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ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

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Miramare - Trieste, Italy

Excited Electronic States of Surfaces and Molecules

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Excited Electronic States of Surfaces and Molecules

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- Introduction
- Surface Excitons
- Excited Molecules
- Interrelation with the Geometry

In cooperation with

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Outline:

- Theoretical Description of Optical Spectra

  $\Longleftrightarrow$ Hierarchy of *ab-initio* Techniques:

1. Density-functional Theory DFT (LDA + Pseudopotentials)

   $\Longrightarrow$ Electronic Ground State $|N, 0\rangle$

   [+ geometric structure]

2. Electronic Self Energy Σ (within GW Approx.)

   Dyson's equation for G_1

   $\Longrightarrow$ Single-particle Excitations $N \rightarrow N \pm 1$

   Electronic Spectrum; Band Structure

   M. S. Hybertsen and S. G. Louie, PRL 55, 1418 (1985);
   R. W. Godby et al., PRL 56, 2415 (1986).

3. Electron-Hole Interaction K^{eh}

   Bethe-Salpeter equation for G_2

   $\Longrightarrow$ Coupled Electron-Hole Excitations $N \rightarrow N^*$

   Optical Spectrum, Excitons, etc.

   G. Strinati, PRB 29, 5718 (1984);
   S. Albrecht et al., PRL 80, 4510 (1998);
   L. X.Benedict et al., PRL 80, 4514 (1998);
   M. Rohlfing and S. G. Louie, PRL 80, 3320 (1998),
   PRL 82, 1959 (1999).

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:

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

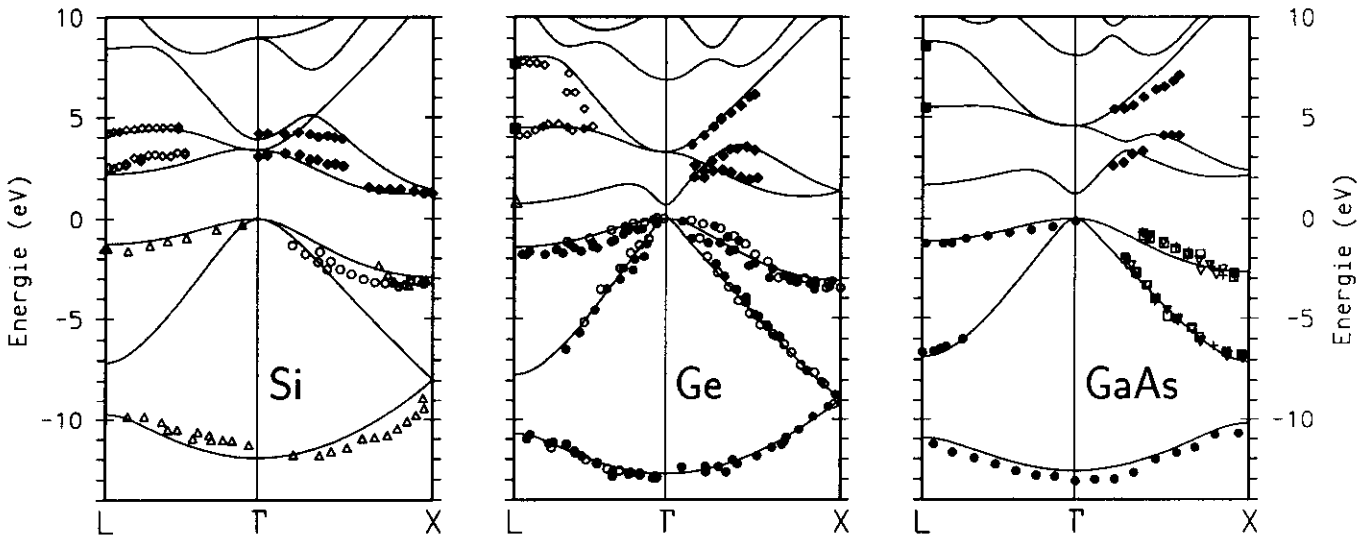
$\Sigma = iG_1W$ GW approximation for the self energy

G_1 one-particle Green function

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

Hedin 1965, Hybertsen and Louie 1985

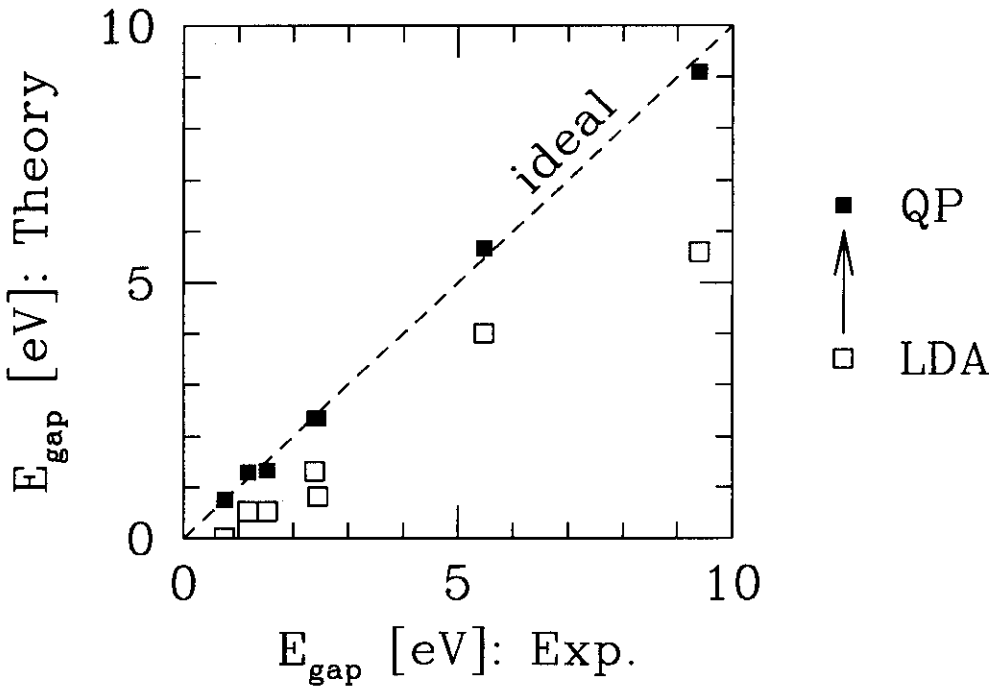
QP band structures of Si, Ge, and GaAs:



——— calculated

● ◁ ◇ experimental data (ARPES, ARIPES)

QP gap energies of various semiconductors:



