Spezialvorlesung zur Theoretischen Physik:

Ab-initio Methoden in der Festkörperphysik

(2 VO)

653.534

Peter Puschnig

Contents of Lecture

Literature

[1] A Primer in Density Functional Theory, Lecture Notes in Physics, C. Fiolhais, F. Nogueira, M. Marques (Eds.), Springer (2003).

[2] Density Functional Theory – A Practical Introduction, David S. Sholl, Janice A. Steckel, Wiley (2009).

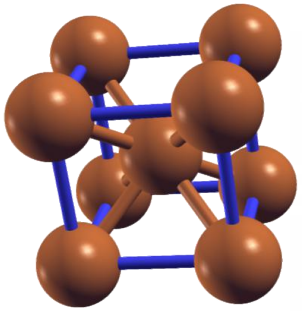
[3] Walter Kohn, Nobel Lecture: Electronic structure of matter-wave functions and density functionals, Rev. Mod. Phys. 71, 1253 (1999).

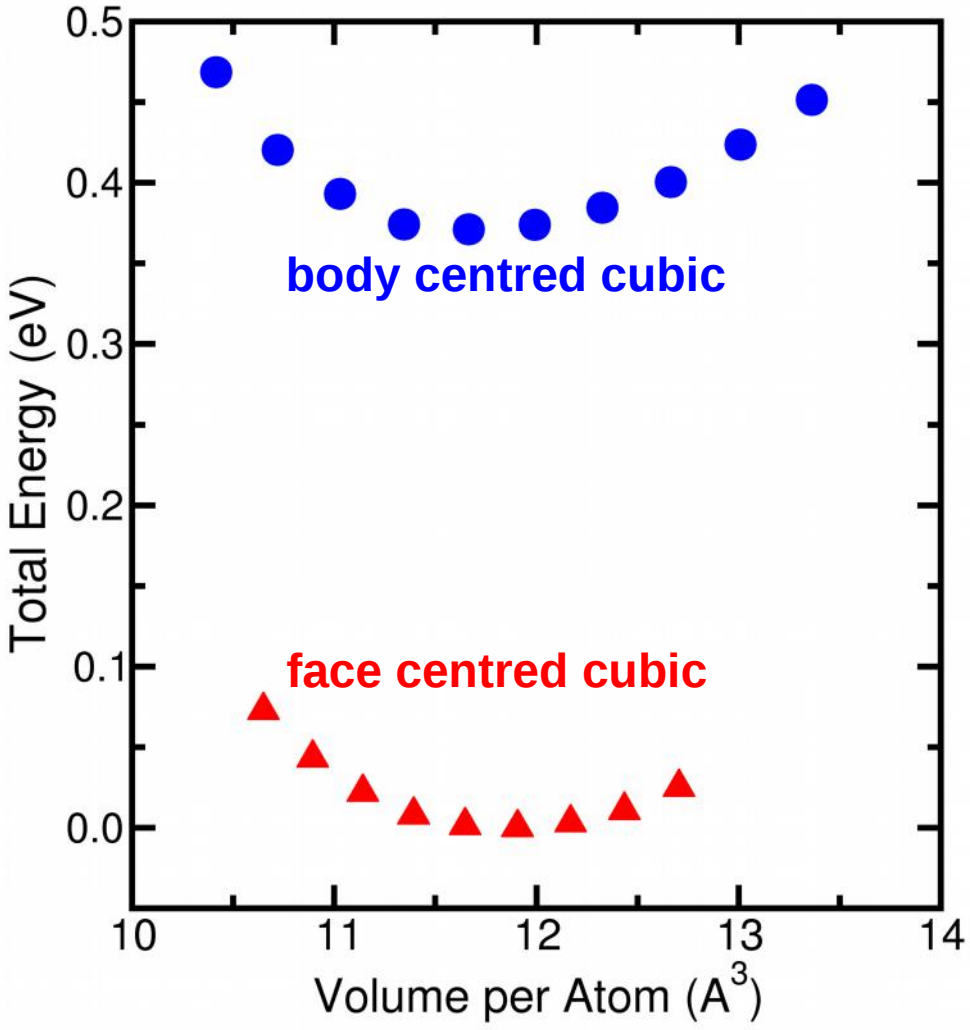
[4] R. O. Jones, O. Gunnarsson,cThe density functional formalism, its application and prospects, Rev. Mod. Phys. 61, 689 (1989).

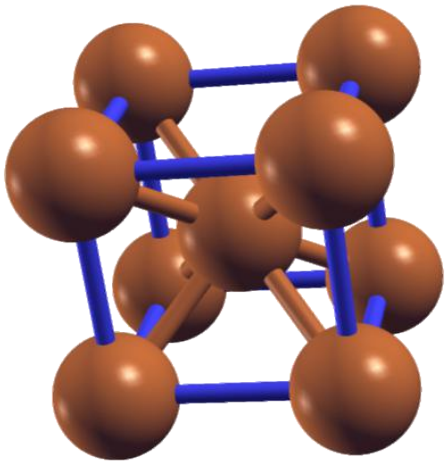
[5] Peter Hohenberg, Walter Kohn, Inhomogeneous Electron Gas, Phys. Rev. 136, B864 (1964).

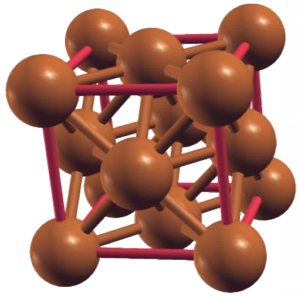
[6] W. Kohn, L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, Phys. Rev. 140, A1133-A1138 (1965).

