
$E_{4,5}$	5.3, 6.5–6.9	6.0

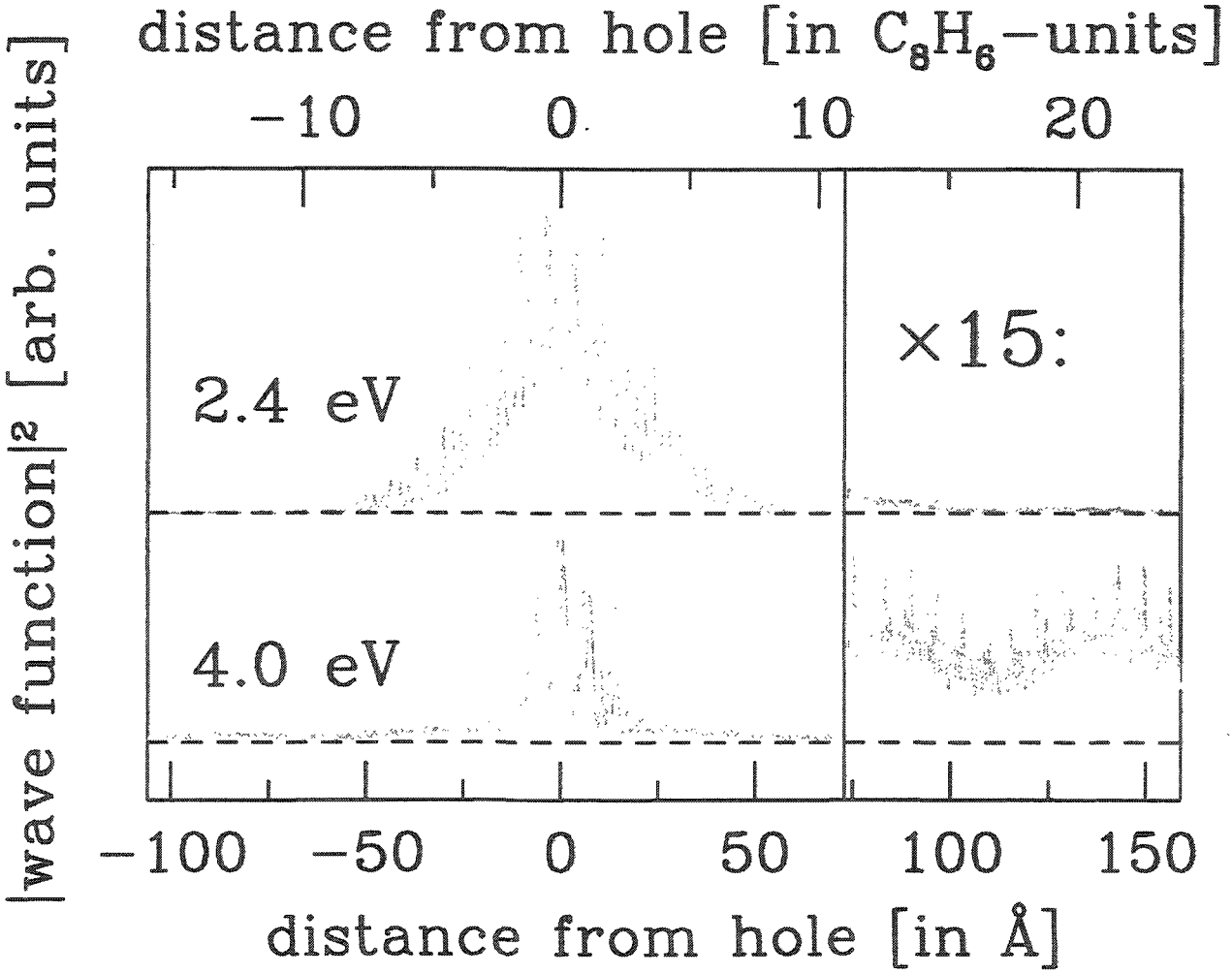
$E_g^{QP} = 3.3$ e!

Exp.: D. A. Halladay *et al.*, Synthetic Metals 55-57, 954 (1993).

Electron-hole Wavefunctions in PPV

- Electron distribution with respect to the hole:

$$\chi(\vec{r}_h, \vec{r}_e) = \sum_{cv\vec{k}} A_{vc\vec{k}}\, \phi^*_{v\vec{k}}(\vec{r}_h)\, \phi_{c\vec{k}}(\vec{r}_e)$$



- At 2.4 eV (below E_g): Exciton
- At 4.0 eV and higher: Resonant states

Singlet and Triplet Excitons

- Spin-singlet excitons (excitable by light): observe repulsive exchange interaction
- Spin-triplet excitons: No exchange interaction