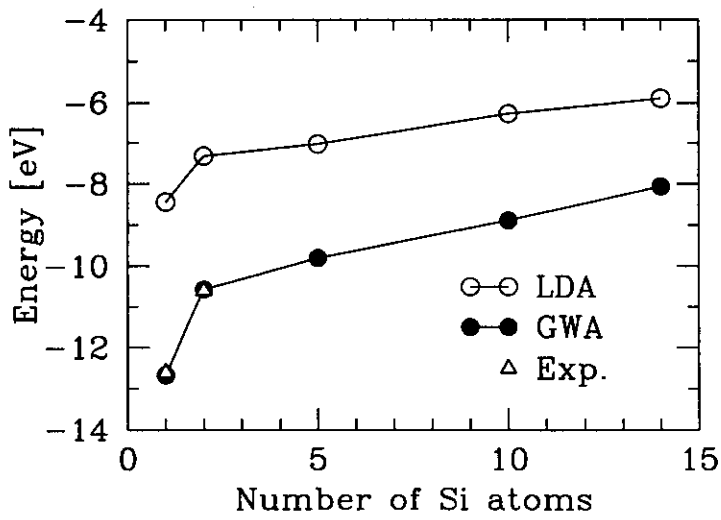
Ionisation Energies of Atoms and Molecules:

[eV]	LDA[a]	GWA	Exp.[b]
He	15.48	24.68	24.586
Ne	13.06	21.47	21.564
Ar	10.35	15.94	15.759
CO	9.1	14.3	14.01
HCl	8.0	12.6	12.75
CH_4	9.3	12.5	12.99
C_2H_4	6.9	10.4	10.5

[a]LDA: $-E_{\text{HOMO}}$

[b]Exp.: Landolt-Börnstein, Vol. I-1 (Springer, Berlin 1950);
G. Herzberg, *Molecular Spectra* (Van Nostrand, N.Y. 1966).

Si_mH_n: Quasiparticle HOMO Energies

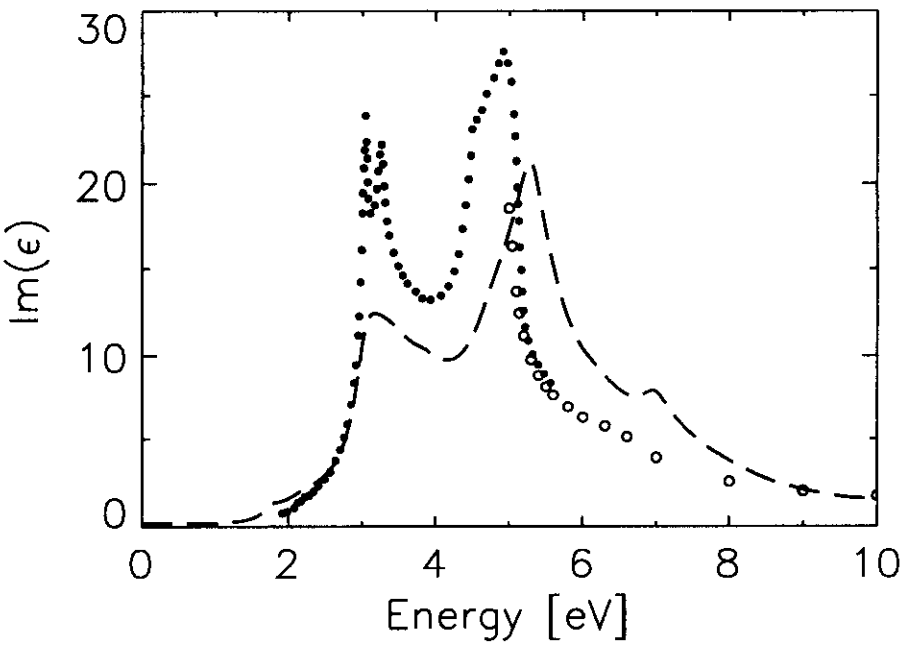


Exp.: U. Itoh et al., J. Chem. Phys. 85, 4867 (1986).

GaAs: Absorption Spectrum ?

- Usual evaluation of the optical spectrum:

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



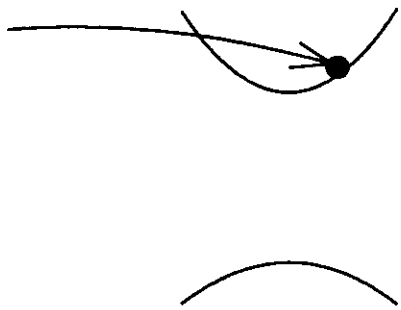
• ○ ○ Exp.

- The "form" of the spectrum is not correct.
- Bound excitons are not described.

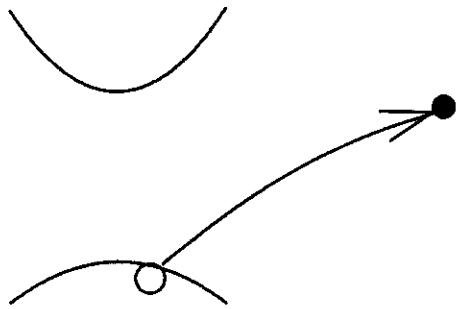
- Quasiparticle band structure:

  describes individually excited holes and electrons
  ($\leftrightarrow$ One-particle Green function G_1)

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

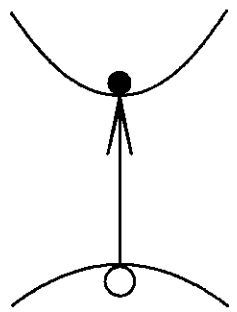


Quasi-hole: $N \rightarrow N-1$
(photoemission; tunneling)

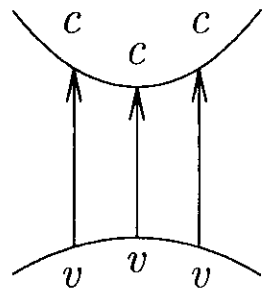


- Optical experiment (e.g., absorption):

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



Coupled Electron-hole excitations:



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

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

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

$A^{S}_{vc\mathbf{k}}$ coupling coefficients

$|S\rangle$ corresponds to the two-particle Green function:

$$G_2(\omega) \hat{=} \sum_{S} \frac{|S\rangle\langle S|}{\omega - \Omega_S} \quad , \qquad \Omega_S \text{ excitation energy}$$

The Bethe-Salpeter Equation for G_2 leads to

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

Strinati 1984

$\varepsilon^{\text{QP}}_{v\mathbf{k}}$, $\varepsilon^{\text{QP}}_{c\mathbf{k+Q}}$ single-QP energies