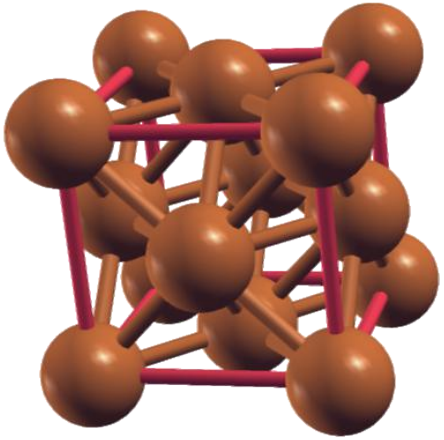
Elastic Properties: Bulk Modulus



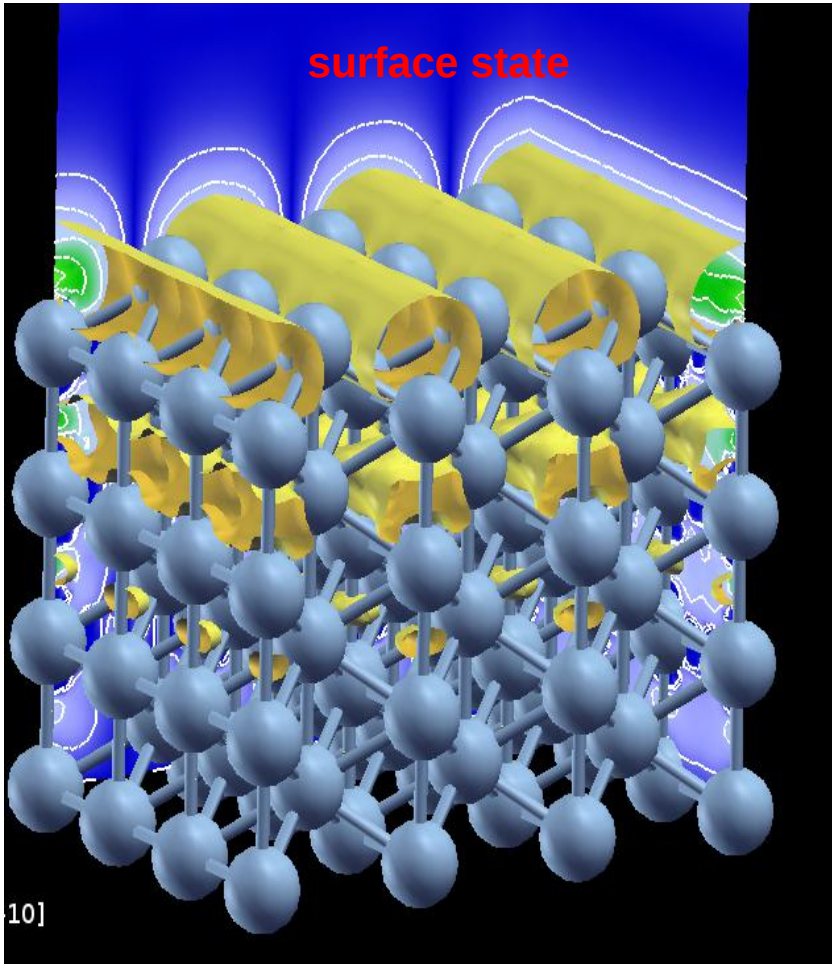


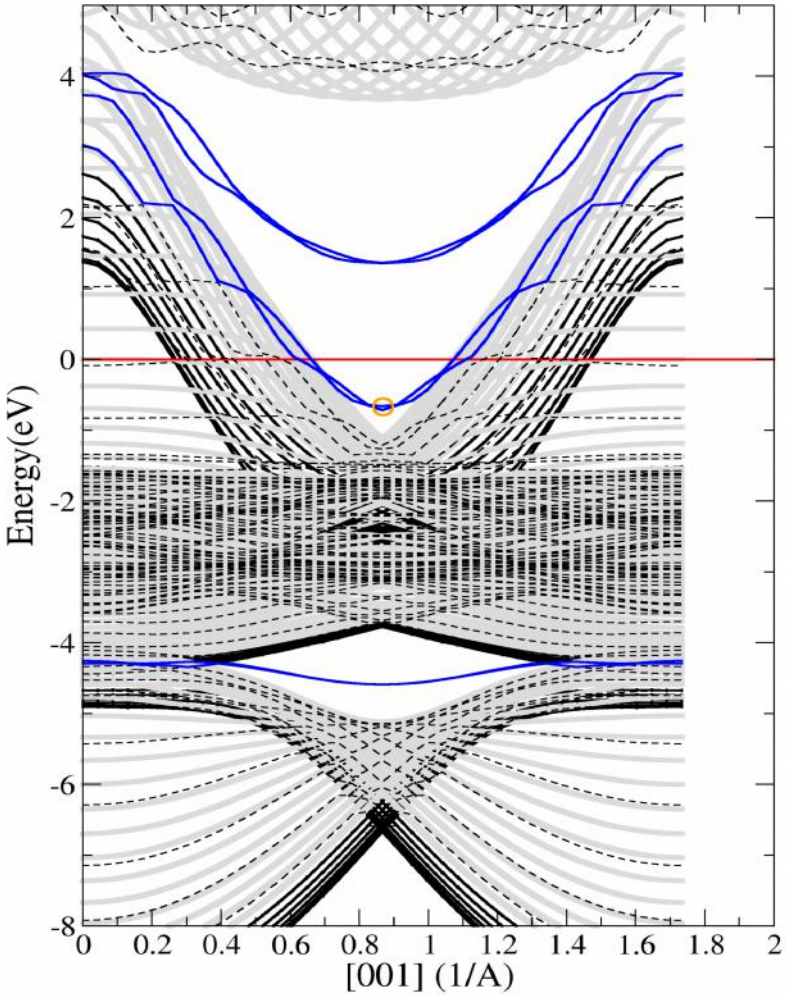






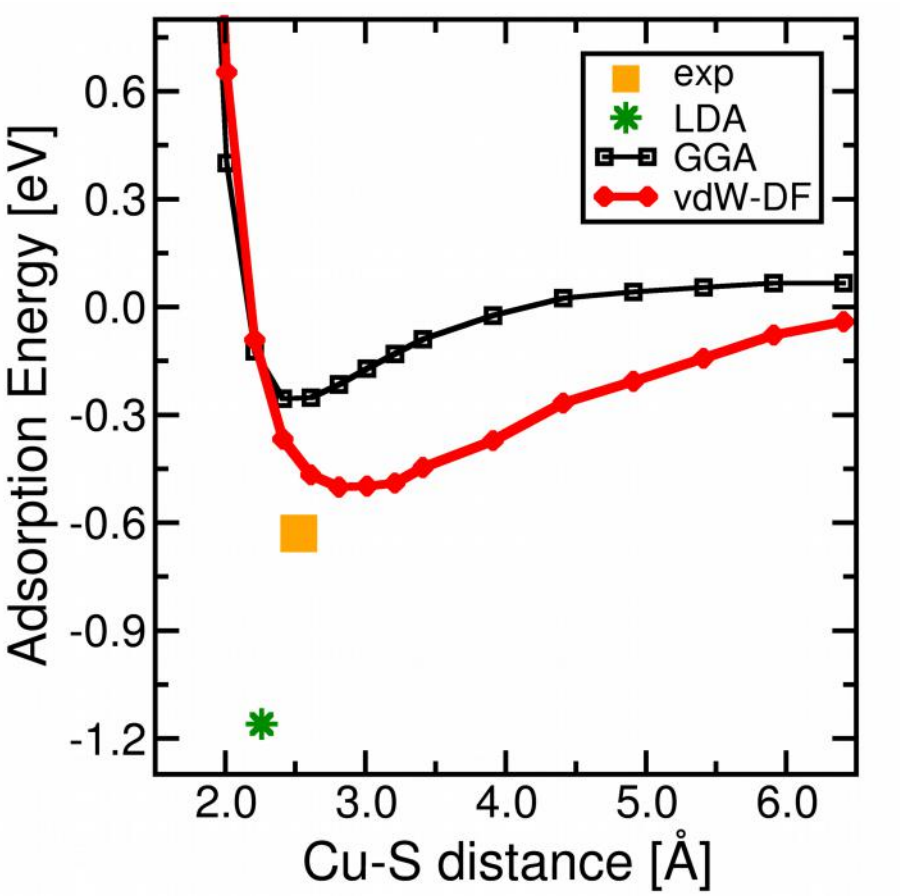
Surface State at a Cu(110) Surface

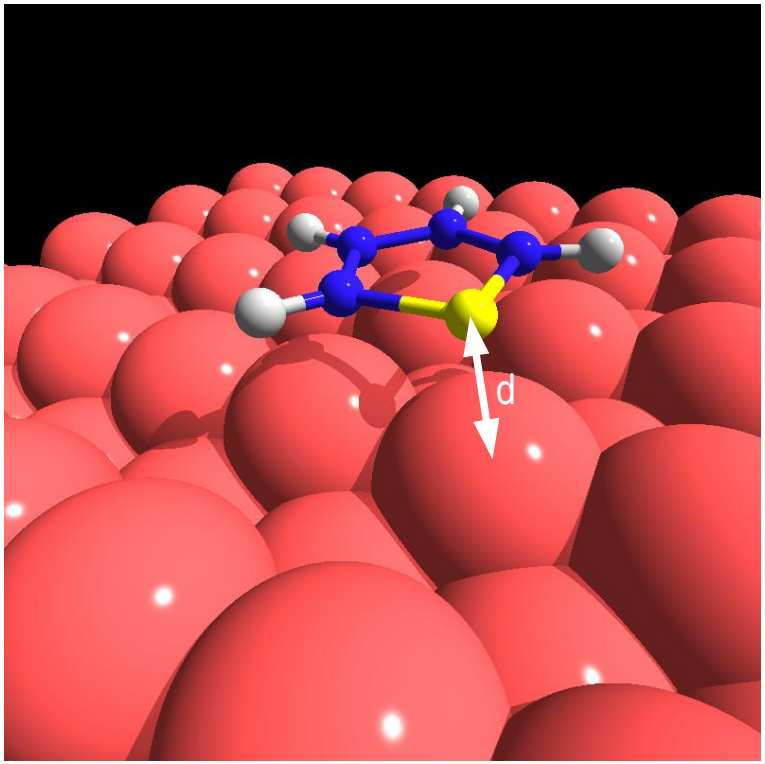




Surface state (left) and electronic band structure of a Cu(110) surface

Molecules Adsorbed at Surfaces

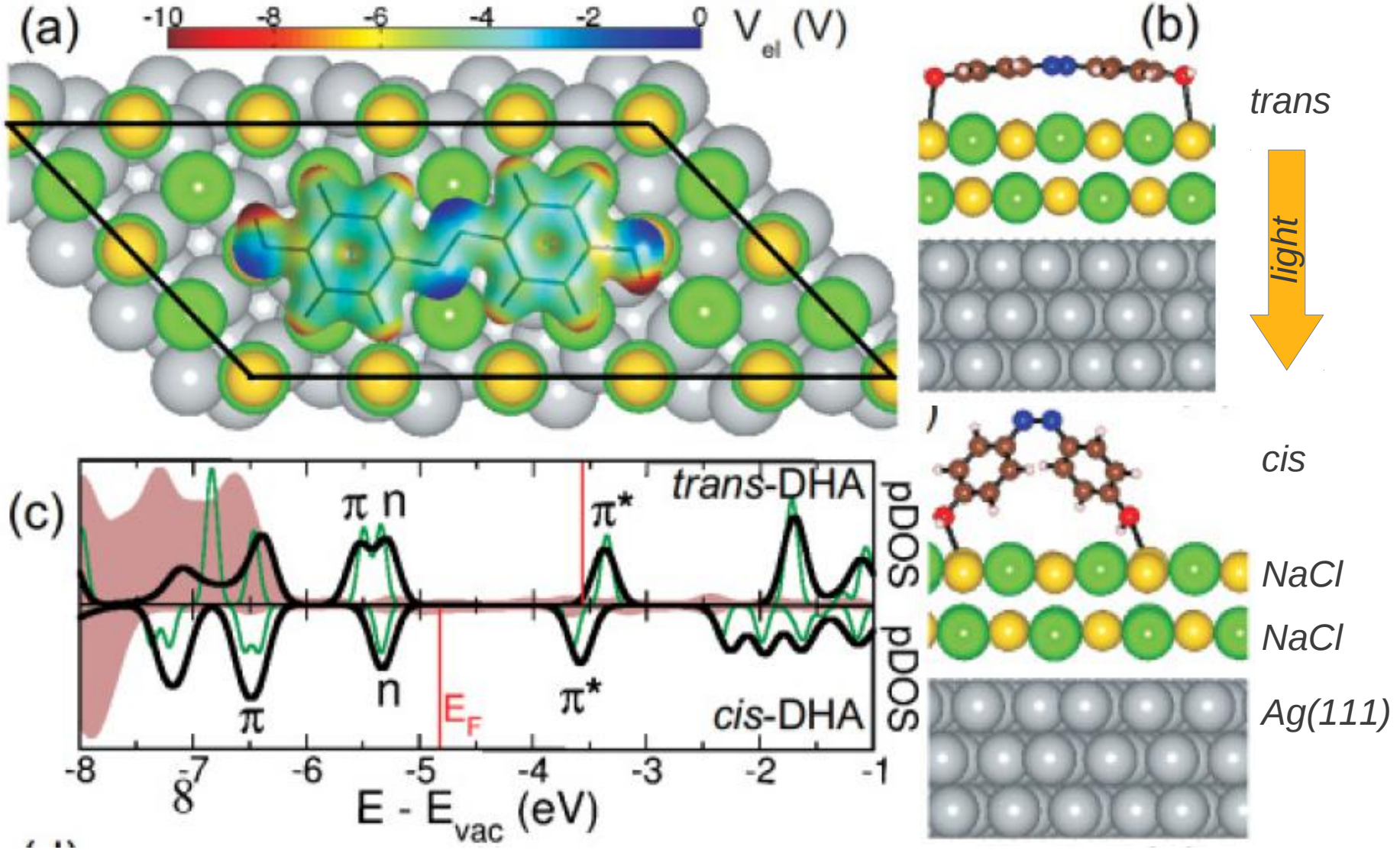




Thiophene@Cu(110): Sony et al., *Phys. Rev. Lett.* ***99****, 176401 (2007).*

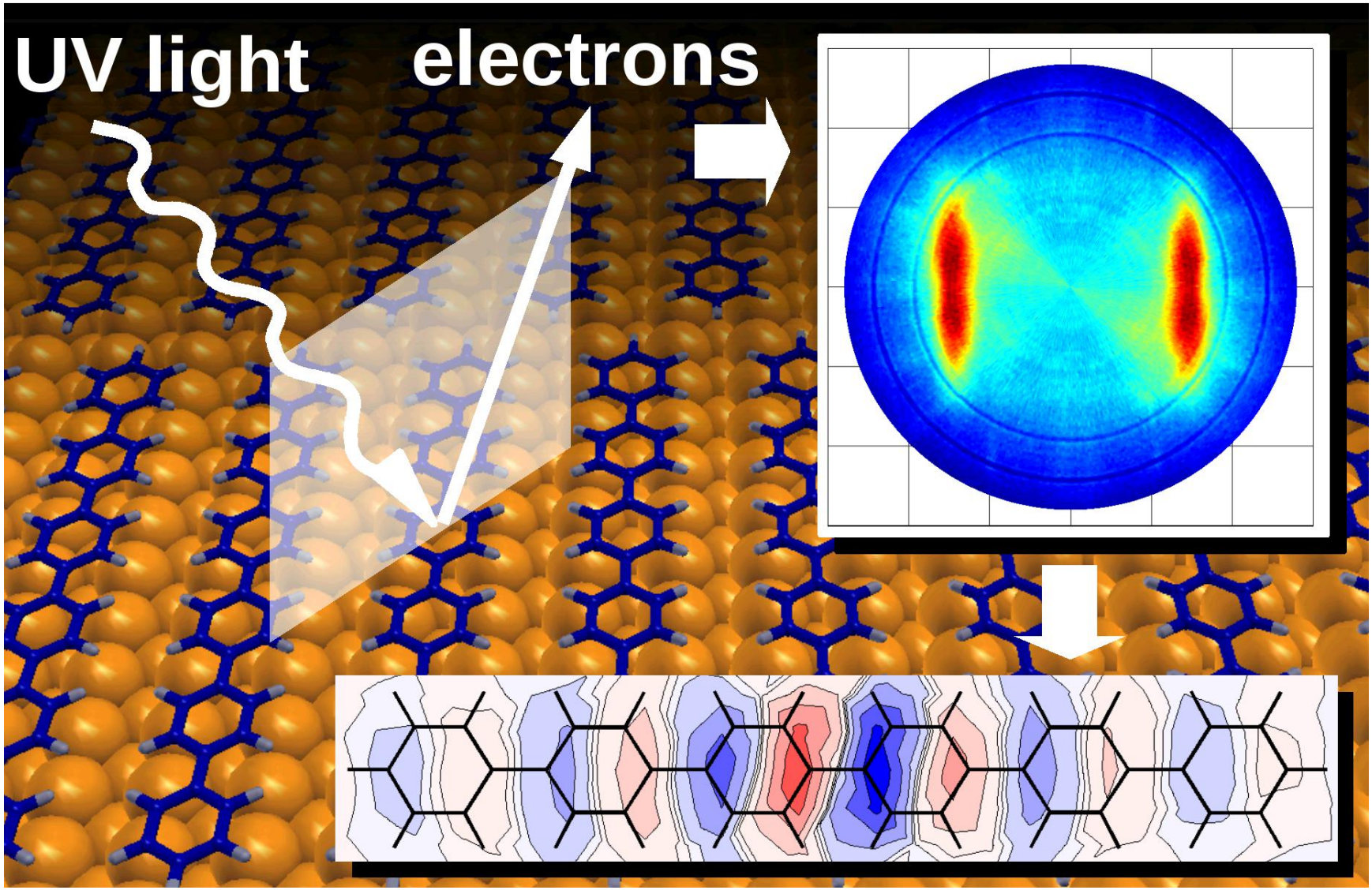
PTCDA@Cu,Ag,Au(111): Romaner et al., New. J. Phys. ***11****, 053010 (2009).*

Molecules Adsorbed at Surfaces



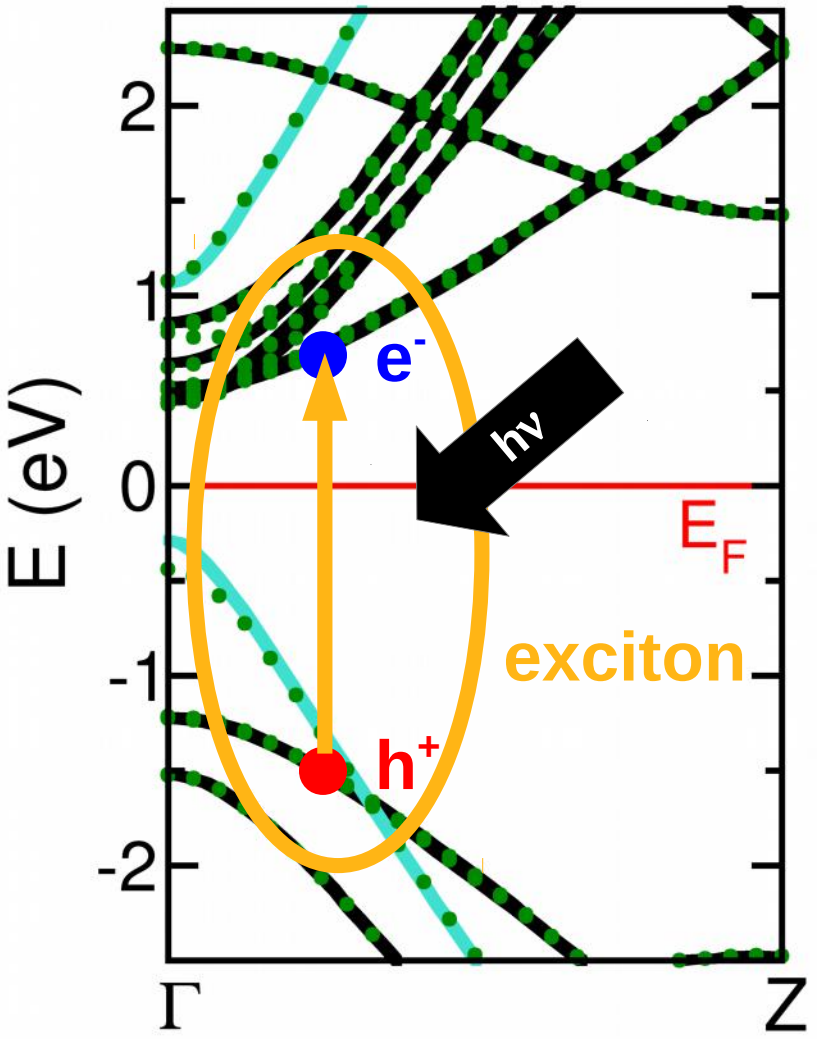
Henzl et al., *Phys. Rev. B* ***85****, 035410 (2010).*

Simulation of Photoemission Process

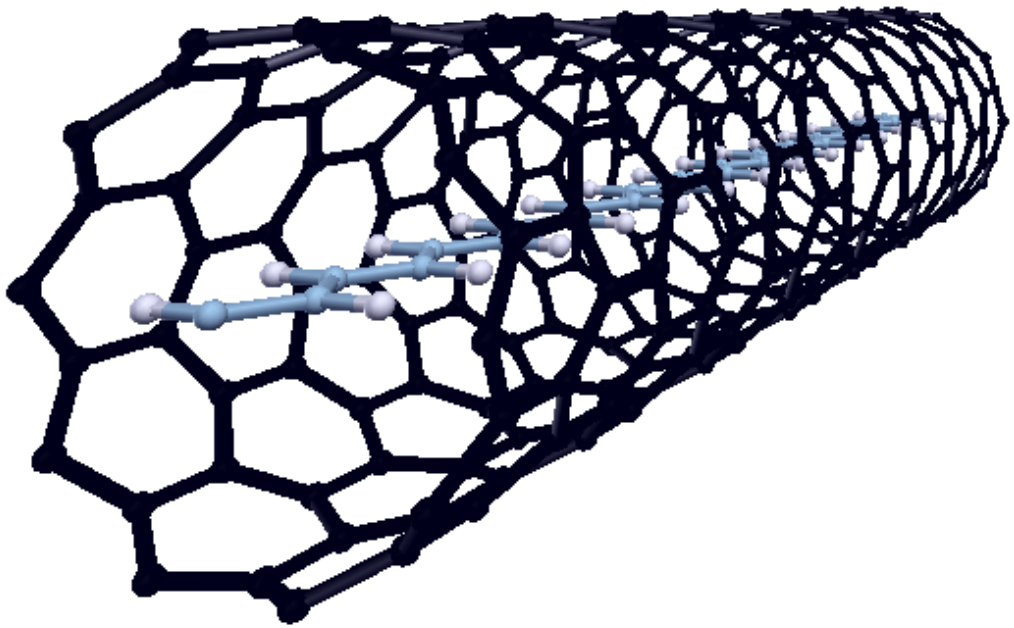


Puschnig et al., Science ***326***, *702 (2009).*

A Polymer Inside a Carbon Nanotube



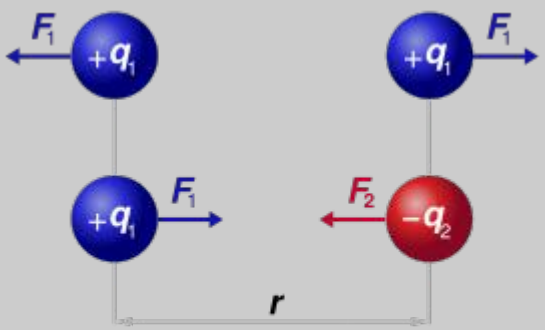
Puschnig, unpublished



trans-polyacetylene
inside a
(10,0) CNT

The Quantum Mechanical Many-Body Problem

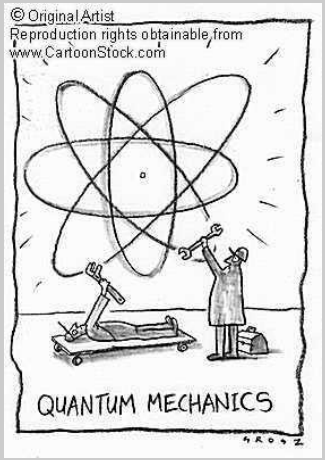
Coulomb Force



$$F_1 = F_2 = k_c \frac{q_1 \times q_2}{r^2}$$

+

Quantum Mechanics



Band structure

Elastic properties

vibrations

Magnetic properties

Optical properties

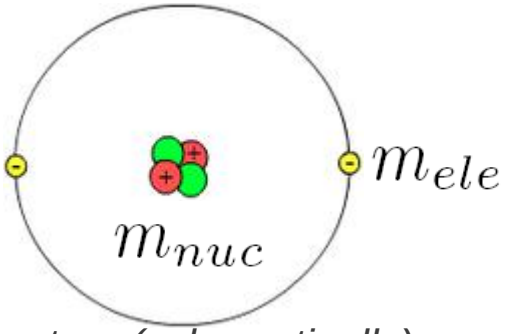
The Quantum Mechanical Many-Body Problem

The material world of everyday experience, as studied by chemistry and condensed-matter physics, is built up from electrons and a few (or at most a few hundred) kinds of nuclei . The basic interaction is electrostatic or Coulombic: An electron at position $\mathbf{r}$ is attracted to a nucleus of charge Z at $\mathbf{R}$ by the potential energy $-Z/|\mathbf{r}-\mathbf{R}|$, a pair of electrons at $\mathbf{r}$ and $\mathbf{r}'$ repel one another by the potential energy $1/|\mathbf{r}-\mathbf{r}'|$, and two nuclei at $\mathbf{R}$ and $\mathbf{R}'$ repel one another as $Z'Z/|\mathbf{R}-\mathbf{R}'|$. The electrons must be described by quantum mechanics, while the more massive nuclei can sometimes be regarded as classical particles. All of the electrons in the lighter elements, and the chemically important valence electrons in most elements, move at speeds much less than the speed of light, and so are non-relativistic.