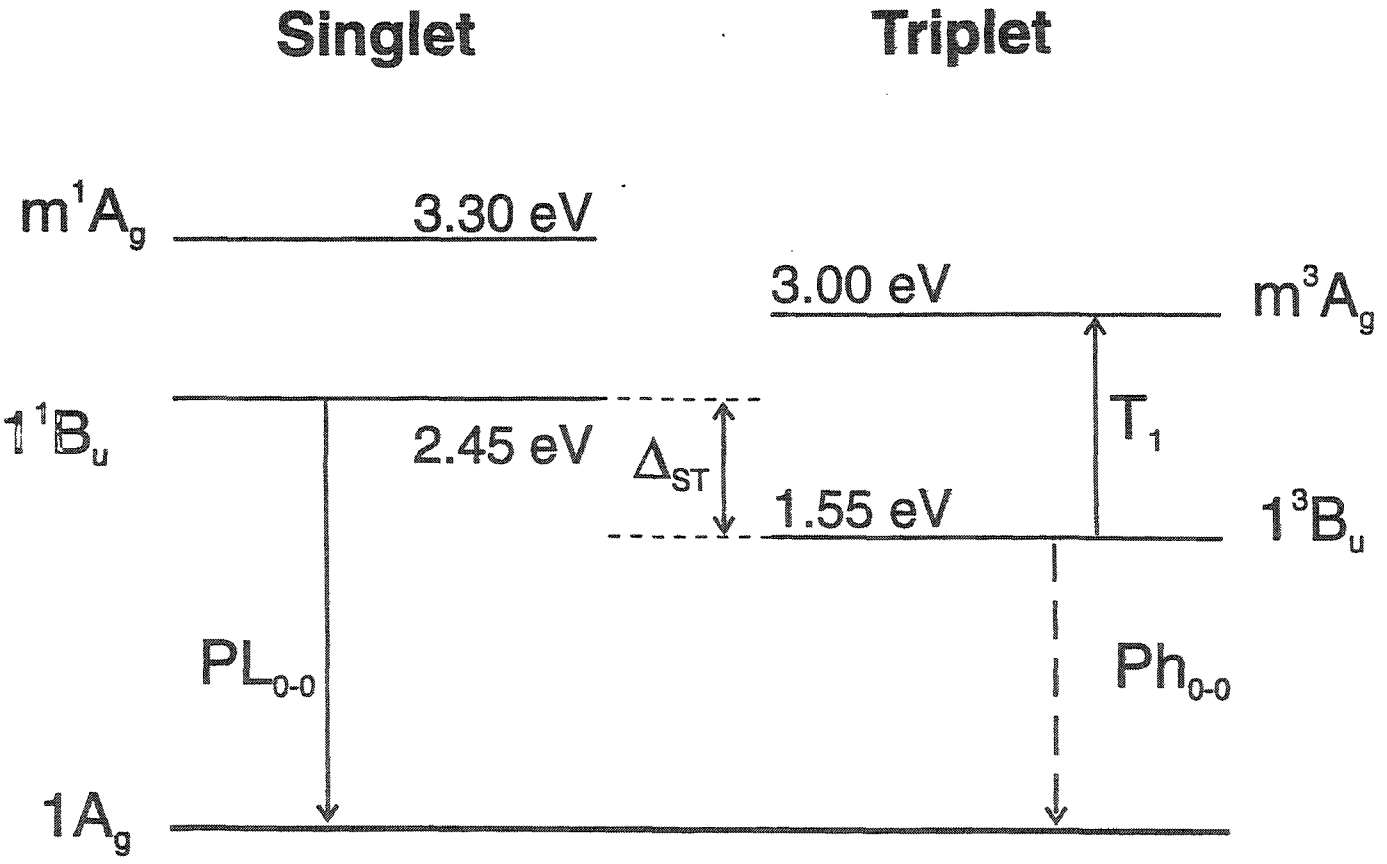
Polyacetylene:

	Singlet		Triplet		
Dipole	E_i^S	$E_g - E_i^S$	E_i^T	$E_g - E_i^T$	$\Delta_{S \leftrightarrow T}$
•	1.7	0.4	0.9	1.2	0.8
—	1.8	0.3	1.7	0.4	0.1

PPV:

	Singlet		Triplet		
Dipole	E_i^S	$E_g - E_i^S$	E_i^T	$E_g - E_i^T$	$\Delta_{S \leftrightarrow T}$
•	2.4	0.9	1.5	1.8	0.9
—	2.8	0.5	2.7	0.6	0.1

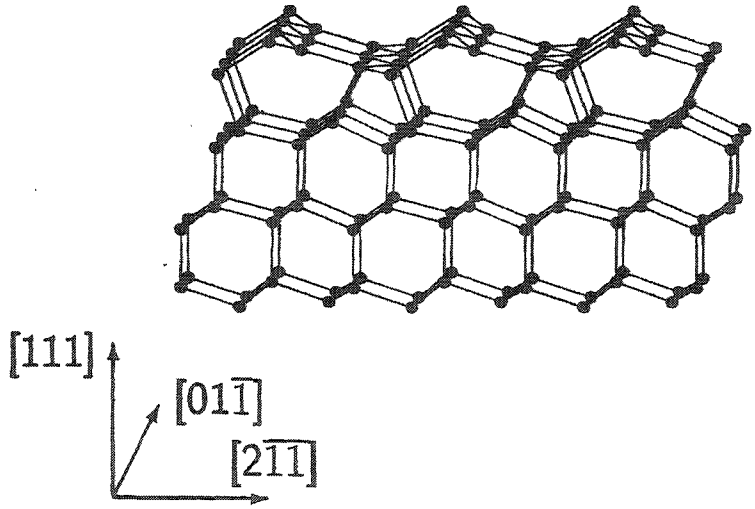
- Even ($\hat{=}$ dipole-allowed) states: Electron and hole are close to each other $\Rightarrow$ Strong exchange interaction