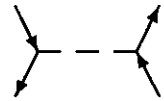
K^{eh} electron-hole interaction

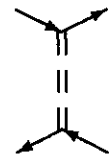
The electron-hole interaction K^{eh}:

$$K^{eh}(12,34) = \frac{\delta[V_{\text{Coul}}(1)\delta(13) + \Sigma(13)]}{\delta G_1(42)} \qquad \mathbf{1}=(\mathbf{r}_1, \sigma_1, t_1)$$

assume that $\Sigma = iG_1W$ and $G_1 \dfrac{\delta W}{\delta G_1} \approx 0$

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





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

$$\int dx dx' \, \psi^*_{c\mathbf{k}+\mathbf{Q}}(\mathrm{x})\psi_{v\mathbf{k}}(\mathrm{x}) \, v(\mathbf{r},\mathbf{r}') \, \psi_{c'\mathbf{k}'+\mathbf{Q}}(\mathrm{x}')\psi^*_{v'\mathbf{k}'}(\mathrm{x}') \qquad \text{(I)}$$

$$- \int dx dx' \, \psi^*_{c\mathbf{k}+\mathbf{Q}}(\mathrm{x})\psi_{c'\mathbf{k}'+\mathbf{Q}}(\mathrm{x})\psi_{v\mathbf{k}}(\mathrm{x}')\psi^*_{v'\mathbf{k}'}(\mathrm{x}') \quad \times \qquad \text{(II)}$$

$$\frac{i}{2\pi} \int d\omega e^{-i\omega 0^+} \, W(\mathbf{r},\mathbf{r}',\omega) \quad \times$$

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

$$=: K^{eh,x} + K^{eh,d}$$

(I) repulsive exchange term $K^{eh,x}$

(II) attractive direct term $K^{eh,d}$

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

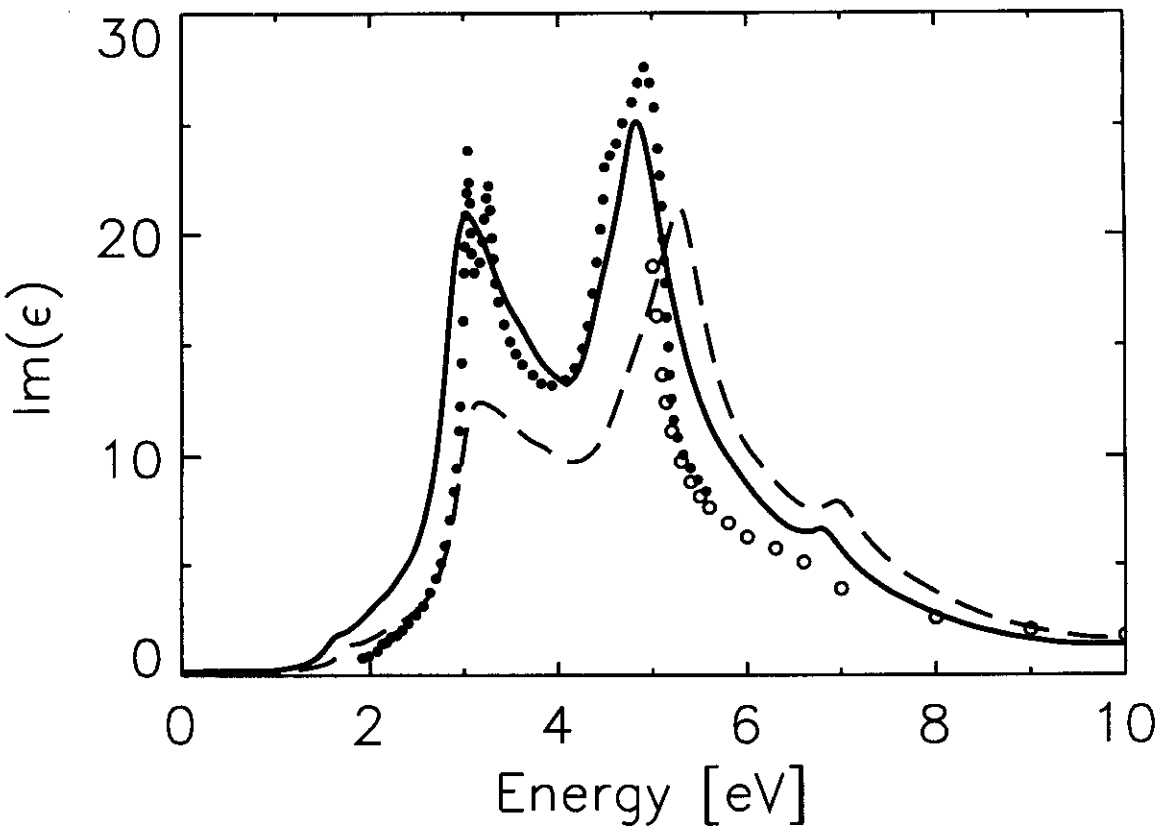
- Coupled transitions $|S\rangle$:

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

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

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

GaAs: Absorption Spectrum



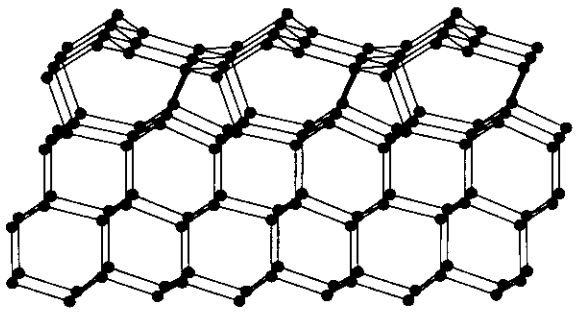
—— with E-H Int. - - - without E-H Int.

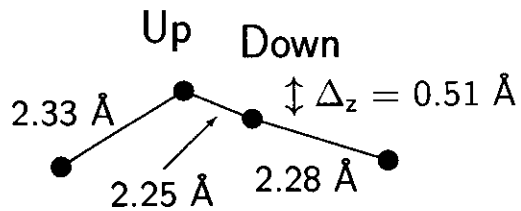
• ○ ○ Exp.: D.E. Aspnes and A.A. Sturge, PRB 27, 985 (1983);
P. Lautenschlager et al., PRB 35, 9174 (1987).