In essence, that is the simple story of practically everything. But there is still a long path from these general principles to theoretical prediction of the structures and properties of atoms, molecules, and solids, and eventually to the design of new chemicals or materials. If we restrict our focus to the important class of ground-state properties, we can take a shortcut through density functional theory.

Quoted from: J. Perdew, "A Primer in DFT"

Electrons and Atomic Nuclei



He atom (schematically)

$$m_{nuc} \gg m_{ele}$$

Born-Oppenheimer approximation

$$\Psi_{total} = \psi_{electronic} \times \psi_{nuclear}$$

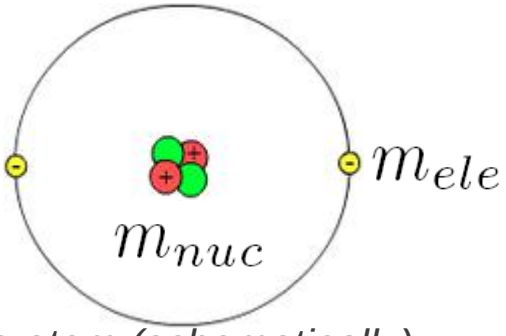
de Broglie wavelength

$$\lambda = \frac{h}{p}$$

electrons QM

nuclei classical (Newton)

The Adiabatic Approximation



He atom (schematically)

$$m_{nuc} \gg m_{ele}$$

The Born-Oppenheimer (=adiabatic) Approximation

- The electrons can follow the much heavier nuclei instantaneously
- Electronic and nuclear motion can be separated
- The nuclear coordinates can be regarded as parameters for the electronic problem
- The electronic energy provides a potential for the nuclear motion

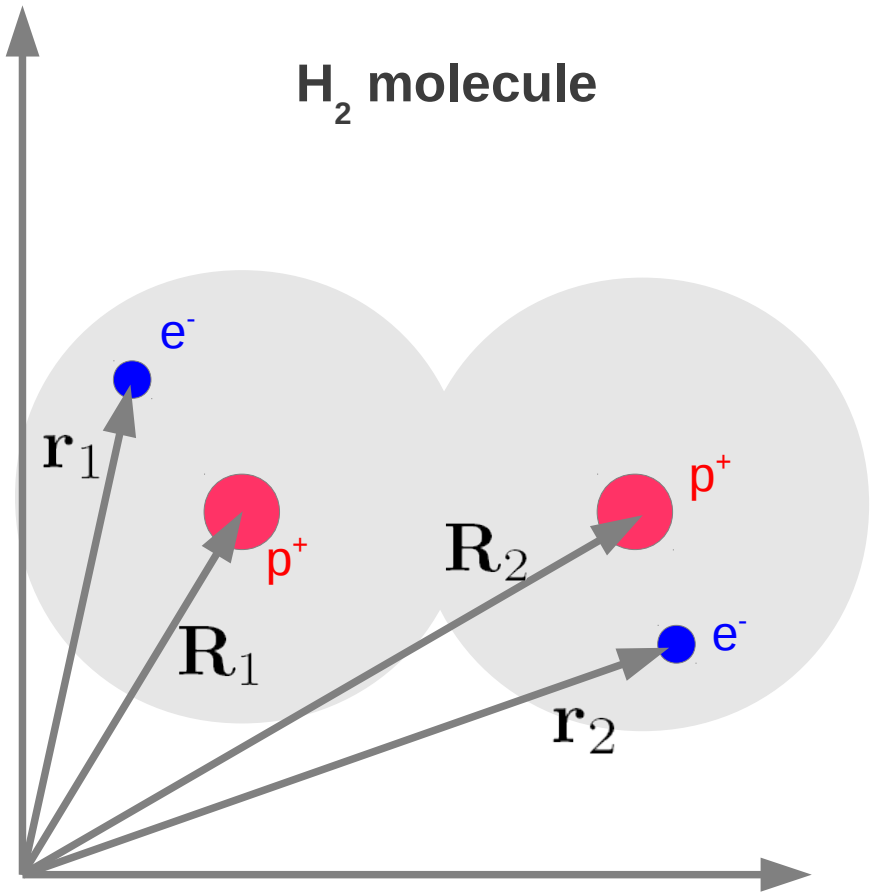
Towards the Many-Electron Problem

Kinetic Energy

$$T = T_e + T_n$$

$$T_e = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} = \sum_{i=1}^{2} \frac{p_i^2}{2m_e}$$

$$T_n = \frac{P_1^2}{2M_n} + \frac{P_2^2}{2M_n}$$



Towards the Many-Electron Problem

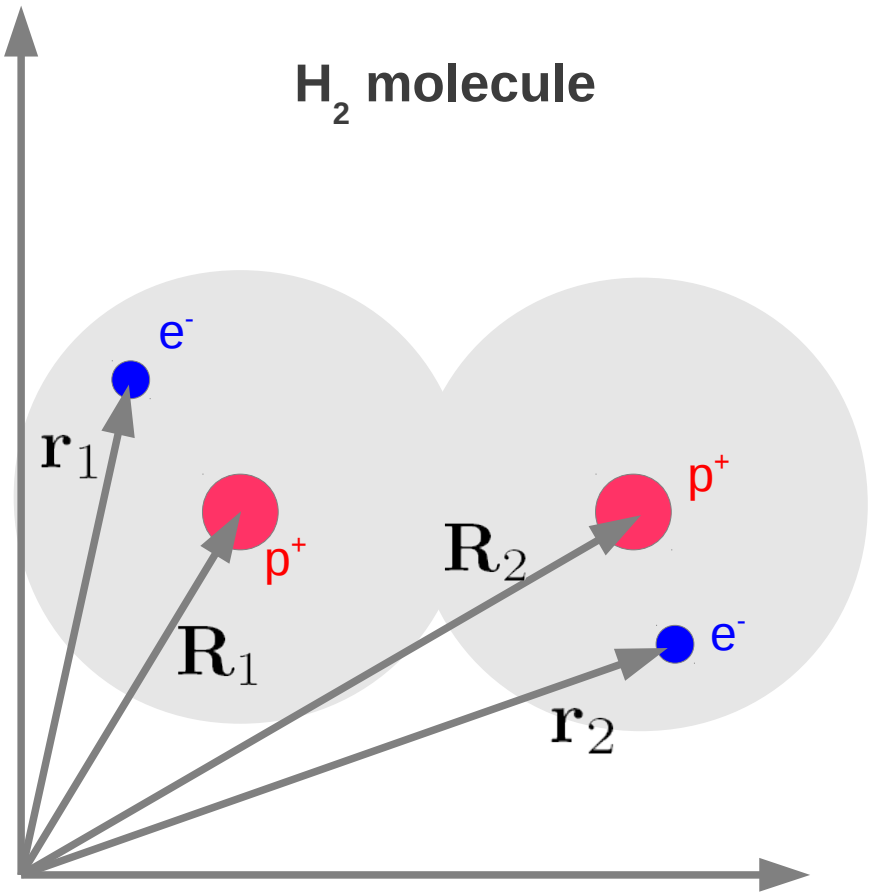
Potential Energy

$$V = V_{n-n} + V_{n-e} + V_{e-e}$$

$$V_{n-n} = \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|}$$

$$V_{e-e} = \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\begin{aligned} V_{n-e} &= -\frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_2|} \\ &\quad -\frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_1|} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_2|} \\ &= -\sum_{i=1}^{2}\sum_{j=1}^{2}\frac{1}{4\pi\epsilon_0}\frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|} \end{aligned}$$



Towards the Many-Electron Problem

Total Electronic Hamiltonian

$$
\begin{aligned}
H &= T_e + V \\
&= \sum_{i=1}^{2} h_i + V_{e-e}
\end{aligned}
$$

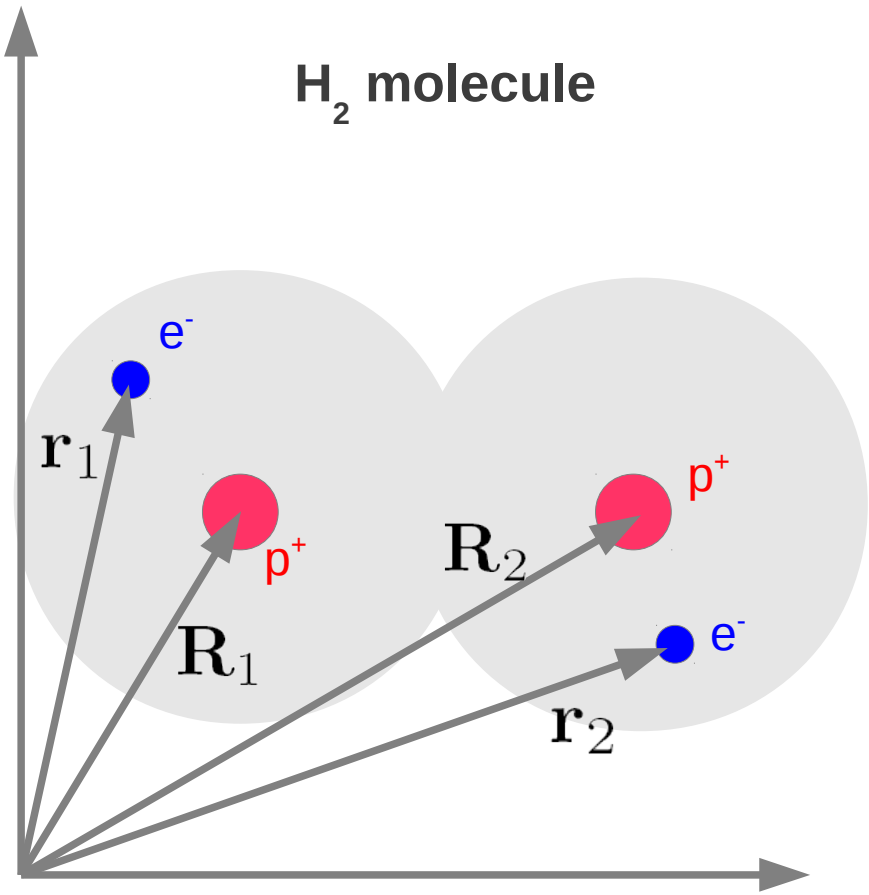
$$h_i = -\frac{\hbar^2}{2m_e}\Delta_i + \sum_{j=1}^{2} \frac{1}{4\pi\epsilon_0}\frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|}$$

$$V_{e-e} = \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

⬇

2-electron Schrödinger equation

$$H\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2)$$



The Many-Electron Problem

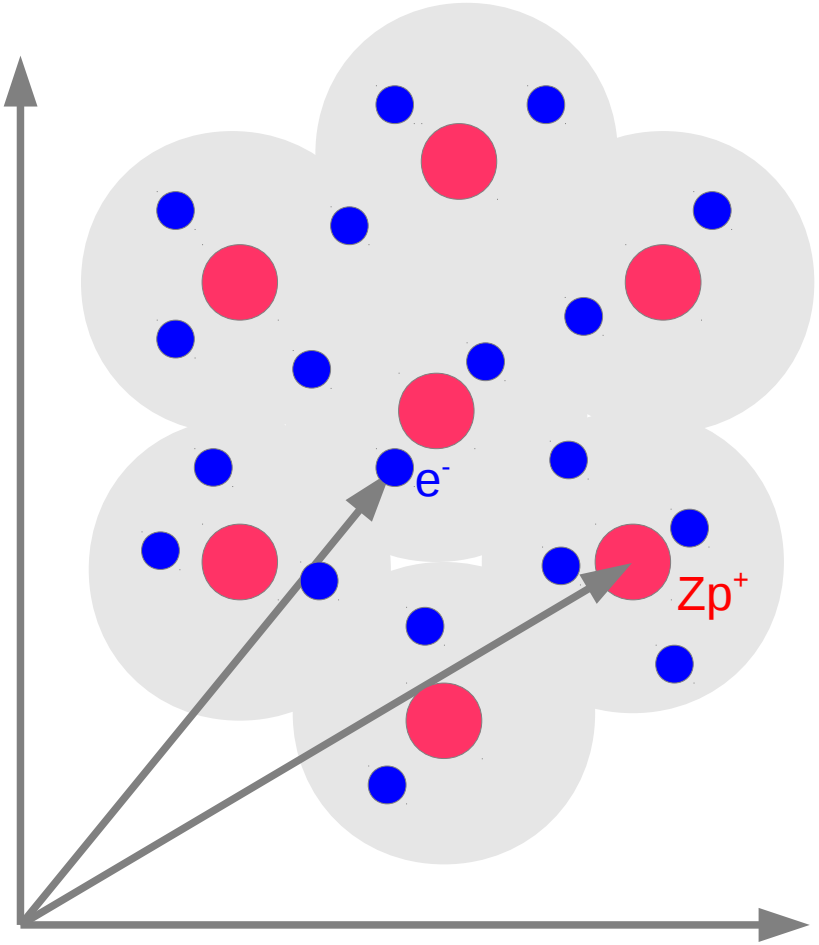
Total Electronic Hamiltonian

$$H = \sum_{i=1}^{n} h_i + V_{e-e}$$

$$h_i = -\frac{\hbar^2}{2m_e}\Delta_i + \sum_{j=1}^{N} \frac{1}{4\pi\epsilon_0}\frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|}$$

$$V_{e-e} = \sum_{i=2}^{n}\sum_{j=1}^{i-1} \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Many-electron Schrödinger equation

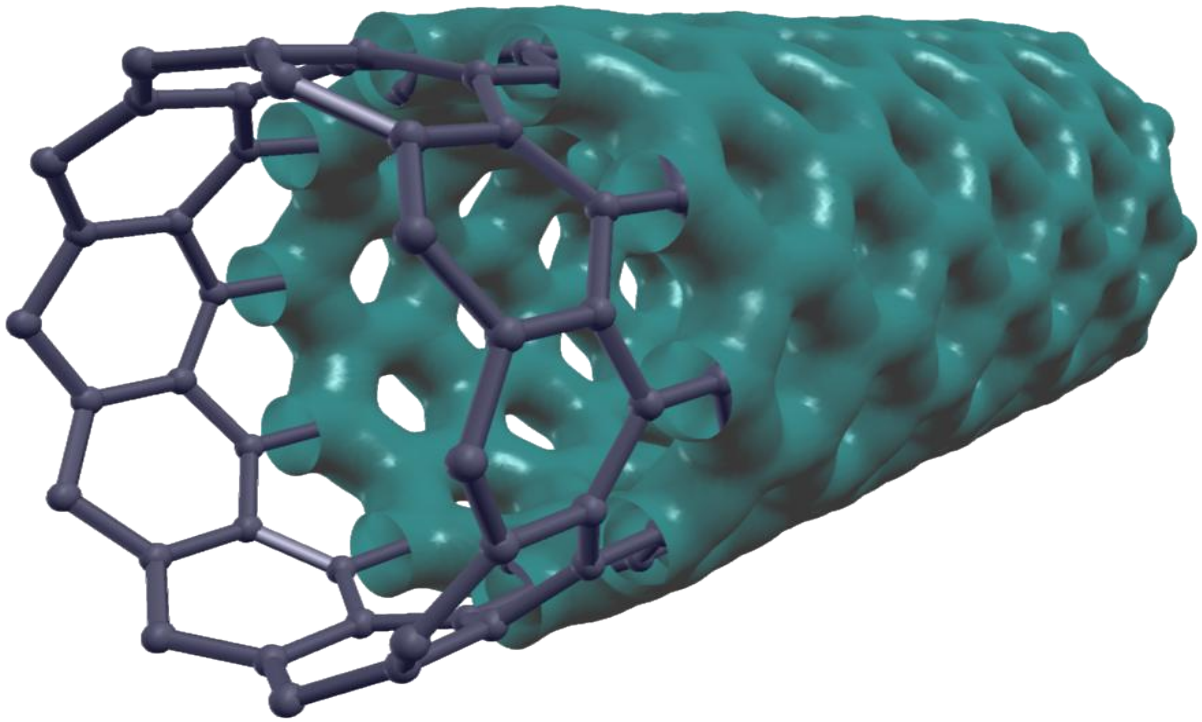


$$H\Psi(\mathbf{r}_1, ..., \mathbf{r}_i, ..., \mathbf{r}_n) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_i, ..., \mathbf{r}_n)$$

Van Vleck Catastrophe

- Small molecules
  - Wave function methods (HF, configuration interaction, ...) give excellent results
  - Number of parameters in many-electron wave function: $M = p^{3N}$
- Large molecules and solids
  - *„Many electron wave function is not a legitimate concept when N > 100“*
  - Number of parameters in wave function: $M = p^{3*100} = 10^{150}$*!!*
  - Accuracy of the wave function becomes a problem!
  - Storage of the results: $B = q^{3*100} = 10^{150}$ *bits required !!*

Electron Density as a Loophole



- Electron density $n(\mathbf{r})$ is the basic variable
- Density Functional Theory (DFT) provides rigorous framework
- All microscopic and macroscopic properties depend on $n(\mathbf{r})$

DFT in a Nutshell: Hohenberg-Kohn-Theorems

1. If two systems of electrons, one trapped in a potential $v_1(\mathbf{r})$ and the other in $v_2(\mathbf{r})$, have the same ground-state density $n(\mathbf{r})$ then necessarily $v_1(\mathbf{r}) - v_2(\mathbf{r}) = const$.