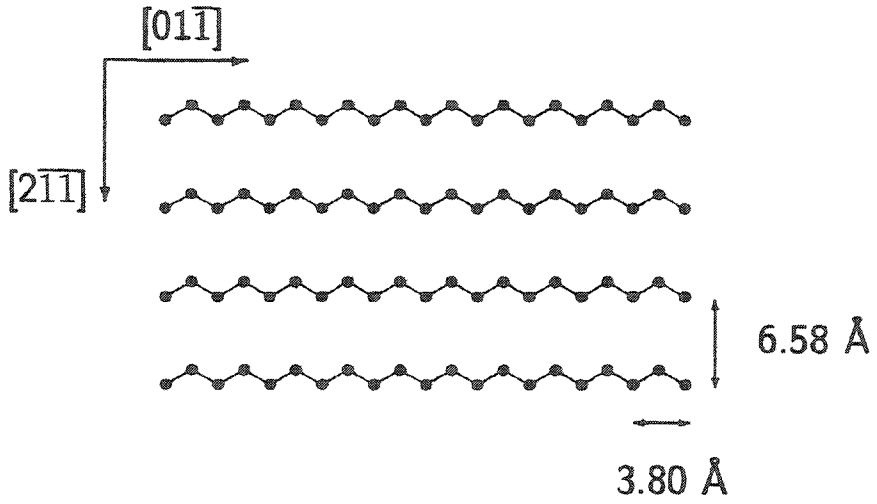
Österbacka, Wohlgenannt, Chinn & Vardeny (1999)