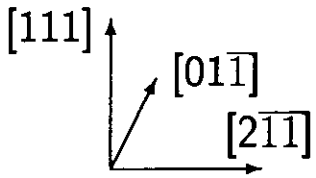
Structure of the Si(111)-(2×1) Surface:

- π-bonded chains ($\leftrightarrow$ K.C. Pandey, Phys. Rev. Lett. 49, 223 (1982)

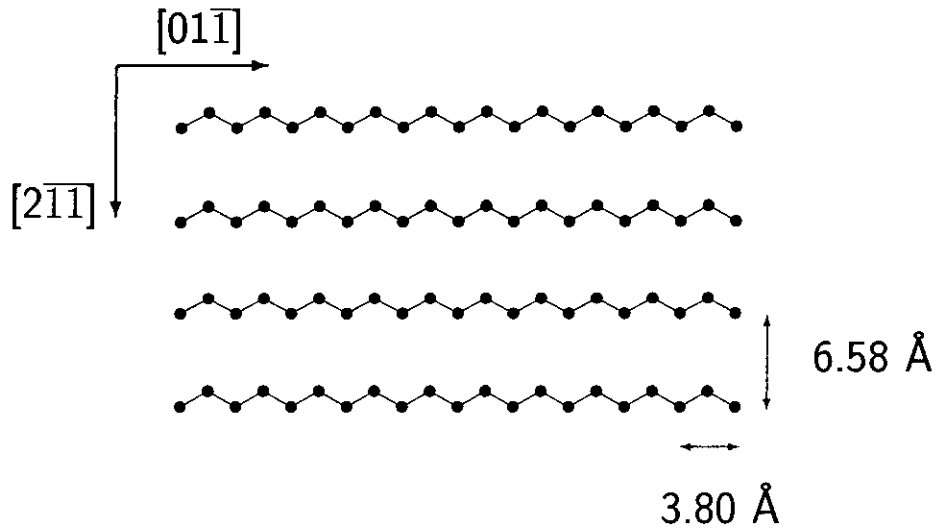
Side view:







Top view:

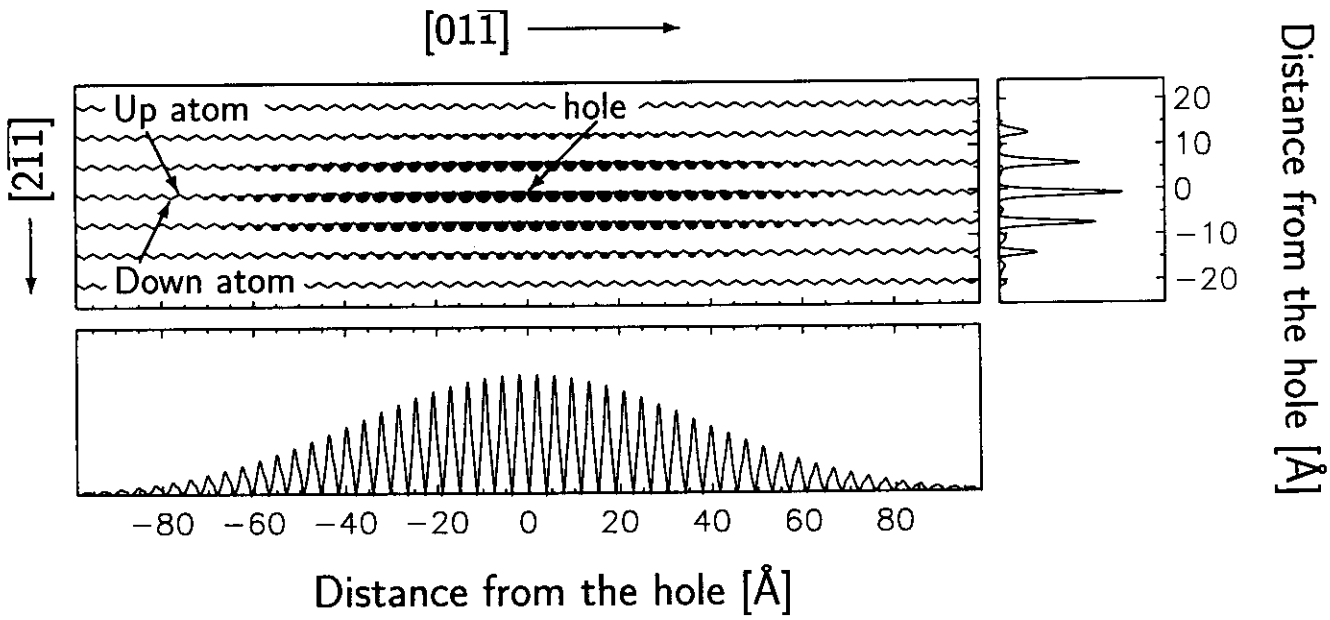


Wave function of the exciton (0.43 eV) – Top view

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

$\mathbf{r}_h$ = coordinates of the hole, $\mathbf{r}_e$ = electron

Distribution of the electron relative to the hole:

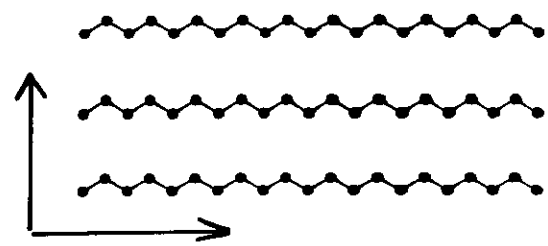


Mean distance Electron—Hole:

- along the chains: 40 Å ($\sim$ Wannier exciton)
- across the chains: 8 Å ($\sim$ Frenkel exciton)

Anisotropy of the Si(111)-(2×1) Surface Exciton

Geometric Structure



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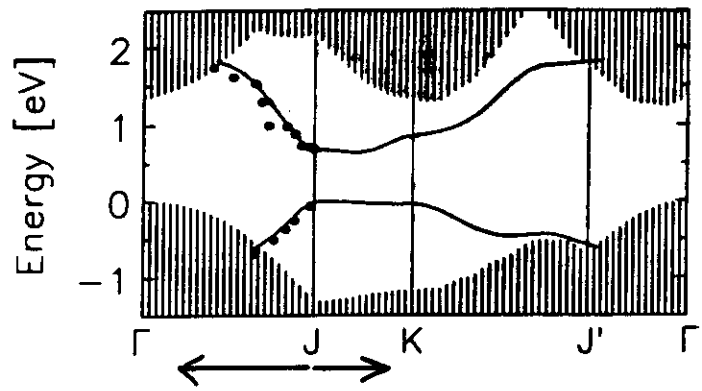
Band Structure