Corollary: the ground state density $n(\mathbf{r})$ uniquely determines the potential and thus all properties of the system, including the many-body wave function. In particular, the "Hohenberg-Kohn" functional, defined as

$$F[n] = T[n] + U[n]$$

is a universal functional of the density (not depending explicitly on the external potential).

2. For any positive integer N and potential $v(\mathbf{r})$ the density functional

$$E[n] = F[n] + \int n(\mathbf{r}) v(\mathbf{r}) \mathrm{d}^3 r$$

obtains its minimal value at the ground-state density of N electrons in the potential $v(\mathbf{r})$. The minimal value $E[n]$ is then the ground state energy of this system.

Peter Hohenberg, Walter Kohn, Inhomogeneous Electron Gas, Phys. Rev. 136, B864 (1964).

DFT in a Nutshell: Kohn Sham Equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$-\frac{Z}{r} \qquad \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r' \qquad \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

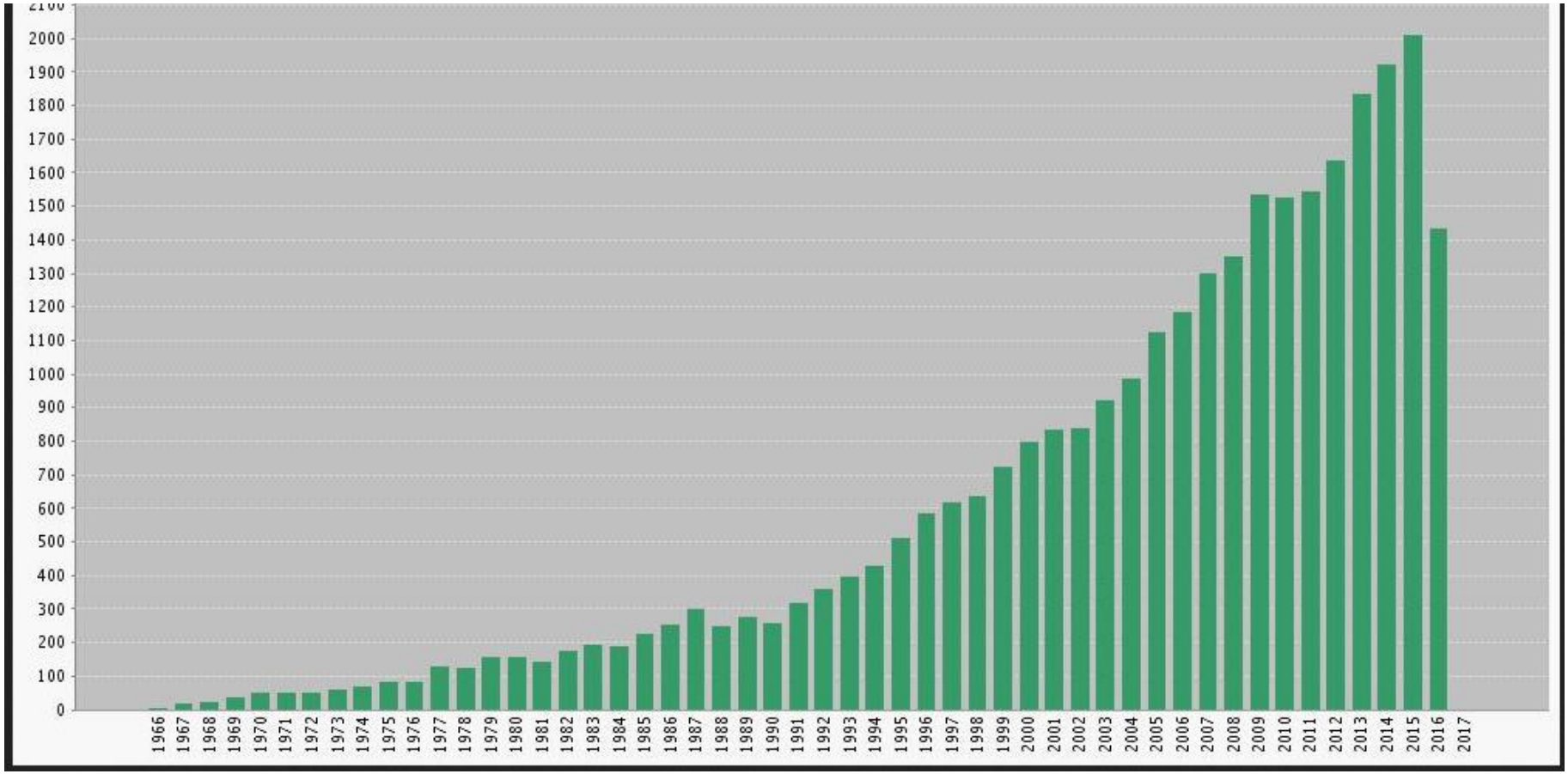
Approximations:
e.g.: LDA, GGA, ...

Self-consistency

$$n(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2$$

W. Kohn, L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, Phys. Rev. 140, A1133-A1138 (1965)

Citation Report of Kohn-Sham paper from 1965



> 30000 citations

W. Kohn, L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, Phys. Rev. 140, A1133-A1138 (1965)

DFT in a Nutshell: Total Energy

$$E = T_{\mathrm{s}}[n_\uparrow, n_\downarrow] + \int \mathrm{d}^3 r\, n(\mathbf{r}) v(\mathbf{r}) + U[n] + E_{\mathrm{xc}}[n_\uparrow, n_\downarrow]$$

kinetic energy

electron-ion interaction

Hartree Energy (self-repulsion of electrons)

Exchange-Correlation-energy

$$T_{\mathrm{s}}[n_\uparrow, n_\downarrow] = \sum_\sigma \sum_\alpha \theta(\mu - \varepsilon_{\alpha\sigma}) \langle \psi_{\alpha\sigma} | -\frac{1}{2}\nabla^2 | \psi_{\alpha\sigma} \rangle$$

$$U[n] = \frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

E_{xc} Defined to include everything else omitted from the first three terms ...

$$E_{\mathrm{xc}}^{\mathrm{LSD}}[n_\uparrow, n_\downarrow] = \int \mathrm{d}^3 r\, n(\mathbf{r}) e_{\mathrm{xc}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}))$$ Local spin density appriximation

Wave Function Theory

One Electron

$$\hat{h} = -\frac{1}{2}\nabla^2 + v(\mathbf{r})$$ Hamiltonian

$$\hat{h}\psi_\alpha(\mathbf{r},\sigma) = \varepsilon_\alpha \psi_\alpha(\mathbf{r},\sigma)$$ Stationary Schrödinger Equation (SE)

$$\sum_\sigma \int \mathrm{d}^3 r \, |\psi_\alpha(\mathbf{r},\sigma)|^2 = \langle \psi | \psi \rangle = 1$$ Normalization

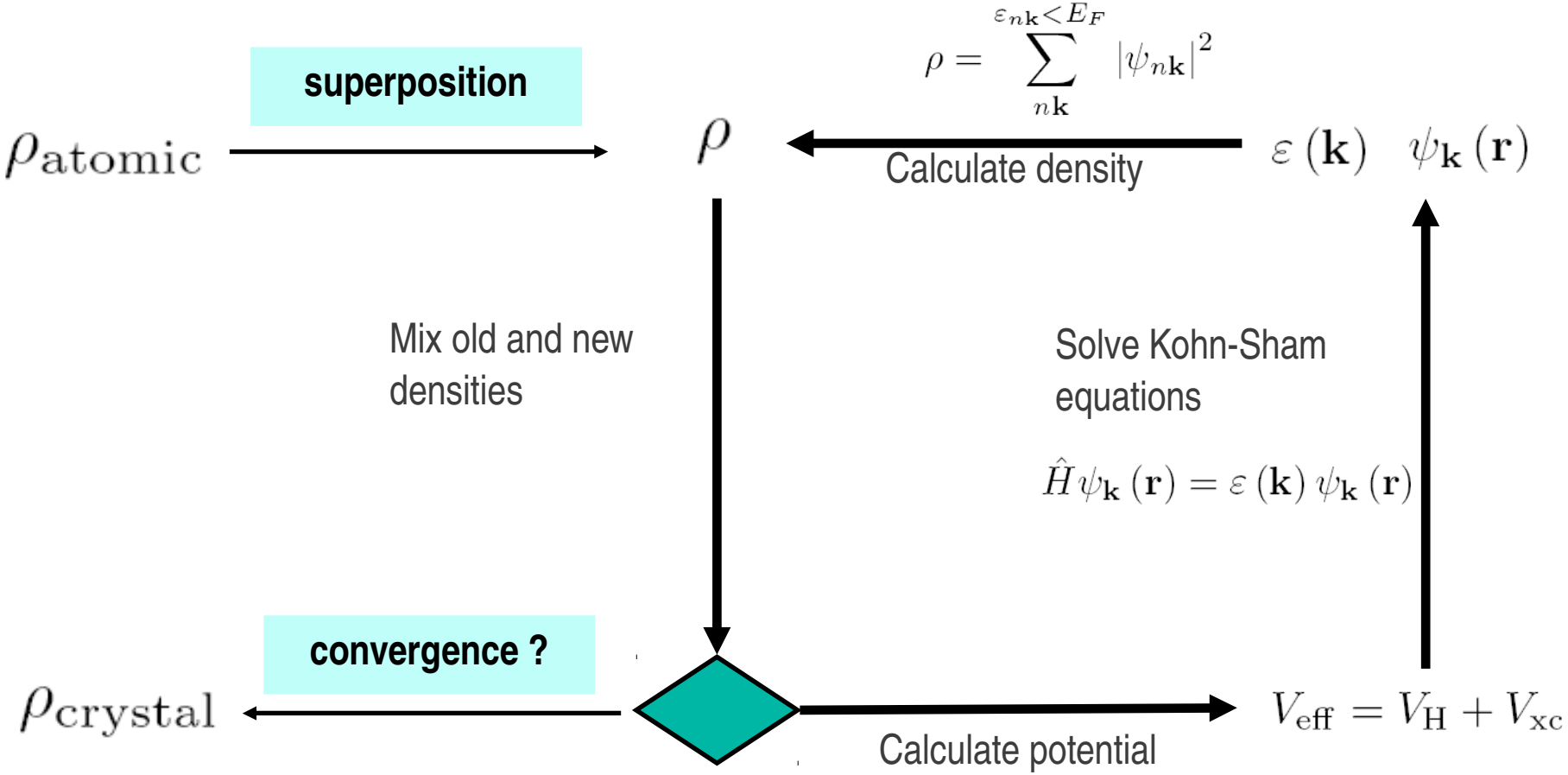
Many Electrons

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} v(\mathbf{r}_i) + \frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$ Hamiltonian

$$\hat{H}\Psi_k(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N) = E_k \Psi_k(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)$$ SE

$$\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_i\sigma_i,\ldots,\mathbf{r}_j\sigma_j,\ldots,\mathbf{r}_N\sigma_N) = -\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_j\sigma_j,\ldots,\mathbf{r}_i\sigma_i,\ldots,\mathbf{r}_N\sigma_N)$$ Pauli Principle

$$\frac{1}{N!}\sum_{\sigma_1\ldots\sigma_N}\int \mathrm{d}^3 r_1 \ldots \int \mathrm{d}^3 r_N \, N! \, |\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)|^2 = \int |\Psi|^2 = \langle \Psi | \Psi \rangle = 1 \, .$$ Normalization



2.1 Self Consistency

Kohn-Sham equation
(differential eigenvalue equation)

$$\hat{H}\psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r})$$

Linear expansion in
known basis functions

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_j c_j(\mathbf{k})\phi_j(\mathbf{r})$$

$$\phi_j(\mathbf{r}+\mathbf{R}) = \phi_j(\mathbf{r})$$

Kohn-Sham equation
(matrix eigenvalue equation)

$$\sum_j H_{ij}(\mathbf{k})c_j(\mathbf{k}) = \varepsilon(\mathbf{k})\sum_j S_{ij}(\mathbf{k})c_j(\mathbf{k})$$

Hamilton matrix

$$H_{ij}(\mathbf{k}) = \int_\Omega d^3r e^{-i\mathbf{kr}}\phi_i^*(\mathbf{r})\hat{H}e^{i\mathbf{kr}}\phi_j(\mathbf{r})$$

Overlap matrix

$$S_{ij}(\mathbf{k}) = \int_\Omega d^3r \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})$$

Plane Wave Basis

Plane wave basis:

$$\phi_j(\mathbf{r}) \rightarrow \phi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}\mathbf{r}}$$

Lattice periodicity

$$\phi_{\mathbf{G}}(\mathbf{r}+\mathbf{R}) = \phi_{\mathbf{G}}(\mathbf{r})$$

Orthogonality

$$\int_{\Omega_0} \phi^*_{\mathbf{G}}(\mathbf{r})\phi_{\mathbf{G}'}(\mathbf{r}) = \delta_{\mathbf{G}\mathbf{G}'}$$

Completeness

$$\sum_{\mathbf{G}} \phi^*_{\mathbf{G}}(\mathbf{r})\phi_{\mathbf{G}}(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$$

Fourier expansion of lattice periodic functions:

$$V(\mathbf{r}) = \frac{1}{\Omega_0} \sum_{\mathbf{G}} \tilde{V}(\mathbf{G})\, e^{i\mathbf{G}\mathbf{r}} \qquad \tilde{V}(\mathbf{G}) = \int_{\Omega_0} d^3r V(\mathbf{r}) e^{-i\mathbf{G}\mathbf{r}}$$