Structure of the Si(111) 2x1 Surface

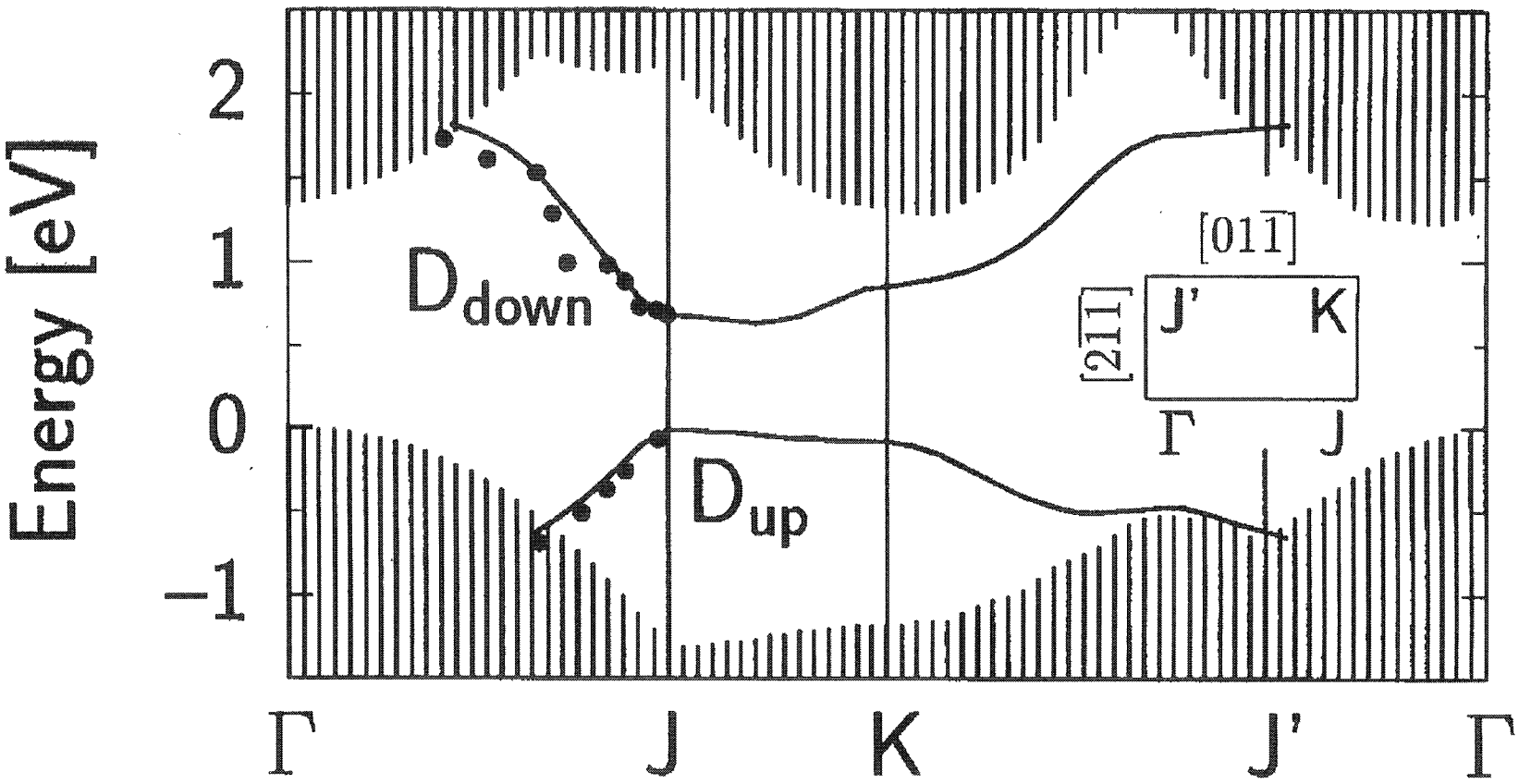
Side view



Top view



Quasiparticle Surface-State Bands of Si(111)2x1



- Exp.: R. Uhrberg et al (1982); P. Perfetti et al (1987)

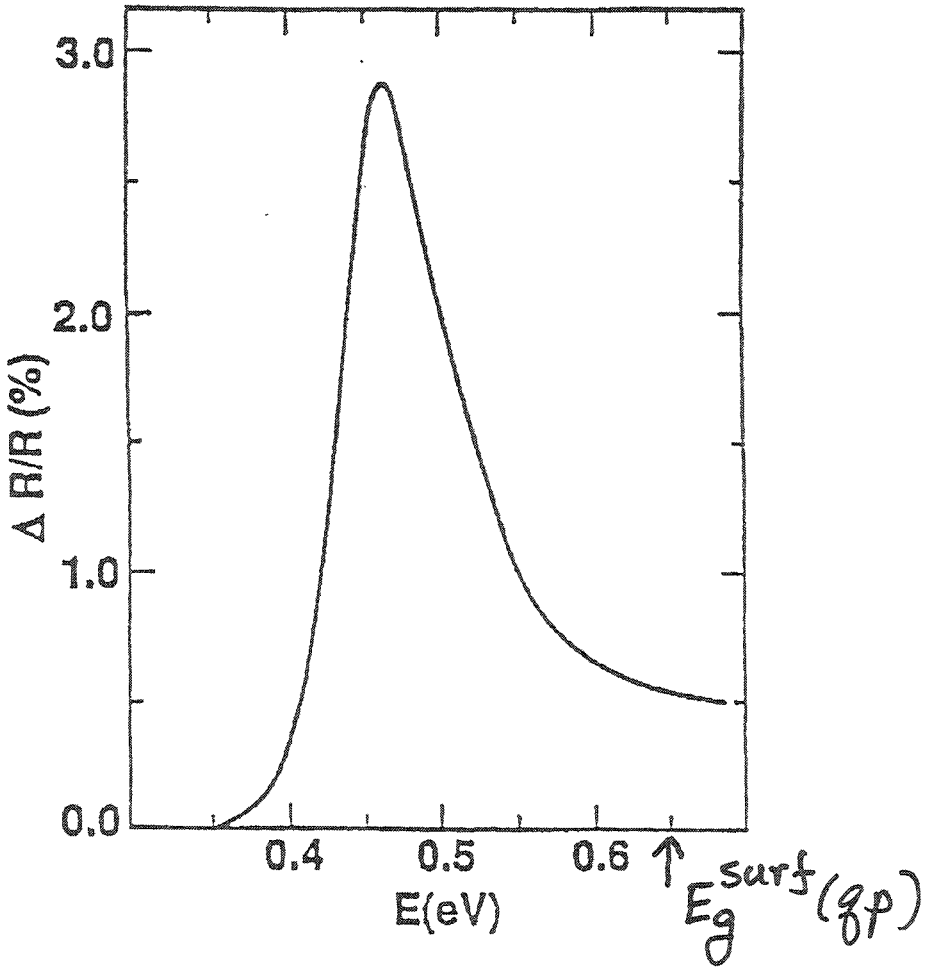
  Eg = 0.65 eV (< Eg(bulk) = 1.17 eV)

  ↖ surface state QP gap

Rohlfing & Louie (1999)