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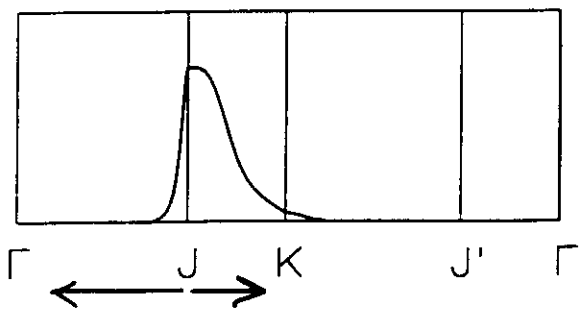
Coupling Coefficients

$A_{\text{up}\to\text{down}}(\mathbf{k})$



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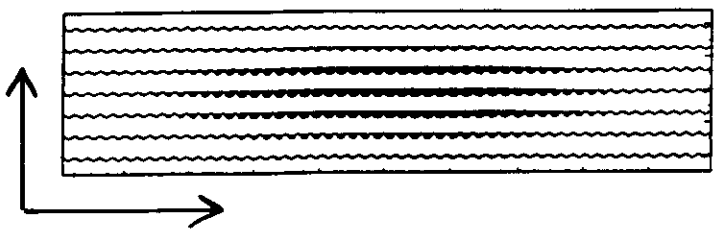
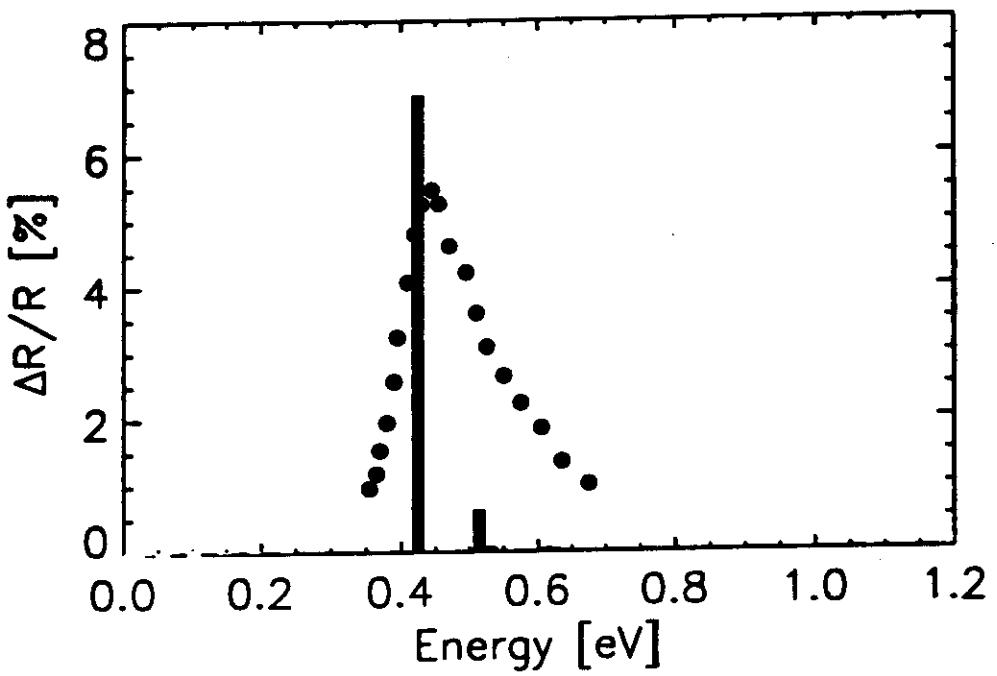
Exciton Wavefunction



Si(111)-(2×1): Line Shape of the DRS



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

- Theory: Discrete exciton levels.
- Exp.: Broadened spectrum
  (FWHM $\sim$ 100 meV at RT).

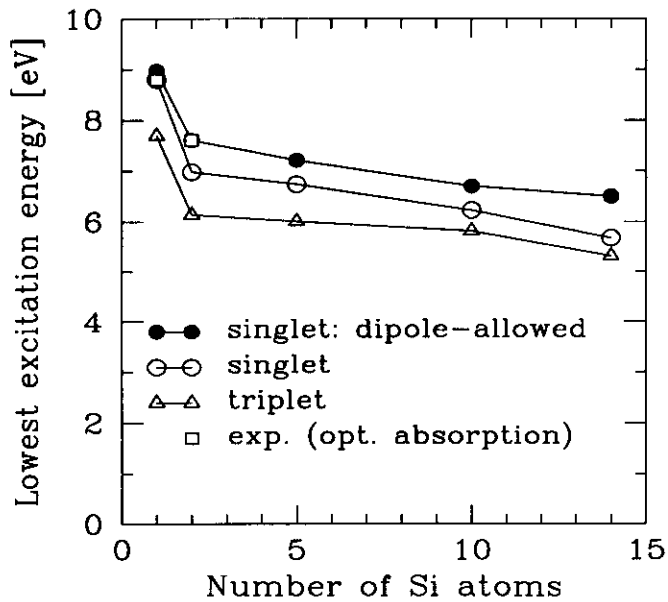
$\Longleftrightarrow$ Coupling to lattice vibrations.

Excitation Energies of Atoms and Molecules

	Spin Singlet		Spin Triplet	
[eV]	GW+BSE	Exp.[a]	GW+BSE	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 (Springer, Berlin 1950);
G. Herzberg, *Molecular Spectra* (Van Nostrand, N.Y. 1966);
L. Serrano-Andres *et al.*, J.Chem.Phys. 98, 3151 (1993).

Si_mH_n: Excitation Energies

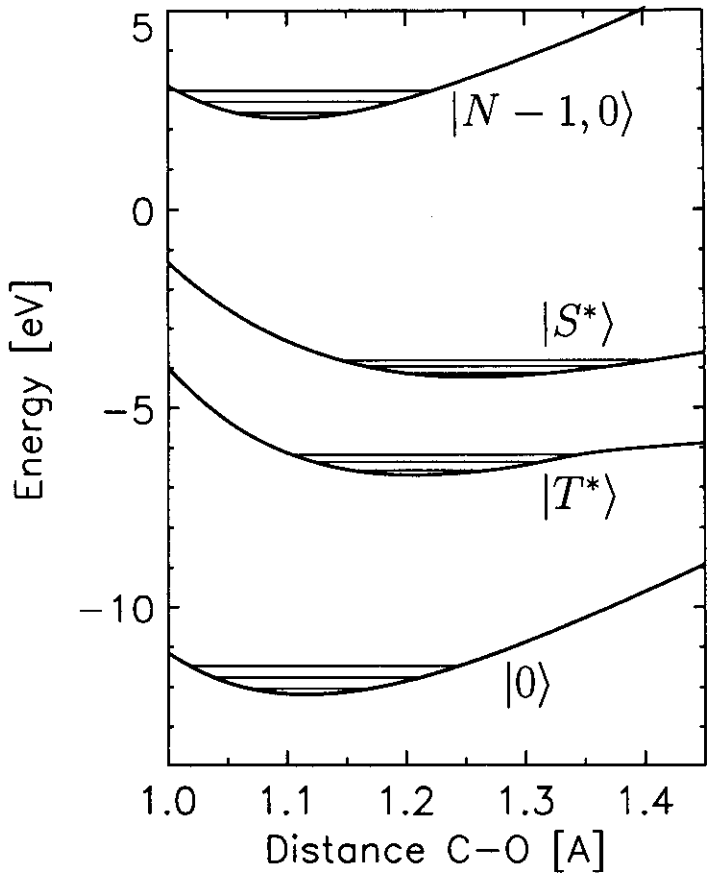


Theor.: M. Rohlfing and S.G. Louie, PRL 80, 3320 (1998).