Plane Wave Basis

Overlap matrix

$$S_{ij}(\mathbf{k}) \rightarrow S_{\mathbf{G}\mathbf{G}'} = \delta_{\mathbf{G}\mathbf{G}'}$$

Hamilton matrix

$$H_{ij}(\mathbf{k}) \rightarrow H_{\mathbf{G}\mathbf{G}'}(\mathbf{k}) = \underbrace{\frac{1}{2}\left(\mathbf{k}+\mathbf{G}\right)^2 \delta_{\mathbf{G}\mathbf{G}'}}_{\text{kinetic energy}} + \underbrace{\frac{1}{\Omega_0}\tilde{V}\left(\mathbf{G}-\mathbf{G}'\right)}_{\text{effective potential}}$$

Secular equation = Matrix eigenvalue equation

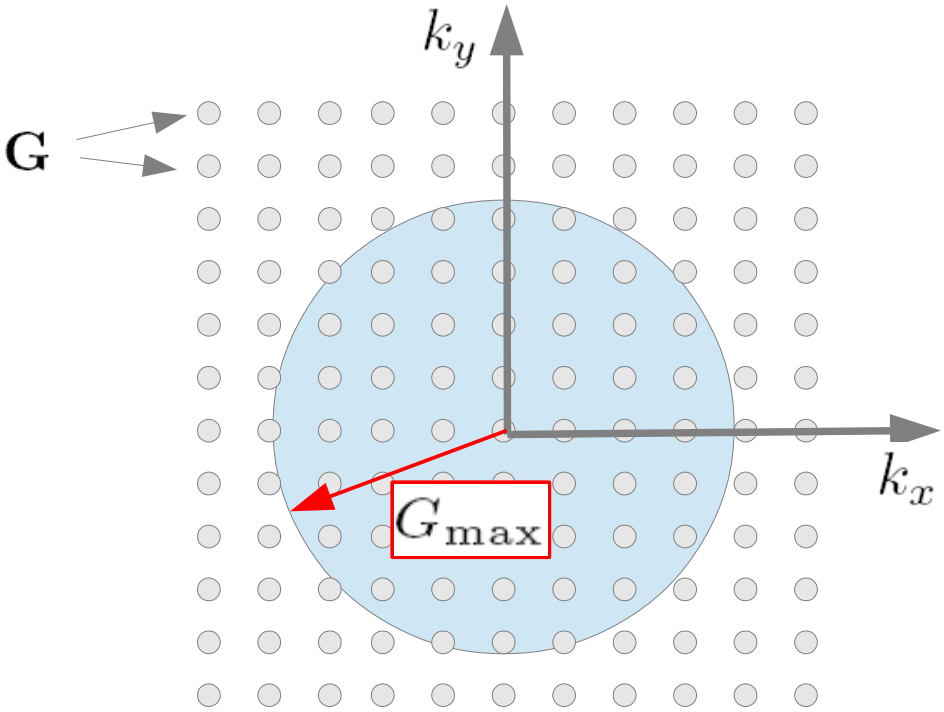
$$\sum_{\mathbf{G}'} \underbrace{H_{\mathbf{G}\mathbf{G}'}(\mathbf{k})}_{\text{matrix}} \underbrace{\tilde{u}_{\mathbf{k}}(\mathbf{G}')}_{\text{vector}} = \underbrace{\varepsilon(\mathbf{k})}_{\substack{\text{eigen}\\ \text{value}}} \underbrace{\tilde{u}_{\mathbf{k}}(\mathbf{G})}_{\text{vector}}$$

= “band structure“

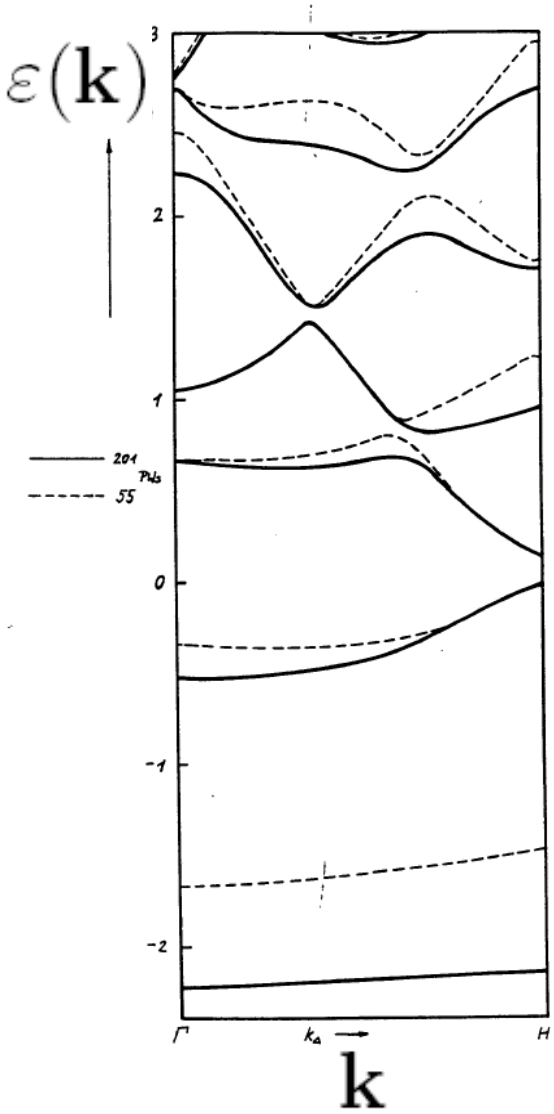
Convergence Problems

Plane wave cut-off

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}}^{|\mathbf{k}+\mathbf{G}|\leq G_{\max}} \tilde{u}_{\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}} \qquad E_{\text{cutoff}} = \frac{1}{2} G_{\max}^2$$

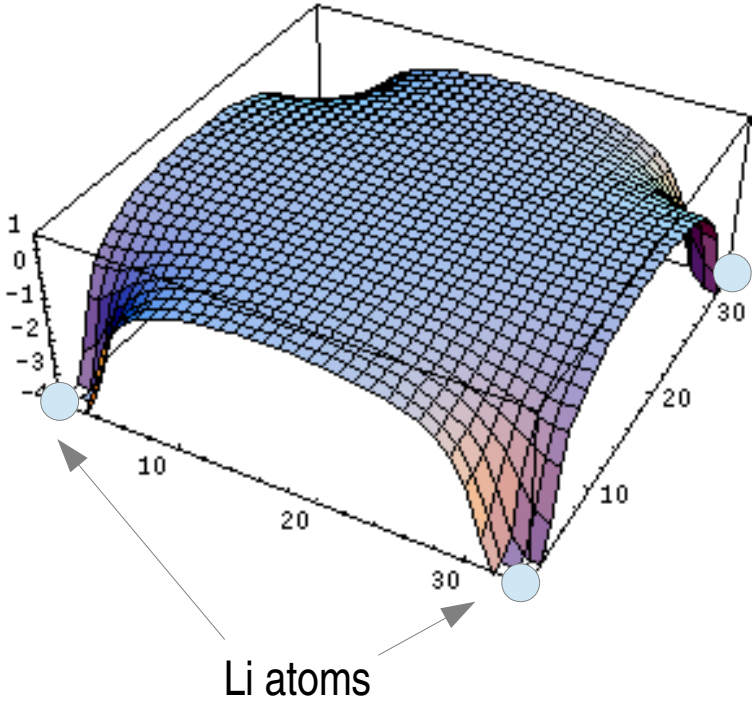


Li-metal

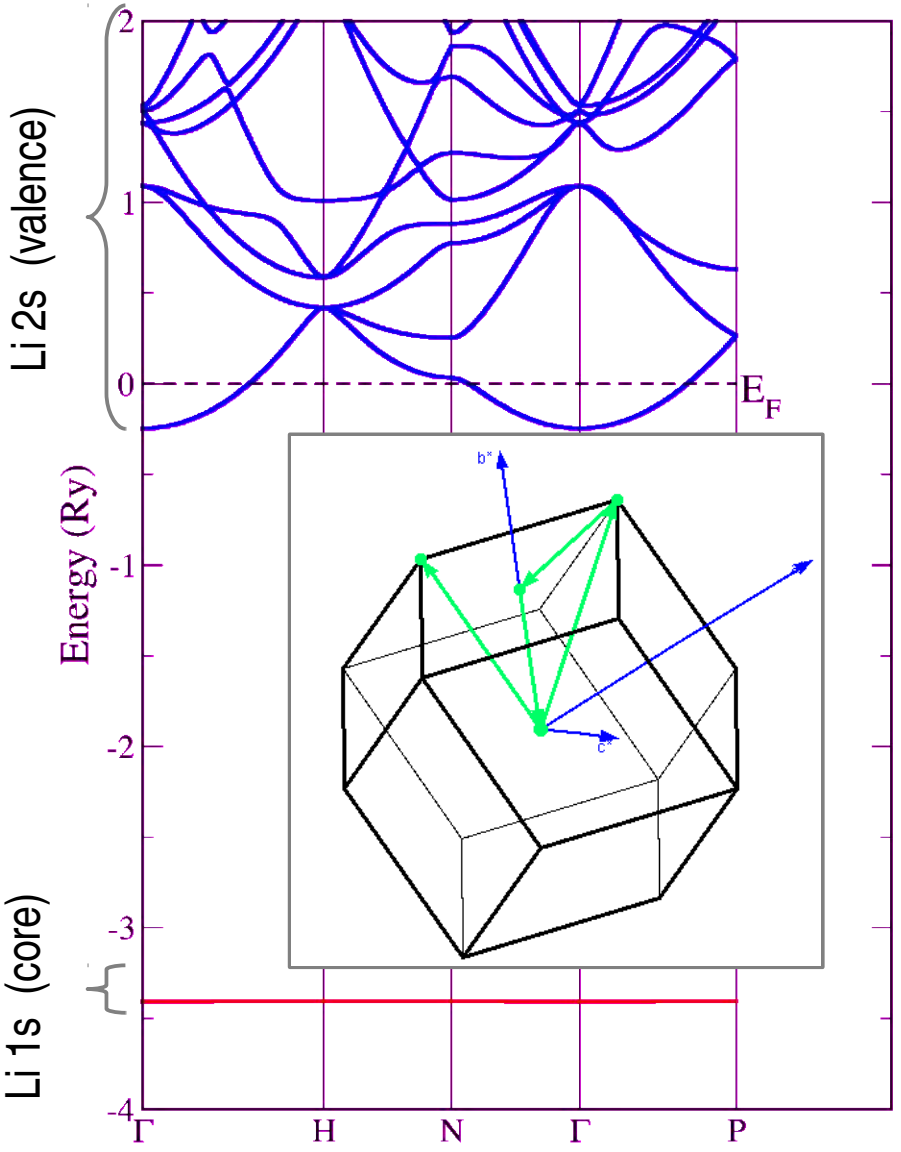


Core States

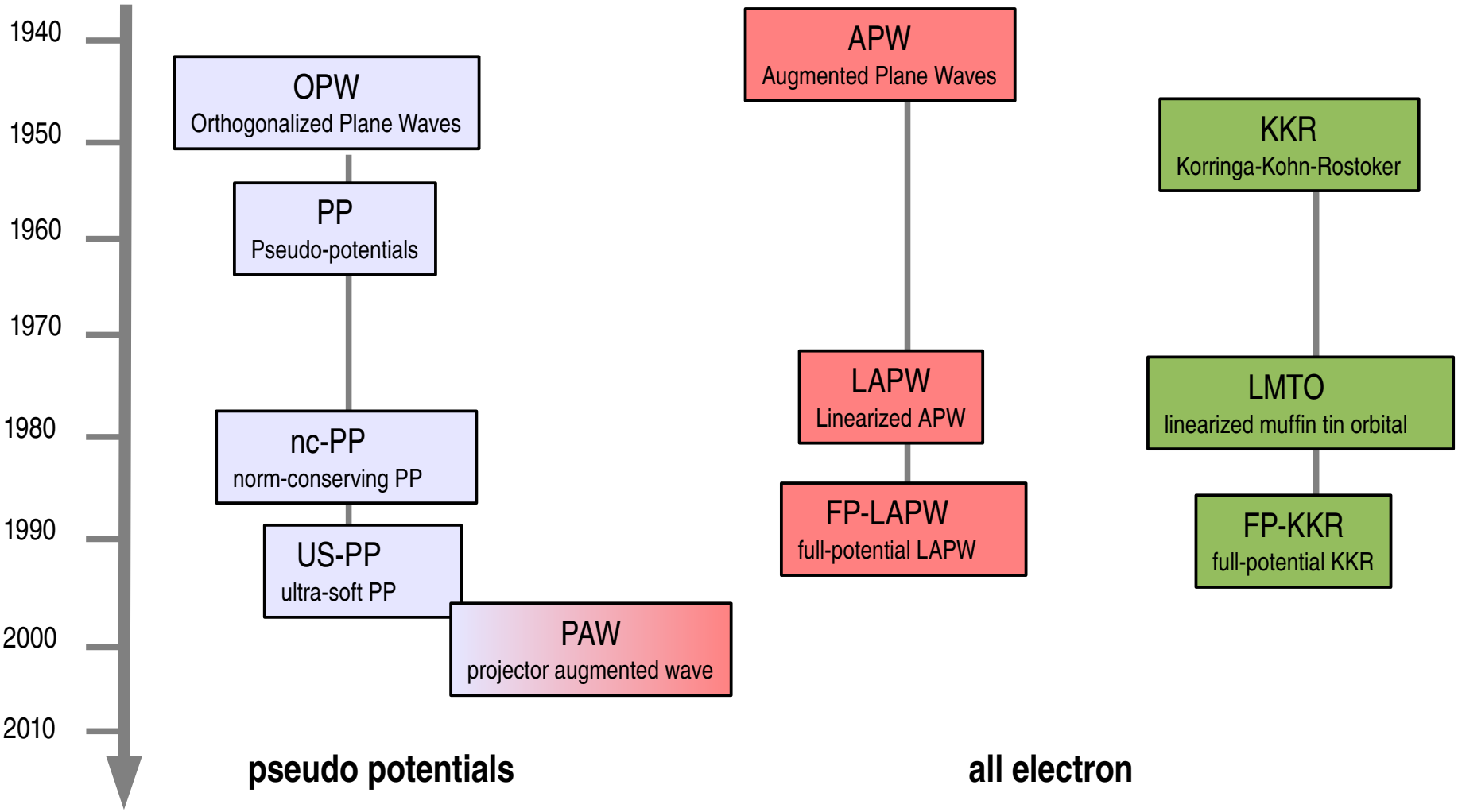
Potential (2D-section)



bcc-Li: accurate band structure



Other Basis Sets - Overview



Some State-of-the-Art Program Packages

PW-PP
plane wave pseudo potentials

PAW
projector augmented wave

FP-LAPW
full-potential LAPW

PWscf
http://www.pwscf.org/

CP-PAW
http://www2.pt.tu-clausthal.de/atp/

WIEN2k
http://www.wien2k.at/

ABINIT
http://www.abinit.org/

EXC!TiNG
http://exciting.sourceforge.net/

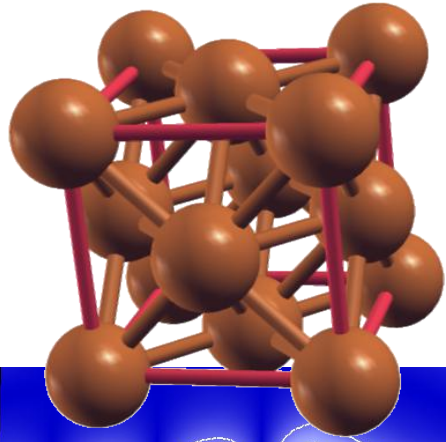
VASP
http://cms.mpi.univie.ac.at/vasp/

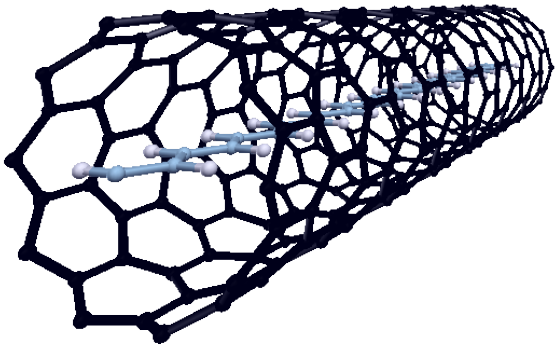
Welche Eigenschaften?