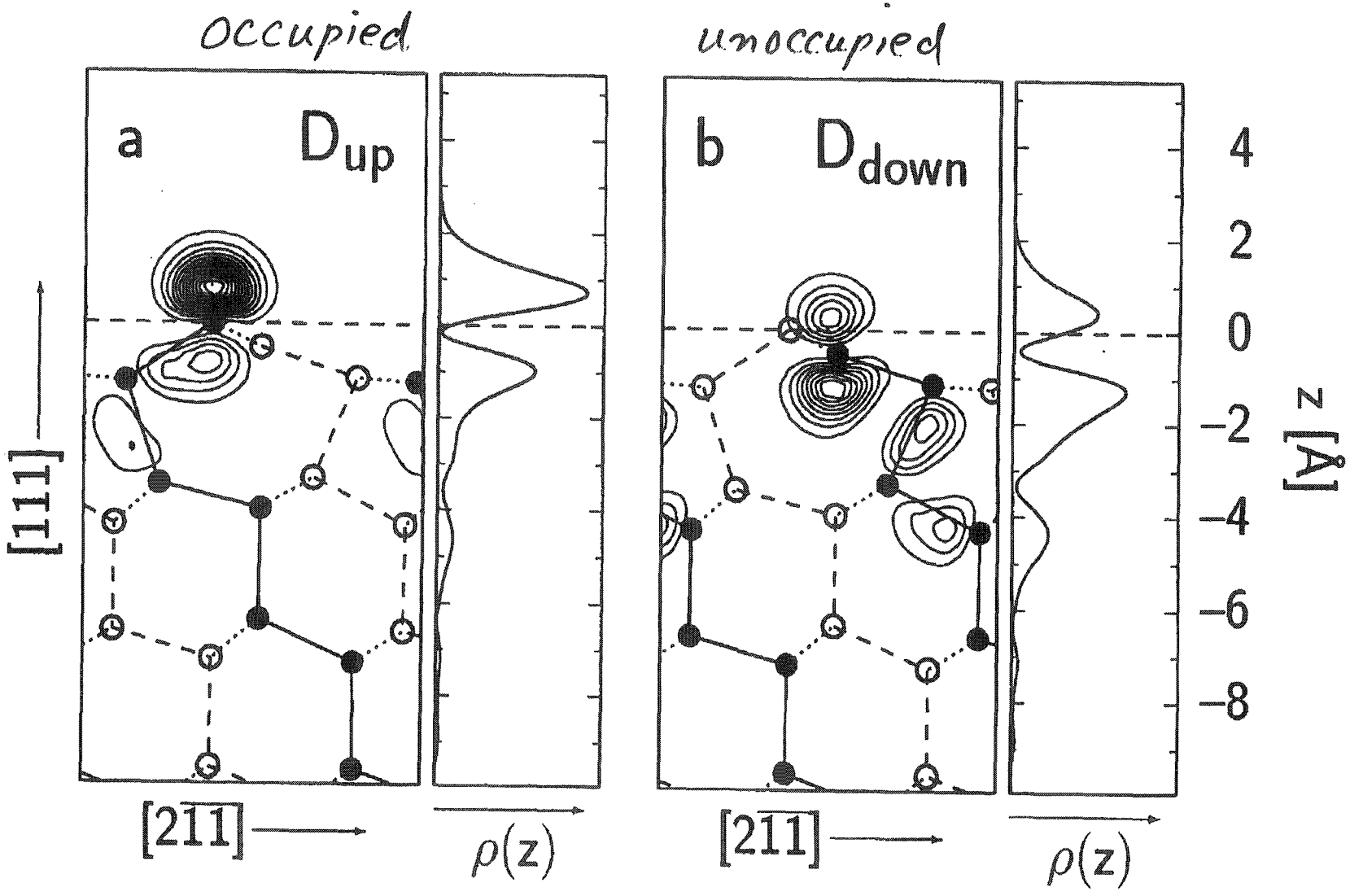
Si(111) 2×1 Surface

Experimental differential reflectivity spectrum (Ciccacci et al., 1986)



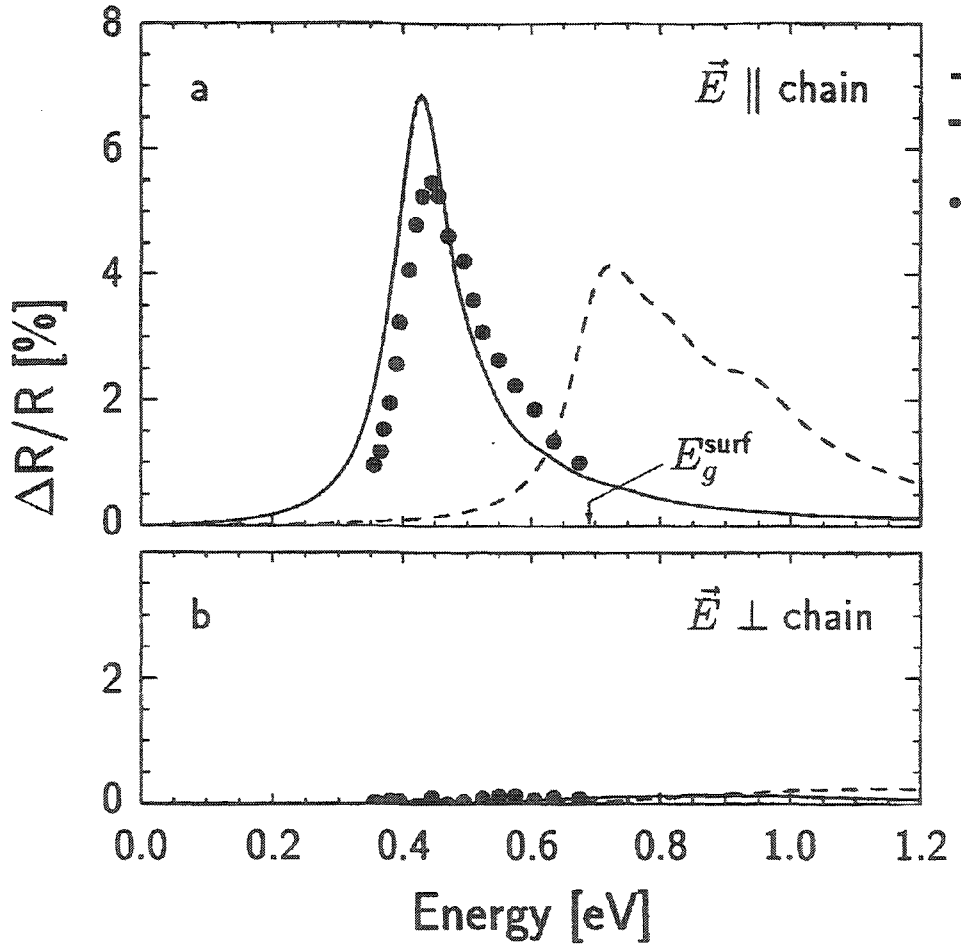
- $\Delta R/R = (R_{clean} - R_{ox})/R_{ox}$
- Reflectivity associated with surface states
- QP results → onset at 0.65 eV
  ← 2-peak structure