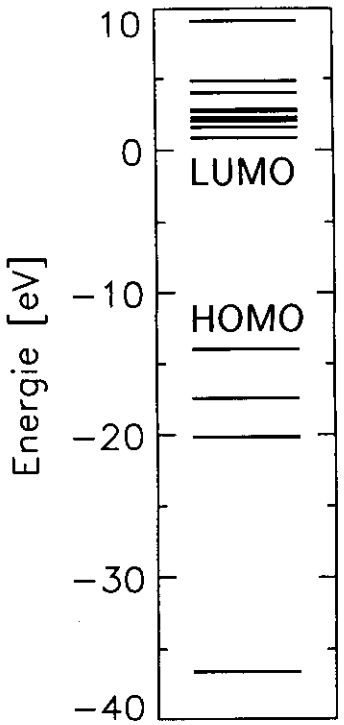
Exp.: U. Itoh et al., J. Chem. Phys. 85, 4867 (1986).

A Diatomic Molecule: CO

Total Energy:



Single-Particle Spectrum (d=1.11Å):



State	d_0 [Å]		ω [cm^{-1}]	
	Theo.	Exp.	Theo.	Exp.
$\|0\rangle$	1.11	1.128	2270	2170
$\|T^*\rangle$	1.21	1.206	1750	1743
$\|S^*\rangle$	1.26	1.235	1480	1518
$\|N-1,0\rangle$	1.10		2240	

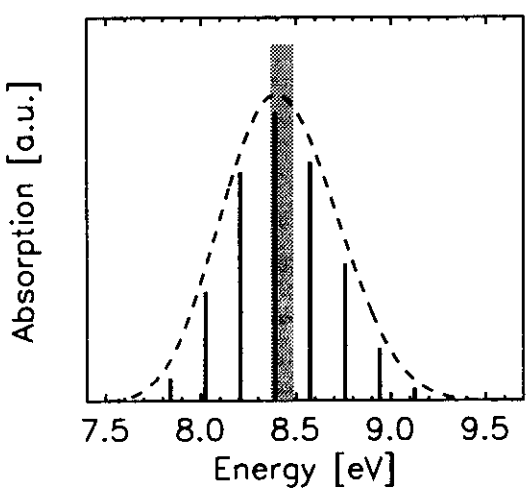
Transitions (ν=0 → ν'=0) [in eV]:

	Theo.	Exp.
CO → C+O	12.0	11.1
$\|0\rangle \rightarrow \|T^*\rangle$	5.5	6.01
$\|0\rangle \rightarrow \|S^*\rangle$	7.9	8.03
$\|0\rangle \rightarrow \|N-1,0\rangle$	14.3	14.01
HOMO-LUMO gap	14.8	

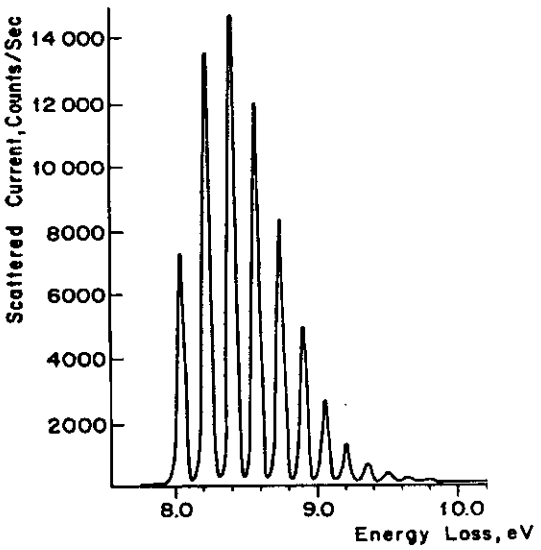
Exp.: K.P. Huber und G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. IV: *Constants of Diatomic Molecules* (Van Nostrand, New York 1979).

Vibrational structure of the spectrum – CO

Theory:



Exp.:



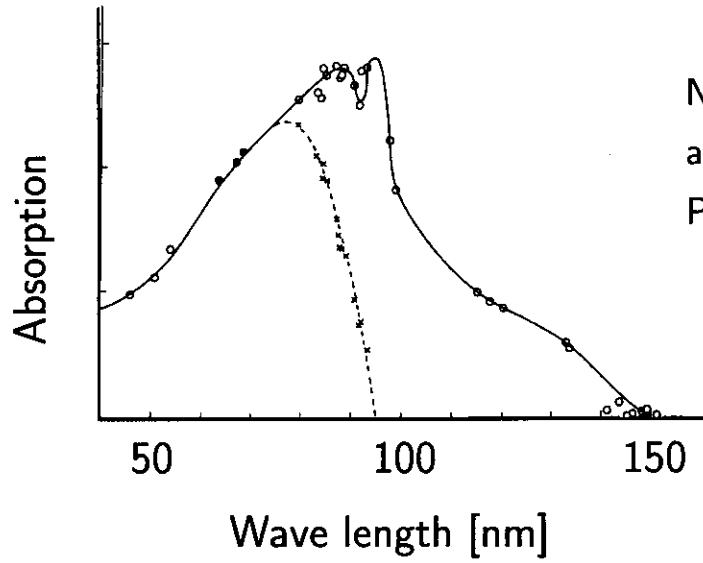
	Theory	Exp.
ΔE [eV]	0.18	0.17
Width [eV]	0.53	0.64
Max. Amplitude at [eV]	8.43	8.47
Maximum Peak	4	3

- Peak of maximum amplitude $\leftrightarrow$ Vertical transition
- Low-energy onset $\leftrightarrow$ Minimum energy in excited state
- Width $\leftrightarrow$ Gain in total energy due to relaxation

Exp.: E.N. Lassettre and A. Skerbele, JCP 54, 1597 (1971).