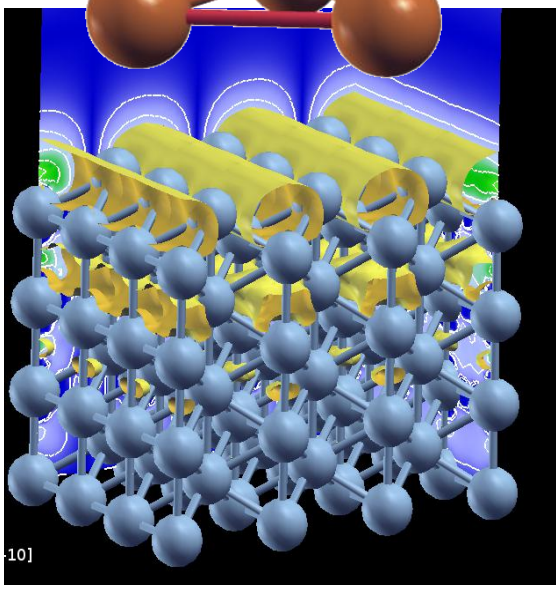
- **Strukturelle Eigenschaften**
  - Gitterkonstanten
  - Phasenstabilität
  - Atomare Kräfte
  - Oberflächenrelaxationen
  - Defekte
- **Gitterdynamik**
  - Schwingungsfrequenzen
  - Phasenübergänge, Thermodynamik
- **Elastische Eigenschaften**
- **Elektronenverteilung**
  - Elektrische Feldgradienten
- **Elektronische Eigenschaften**
  - Bandstruktur
  - Zustandsdichte
- **Spektroskopie**
  - Dielektrische Funktion
  - Optische Absorption
  - Optische Bandlücke
  - Photoemissionsspektren
  - Core level - Spektren
  - Ramanstreuung
  - Comptonstreuung
  - Elektronenspektren
  - Positronstreuung

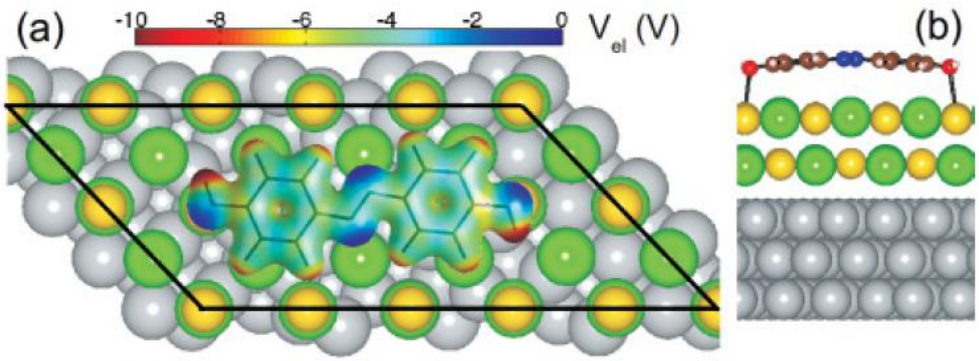
Welche Systeme?

- **Kristalline Festkörper**
  - Isolatoren
  - Halbleiter
  - Metalle
  - Supraleiter
- **Defekte in Festkörpern**
  - Oberflächen
  - Interfaces
  - Versetzungen
  - Punktdefekte
- **Nichtperiodische Systeme**
  - Moleküle, Cluster, ...









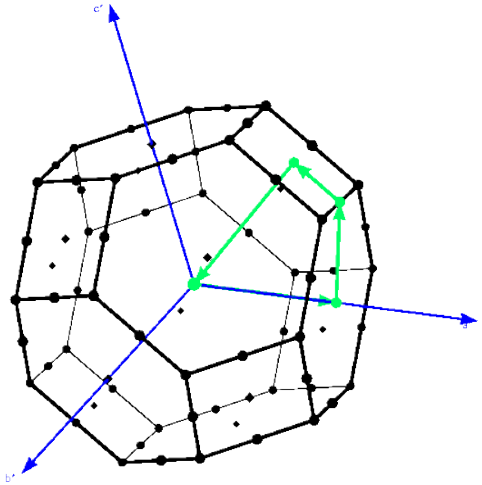
Calculation of the Kohn-Sham Bandstructure

Self-consistent solution of the Kohn-Sham equations

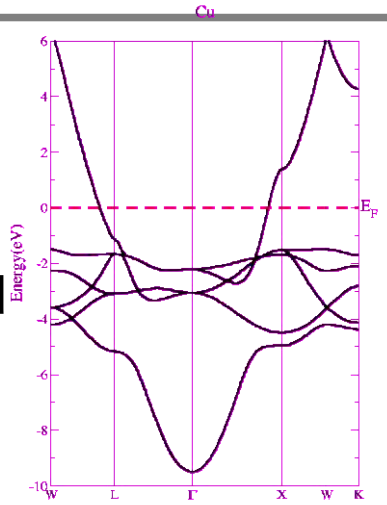
$$\hat{H}\psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r})$$

Self-consistent electron density, total energy, Fermi energy, ...

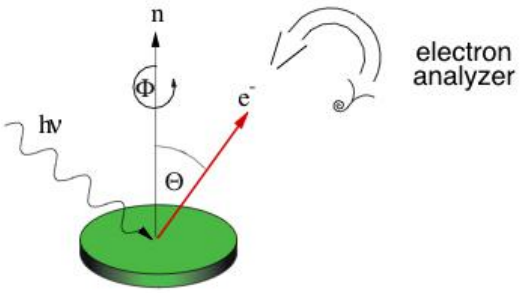
Choose k-path within Brillouin zone

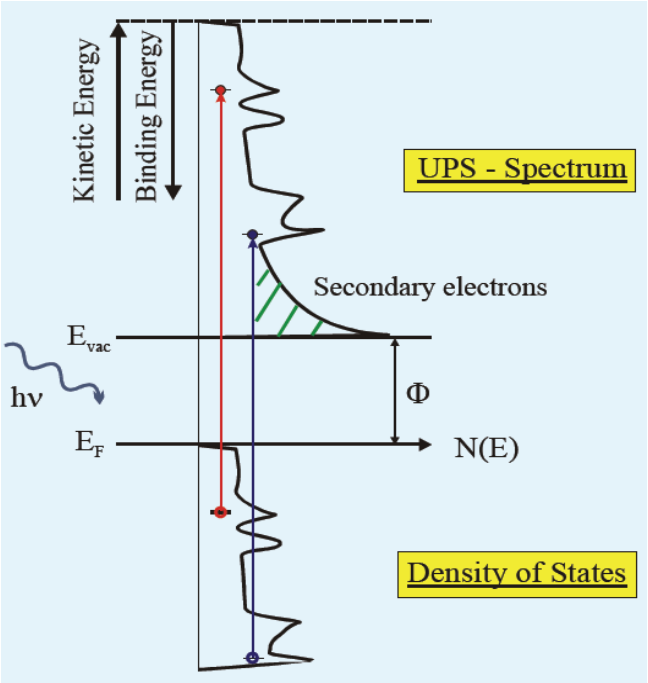


Solve KS-equations for k-points along selected k-path

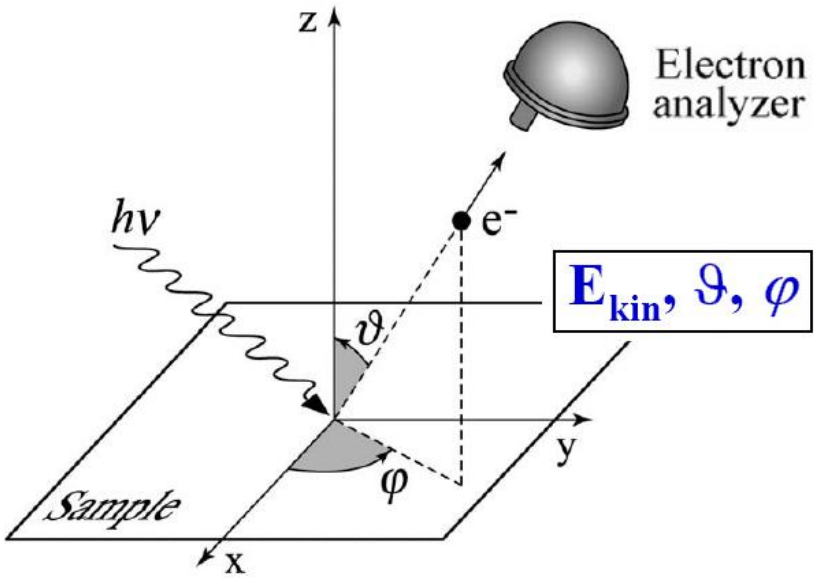


How to measure band structures?





Angle **R**esolved **P**hoto**E**mission **S**pectroscopy



$$\mathbf{K} = \mathbf{p}/\hbar = \sqrt{2mE_{kin}}/\hbar$$

$$K_x = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\cos\varphi$$

$$K_y = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\sin\varphi$$

$$K_z = \frac{1}{\hbar}\sqrt{2mE_{kin}}\cos\vartheta$$

Vacuum

E_{kin}

$\mathbf{K}$

Conservation laws

$$E_f - E_i = h\nu$$

$$\mathbf{k}_f - \mathbf{k}_i = \cancel{\mathbf{k}_{h\nu}}$$

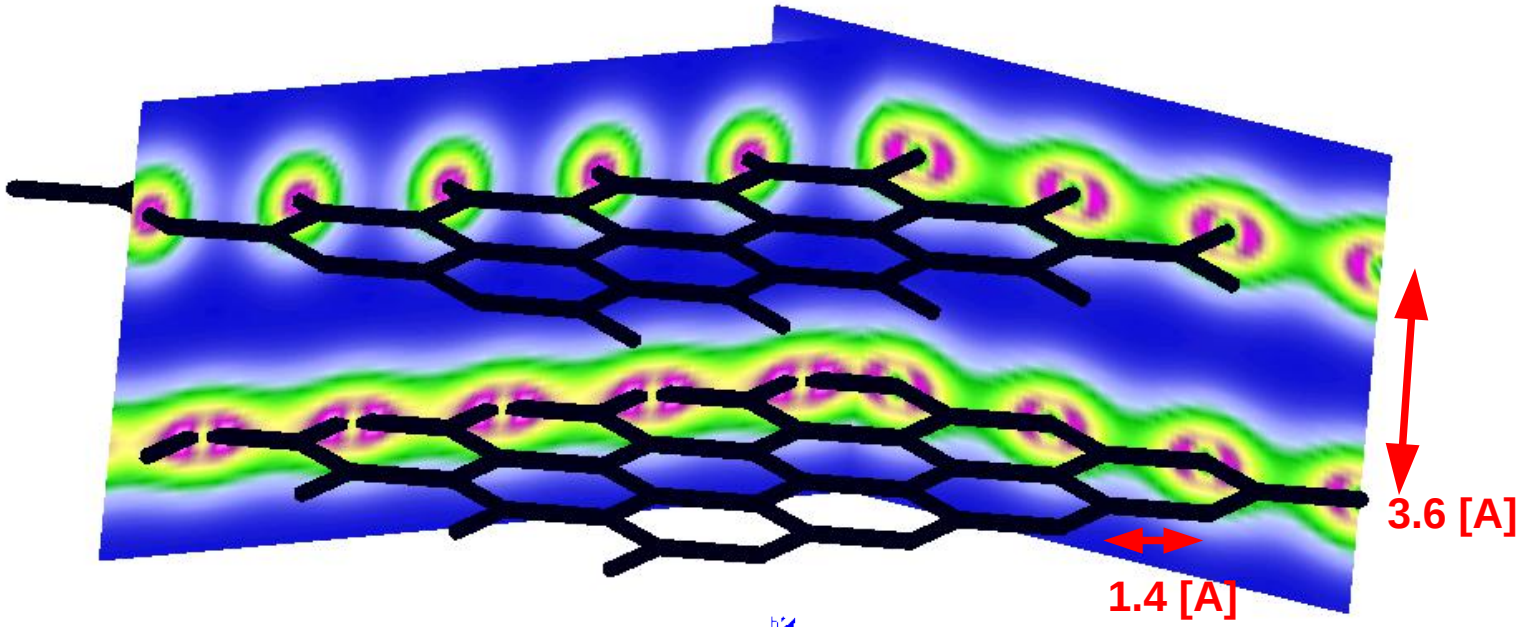
Solid

E_B

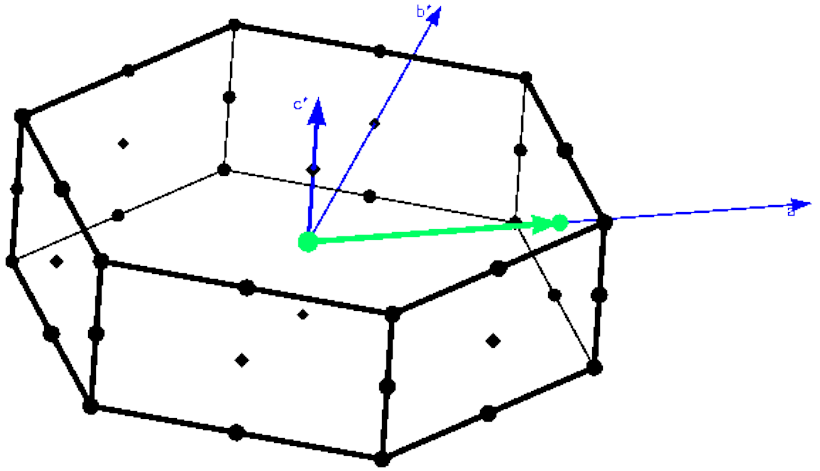
$\mathbf{k}$

Band Structure of Graphite

Layered crystal structure



Brillouin Zone



ABINIT: Input File for Graphite

graphite.in (modified) - /home/pep/LEHRE/AbInitio/sample_inout/graphite/

File Edit Search Preferences Shell Macro Windows Help

/home/pep/LEHRE/AbInitio/sample_inout/graphite/graphite.in byte 1021 of 1661 L: 28 C: 0

```
# C in graphite structure
# Dataset # 1 = scf calculation
# Dataset # 2 = wave functions on a dense mesh: 16x16x8

#Definition of the unit cell
acell   4.639114   4.639114    12.676098

rprim   1.000000   0.000000     0.000000    # hexagonal lattice (to be scaled by ace
       -0.500000   0.866025403  0.000000
        0.000000   0.000000     1.000000

ixc       14   # GGA, revPBE of Y. Zhang and W. Yang, Phys. Rev. Lett. 80, 890 (199
ecut      25.0
nstep     25
diemac    3.0
diemix    0.5
#Definition of the structure
ntypat 1
znucl  6
natom  4                          # There are two atoms
typat  1 1 1 1                    # They both are of type 1, that is, Carbon.
xred  0.00     0.00       1/4     # Triplet giving the REDUCED coordinate of atom 1.
      0.00     0.00       3/4     # Triplet giving the REDUCED coordinate of atom 2.
      1/3      2/3        1/4     # Triplet giving the REDUCED coordinate of atom 3.
      2/3      1/3        3/4     # Triplet giving the REDUCED coordinate of atom 4.
```