Surface-State Charge Density



Si(111) 2×1 Surface

Differential Reflectivity Spectra



— with e-h int.
--- no e-h int.
••• Exp

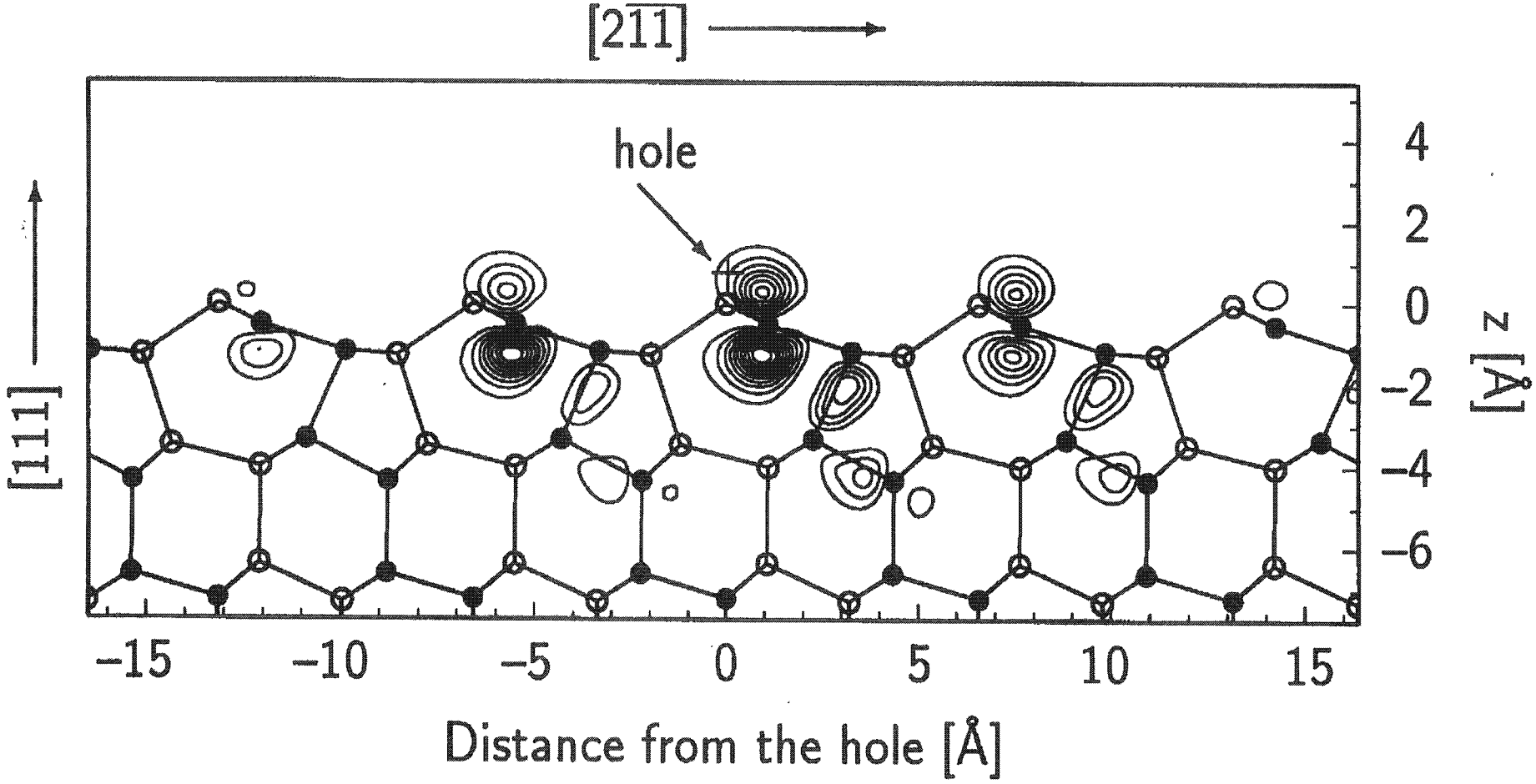
Artificial broadening : 0.05 eV
Exp.: P. Chiaradia et al., PRL **52**, 1145 (1984)