Absorption spectrum of CH_4 and SiH_4

CH_4:

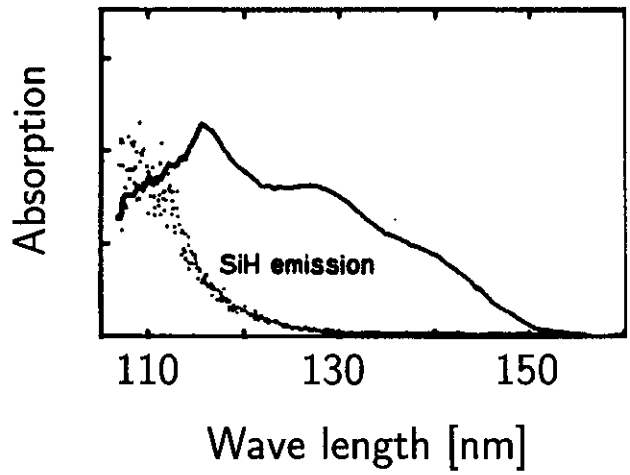


N. Wainfan, W.C. Walker, and G.L. Weissler, Phys.Rev. 99, 542 (1955).

Onset: λ=146 nm $\hat{=}$ 8.5 eV

First maximum: $\lambda\sim$125 nm $\hat{=}$ 9.9 eV

SiH_4:



U. Itoh, Y. Toyoshima, and H. Onuki, JCP 85, 4867 (1986).

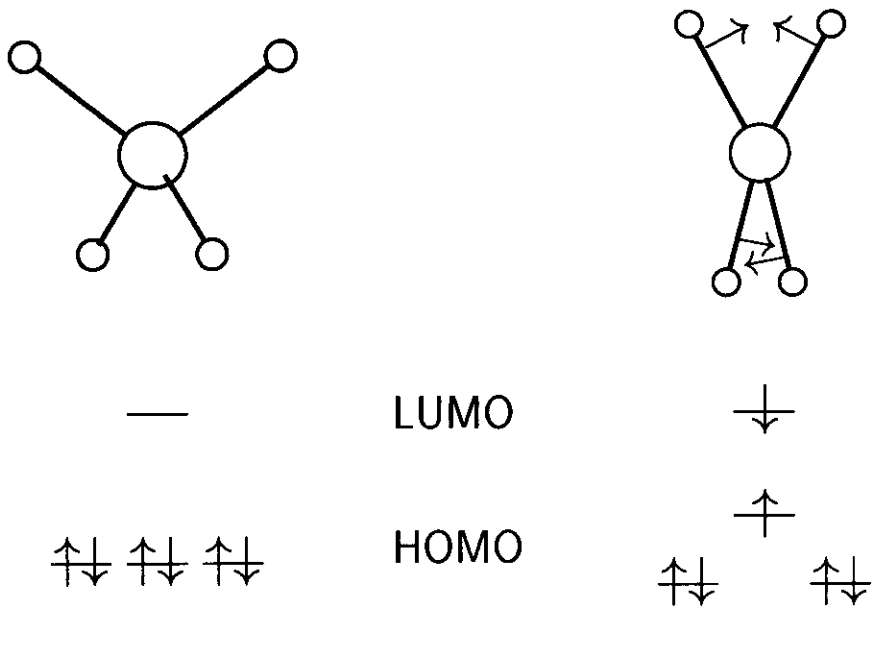
Onset: λ=151 nm $\hat{=}$ 8.2 eV

First maximum: λ=141 nm $\hat{=}$ 8.8 eV

CH_4 and SiH_4: Geometry of the Excited States

- Increase of the C-H distance
- Distortion / Reduction of the symmetry

Ground State: T_d Excited State: C_{2v}

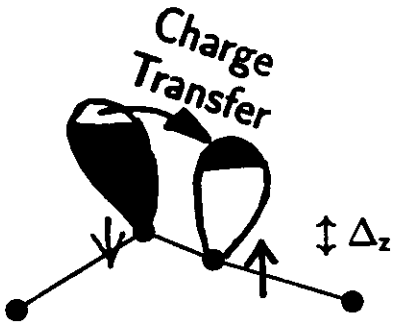


		Vert. Trans.	Energy Gain $d_0 \to d$	Energy Gain $T_d \to C_{2v}$	Min. Trans.	Exp.
CH_4:	Ionization	14.3	–0.2	–1.6	12.5	12.99
	E_S	10.5	–0.3	–1.6	8.6	8.52
	E_T	10.1	–0.4	–1.5	8.2	
SiH_4:	Ionization	12.6	–0.1	–0.6	11.9	
	E_S	9.2	–0.2	–0.7	8.3	8.2
	E_T	8.5	–0.5	–0.3	7.7	

Exp.: G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand 1966); U. Itoh *et al.*, J. Chem. Phys. **85**, 4867 (1986).

Si(111)-(2×1) Surface – Interaction with the Structure

Exciton state:

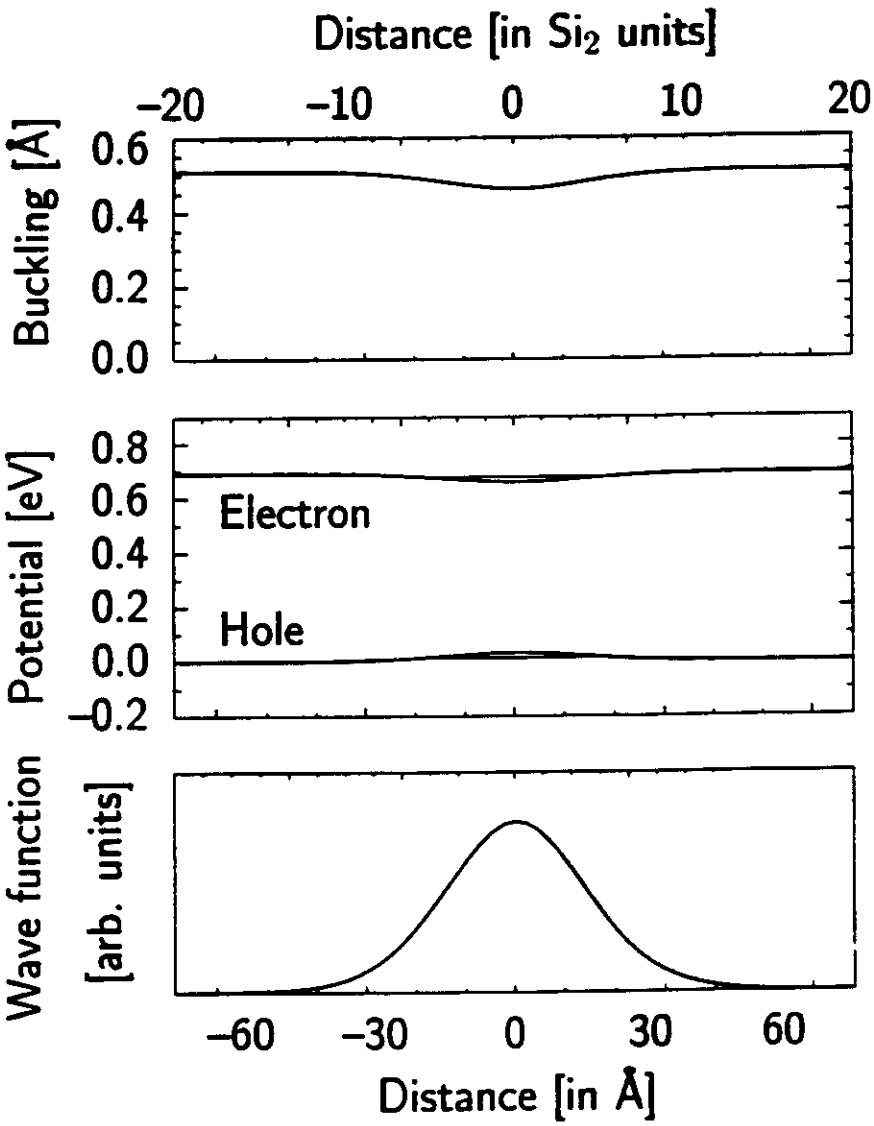


Charge transfer

$\Longrightarrow$ Reduction of buckling

$\Longrightarrow$ Reduction of E_{gap}

$\Longrightarrow$ Self Trapping



Minimization of E^*_{tot}:

$\Delta z = -0.05$ Å

$\Delta E_g = -65$ meV

New VBM: +13 meV

New CBM: E_g – 13 meV

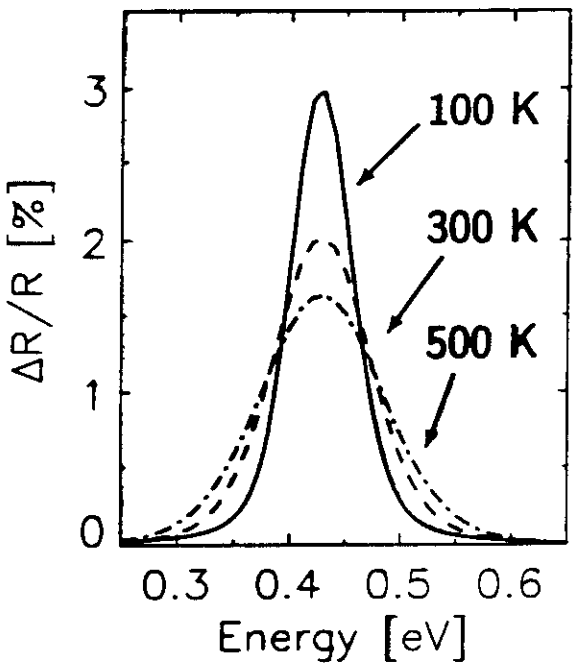
New Exciton: $E_1 - 41$ meV

Lattice Energy: +17 meV

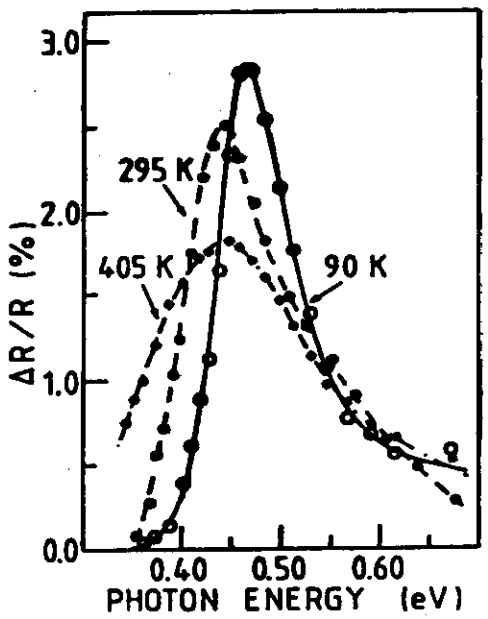
$\Longrightarrow E^*_{\text{tot}} = E_1 - 24$ meV

Si(111)-(2×1) Surface Exciton – Spectral Width

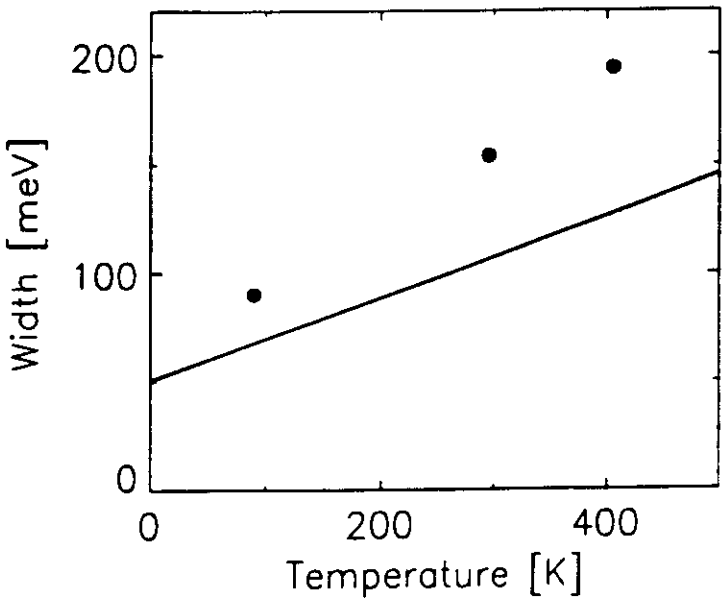
Calculated:



Measured:



Spectral Width (at half maximum):



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

Conclusions

- Three-level ab-initio concept:

  Ground state (LDA)

  $\longrightarrow$ G_1 (GWA); QP spectrum

  $\longrightarrow$ Electron-hole interaction + G_2;

  Electron-hole Excitations; optical spectrum

- Semiconductor surface Si(111)-(2×1):

  Bound surface exciton

  Enhanced electron-hole interaction

- Molecules:

  Interrelation between excitations and geometry

- Outlook:

  Excitations of molecules adsorbed at surfaces