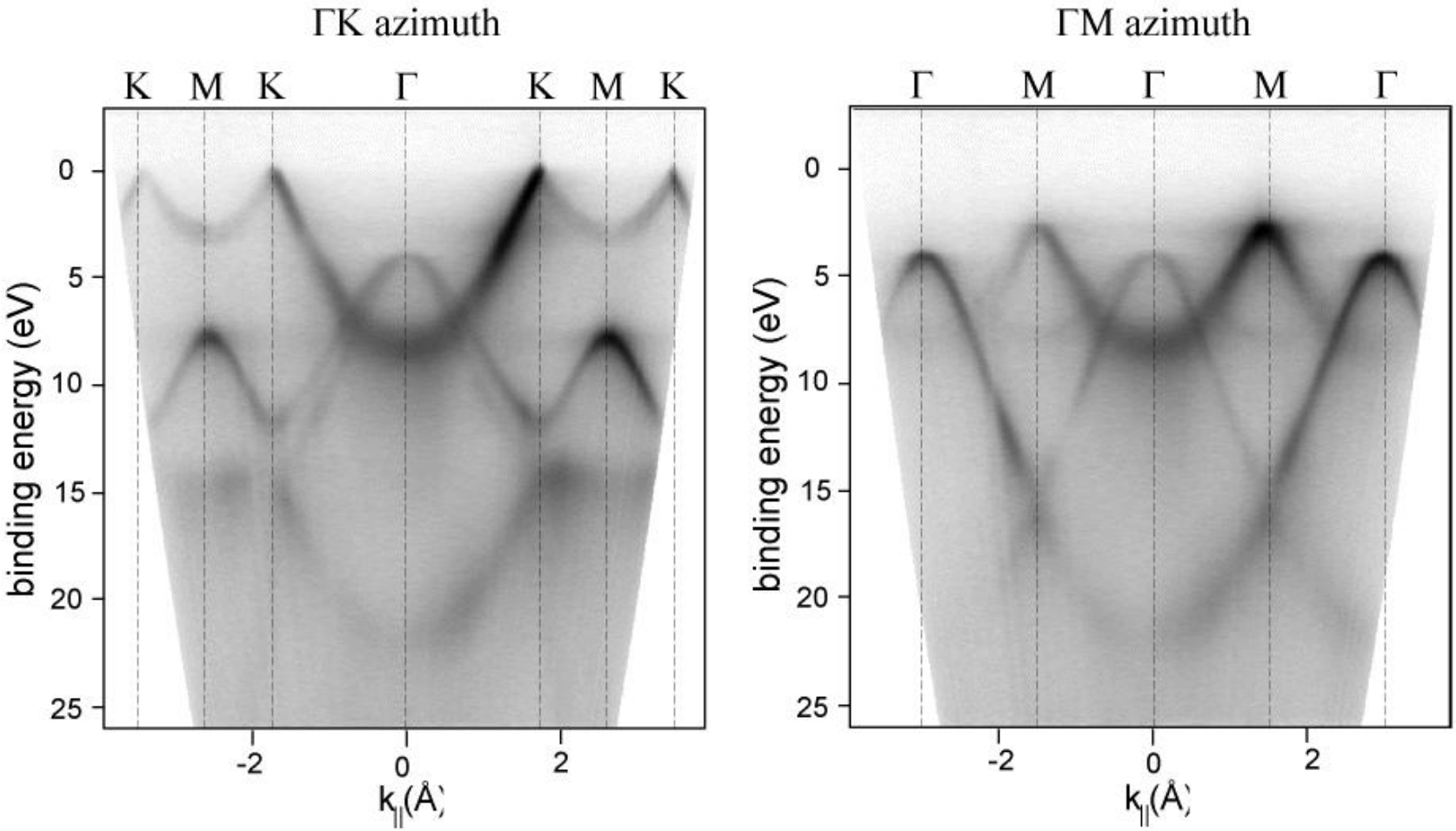
… continued on next slide ...

ABINIT: Input File for Graphite

… continued from previous slide ...

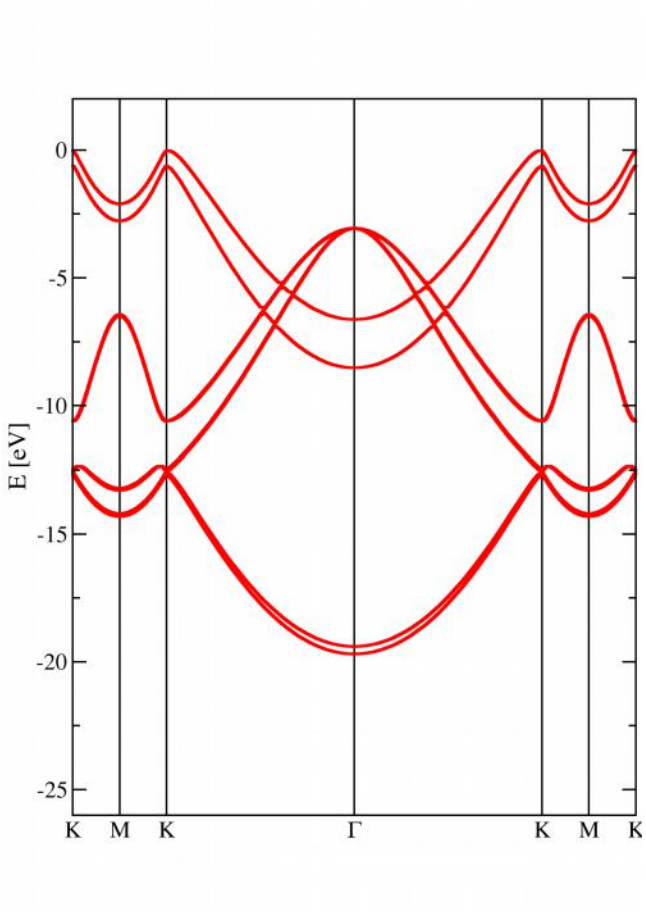
```
28
29 ndtset 2
30
31 #Dataset 1 : self-consistent calculation
32 kptopt1   1
33 ngkpt1   10 10 4
34 nshiftk1  1
35 shiftk1   1 1 1
36 prtden1   1          # Print the density, for use by dataset 2
37 toldfe1   1.0d-10
38
39 #Dataset 2 : the band structure
40 iscf2    -2
41 getden2  -1
42 kptopt2  -4
43 nband2   16
44 ndivk2   40 40 40 20
45 kptbounds2  0.000000000  0.000000000  0.000000000
46             0.500000000  0.000000000  0.000000000
47             0.333333333  0.333333333  0.000000000
48             0.000000000  0.000000000  0.000000000
49             0.000000000  0.000000000  0.500000000
50
51 tolwfr2  1.0d-12
52 enunit2  1                # Will output the eigenenergies in eV
53 prteig2  1
54
55
```

Experimental Band Structure of Graphite

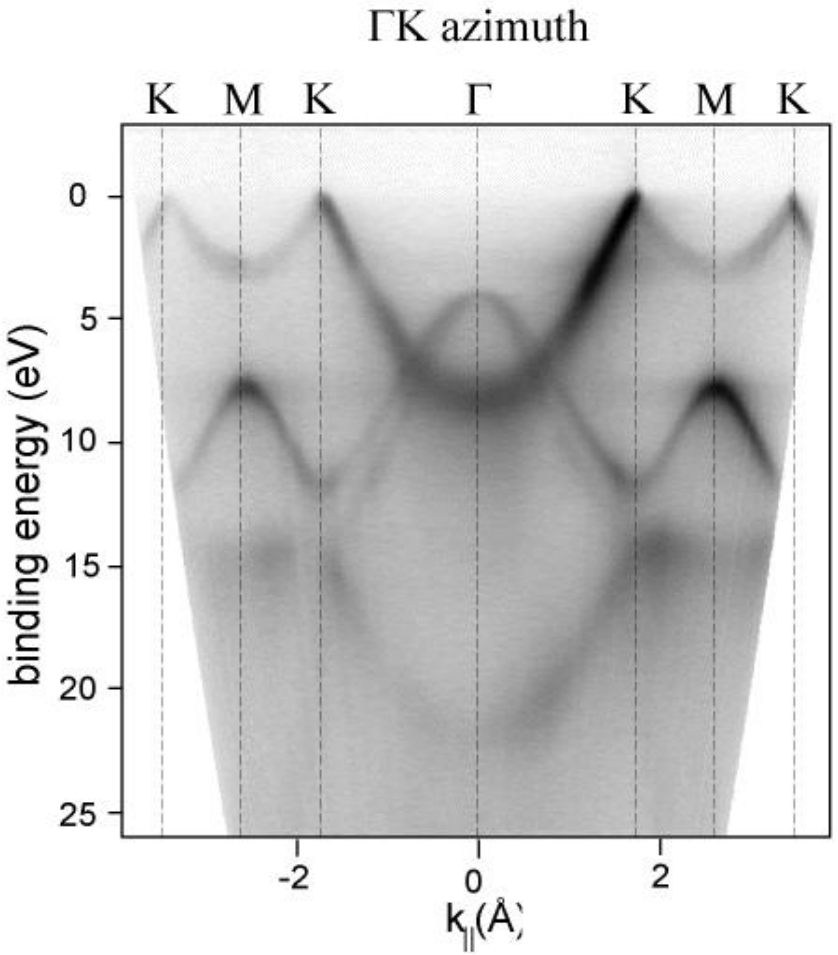


The band structure of graphite along two high symmetry lines Gamma-K and Gamma-M is given below. (measured at the New Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II)