- Discrete exciton spectrum
- Optical spectrum dominated by lowest exciton
- Surface exciton binding energy: 0.25 eV
- Bulk exciton binding energy: 15 meV

Rohlfing & Louie (1999)

Surface Exciton Two-particle Amplitude - Side View

(Distribution of electron relative to the hole for state at 0.43 eV)

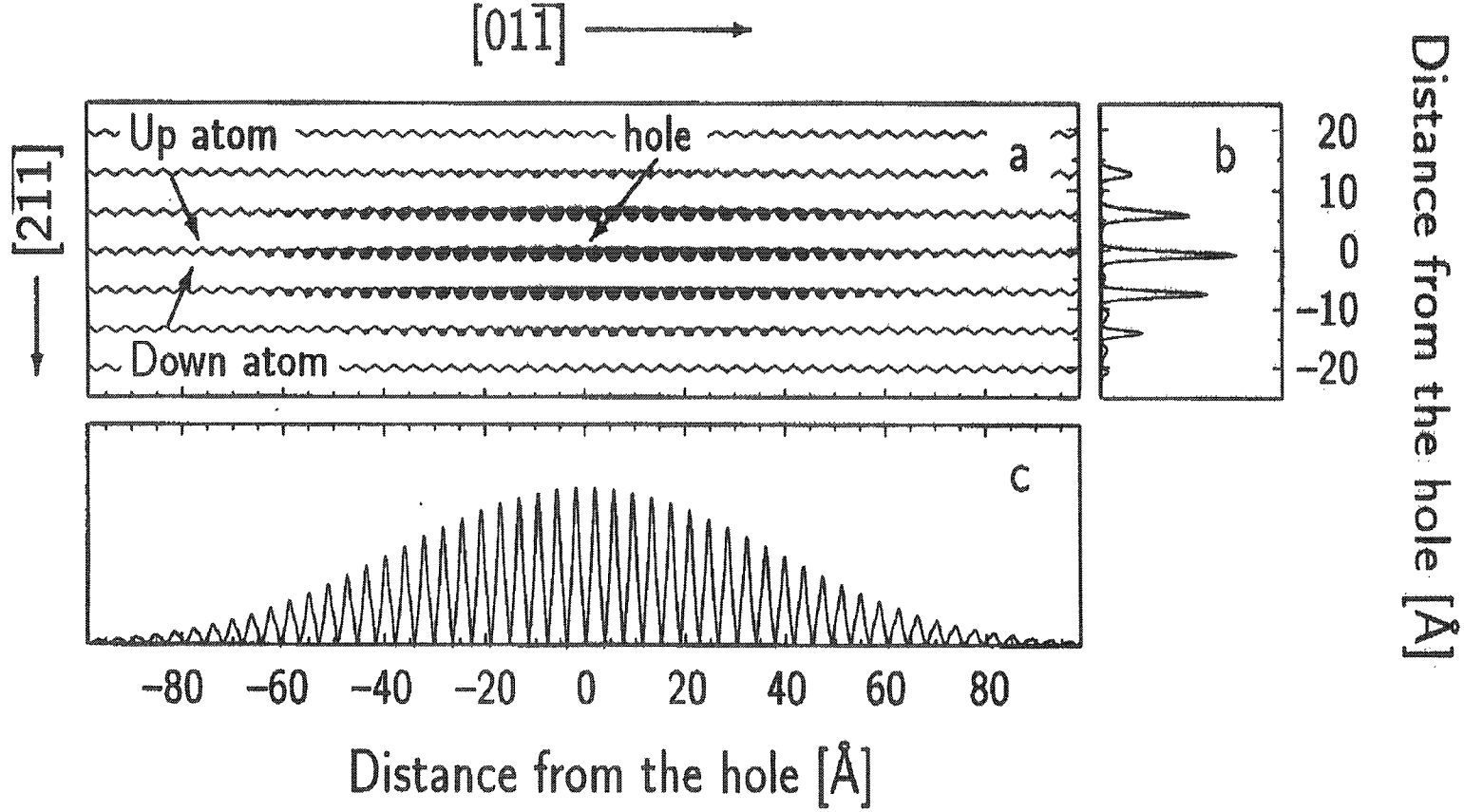


$$A(\vec{r}_h, \vec{r}_e) = \sum_{vc\vec{k}} A_{vc\vec{k}} \psi^*_{v\vec{k}}(\vec{r}_h) \psi_{c\vec{k}}(\vec{r}_e)$$

Rohlfing & Louie (1999)

Surface Exciton Two-particle Amplitude - Top View

(Distribution of electron relative to the hole for state at 0.43 eV)

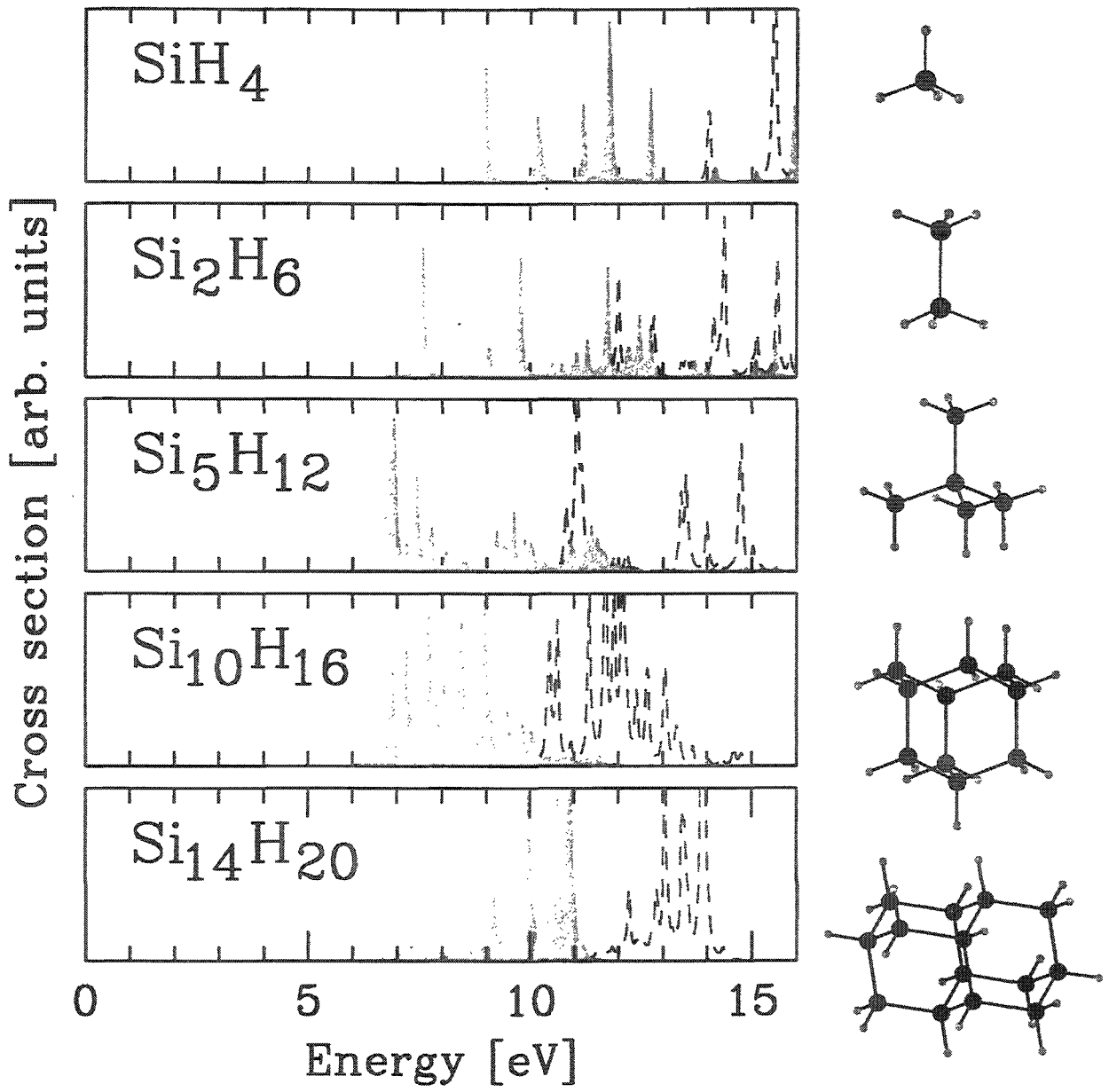


Mean electron-hole distance: Along the chains - 40 A

Across the chains - 8 A

Rohlfing & Louie (1999)

Absorption Spectrum of Si Clusters



—— including electron-hole interaction

– – without electron-hole interaction

- Huge excitonic binding energy: ~ 5 eV

Optical Excitation Energies of SiH_4 and Si_2H_6

	This work [eV]	Experiment [eV]
SiH_4:	9.0	8.8
	10.2	9.7
	11.2	10.7
Si_2H_6:	7.6	7.6
	9.0	8.4
	9.6–9.8	9.5, 9.9

Exp.: U. Itoh, Y. Toyoshima, and H. Onuki,
J. Chem. Phys. 85, 4867 (1986).

Noble-gas Atom Ionization Energies and First Neutral Excitation Energies (in eV)

		This Work	Expt
He:	I	24.7	24.6
	E_S	20.8	20.6
	E_T	19.8	19.8
Ne:	I	21.5	21.6
	E_S	16.9	16.9
	E_T	16.7	16.7
Ar:	I	15.9	15.8
	E_S	12.0	11.8
	E_T	11.8	11.6

I = Ionization energy

E_S = Singlet excitation

E_T = Triplet excitation

Summary

- Density functional theory provides valuable input to many-body perturbation theory calculation of excited-state properties.
- GW approximation yields highly accurate first-principles quasiparticle energies for many materials systems, to a level of ~0.1 eV.
- Evaluation of the Bethe-Salpeter equation provides *ab initio* and quantitative results on exciton states and optical response of crystals, surfaces, polymers, and clusters.
- Combination of DFT and MBPT → excited state properties.