DFT vs. Experiment

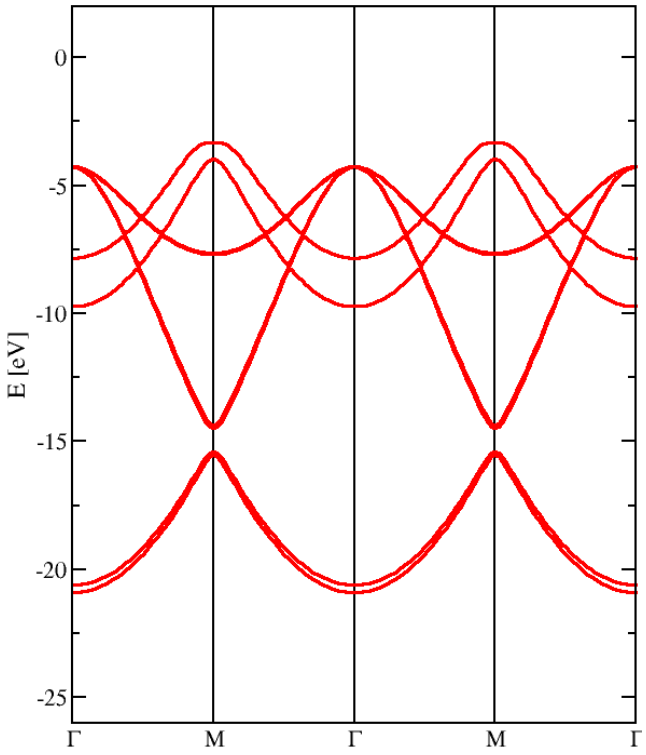


Theory: DFT

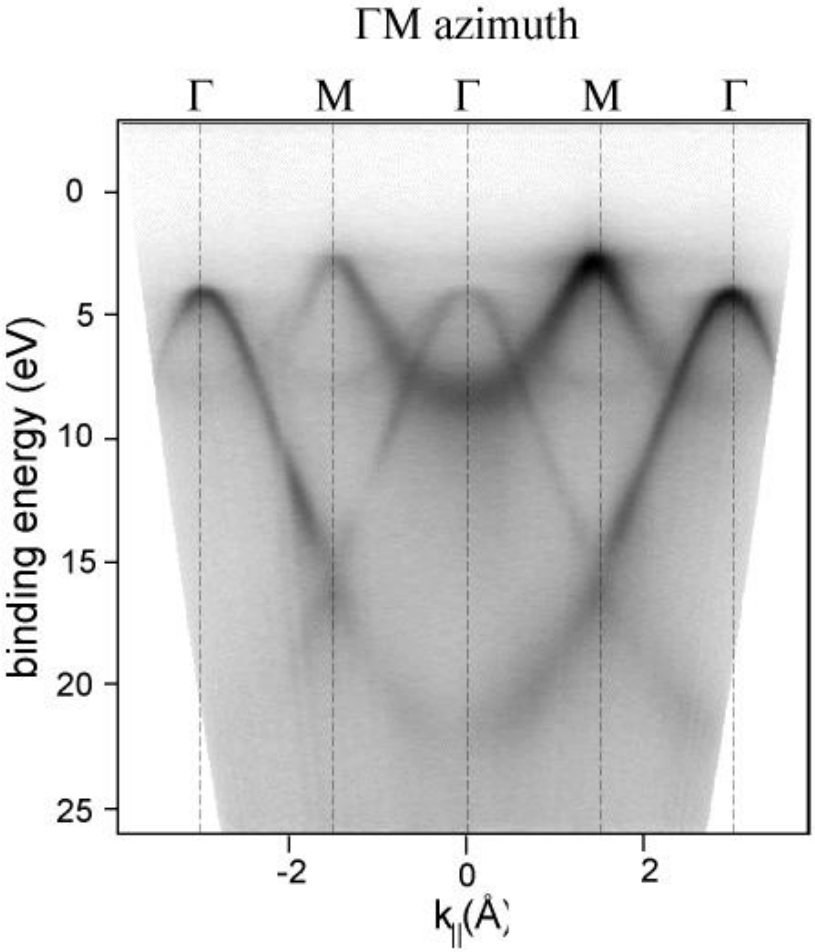


Experiment: ARUPS

DFT vs. Experiment

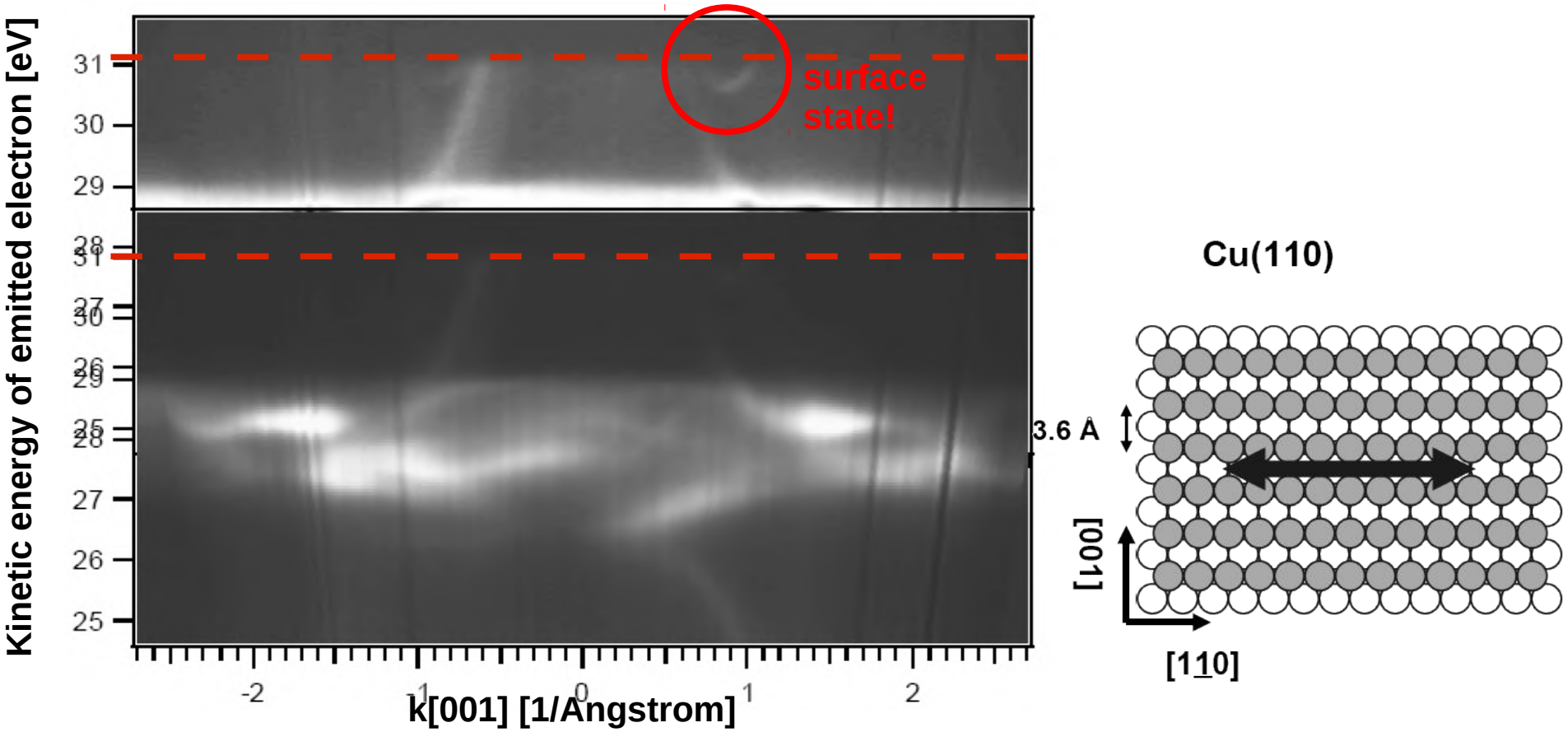


Theory: DFT



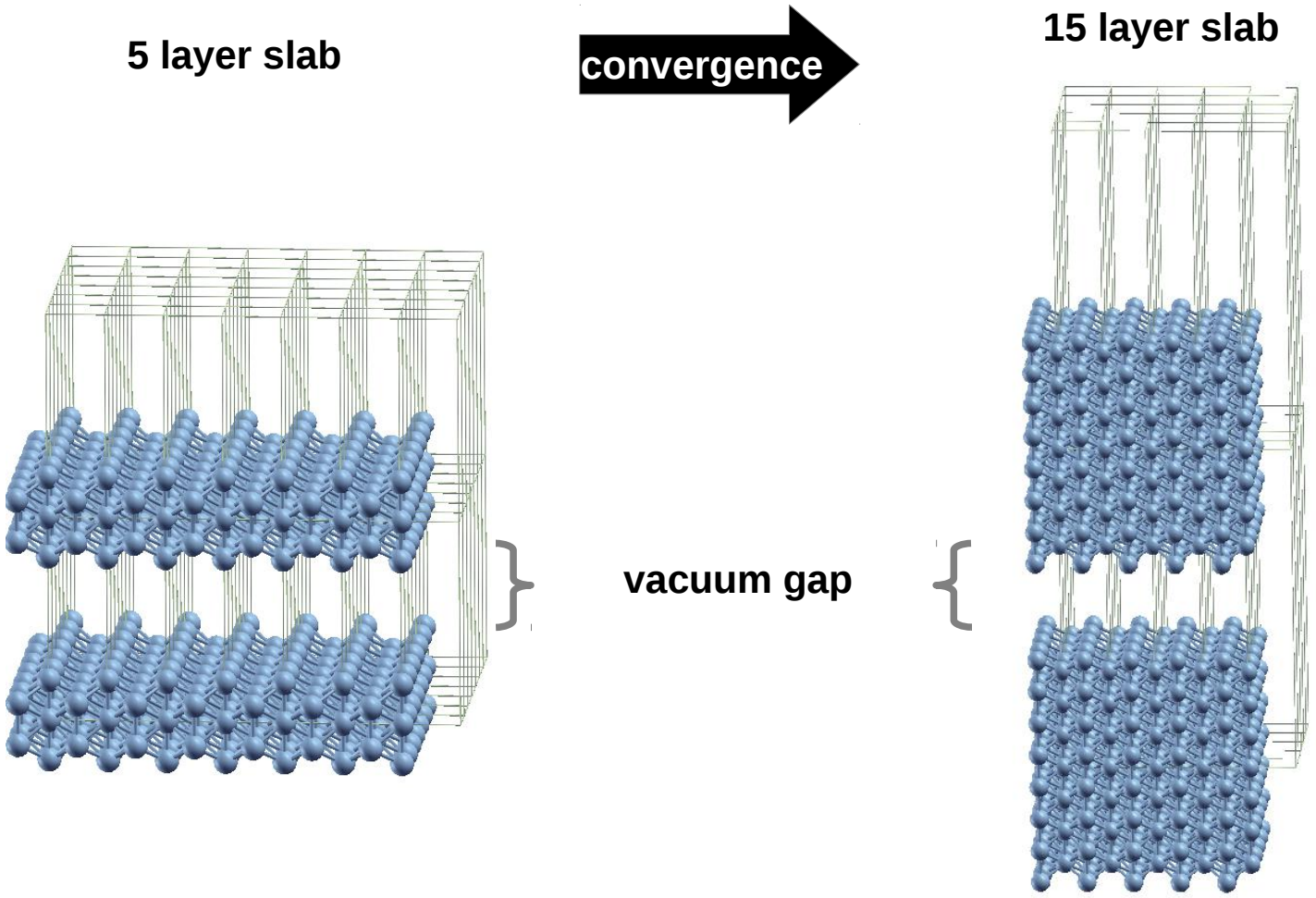
Experiment: ARUPS

Band Structure of Cu(110) Surface

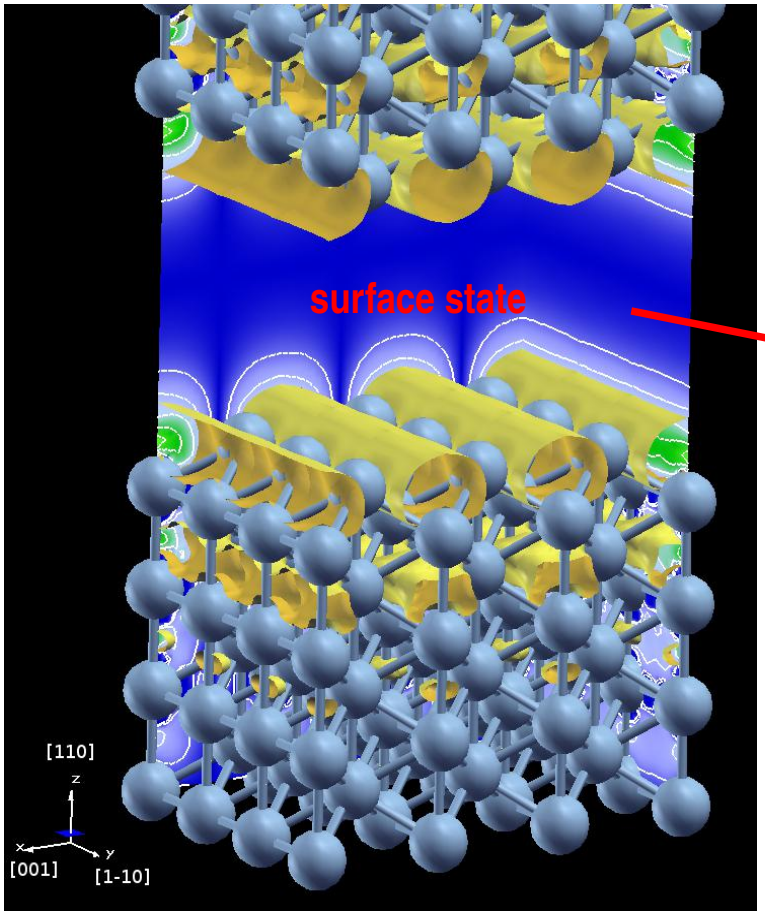


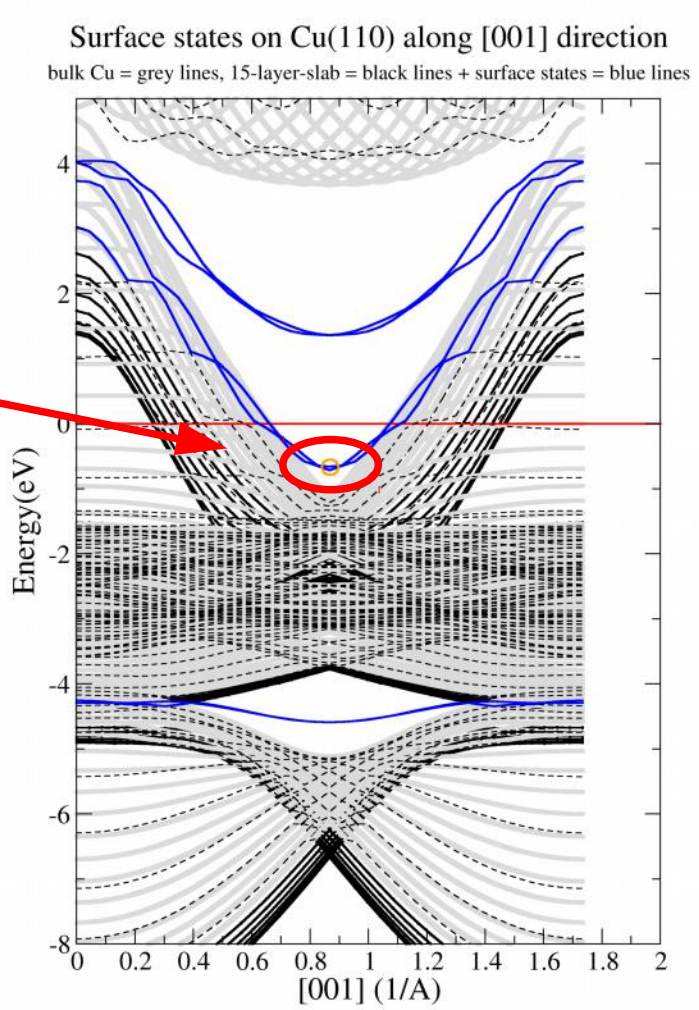
ARUPS band structure for Cu(110) surface measured along the [001] direction (data taken by Stephen Berkebile at BESSY II in Berlin.)

Surface Calculations – Repeated Slab Approach

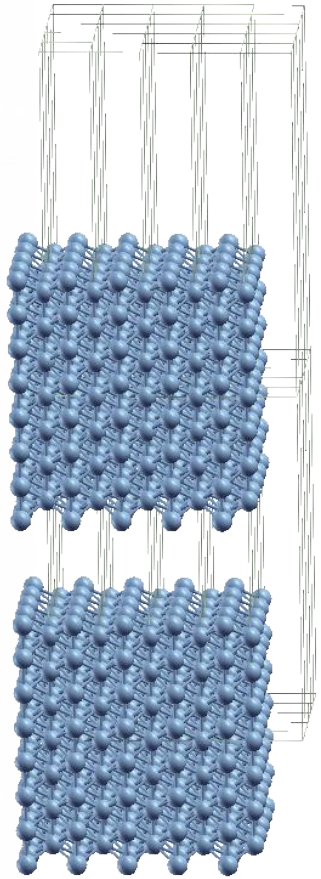


Surface Calculations – Repeated Slab Approach





15 layer slab



Total Energy from DFT

Kohn-Sham wave functions

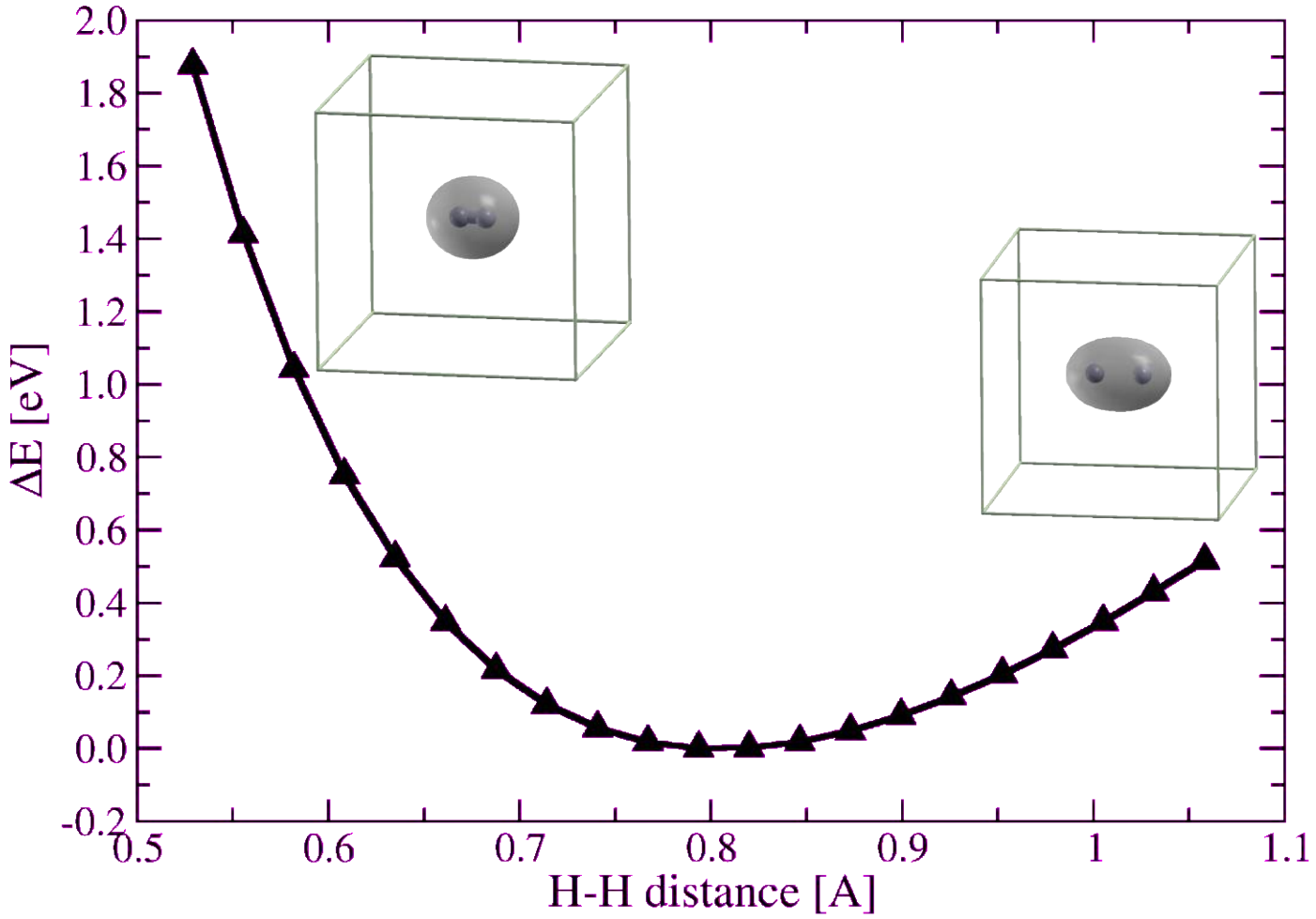
Kinetic **Hartree** **xc**

$$E\left[\{\phi\},\{\mathbf{R}\}\right] = -\frac{1}{2}\sum_{i=1}^{n}\int \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r})\mathrm{d}^3r + \frac{1}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r\mathrm{d}^3r' + E_{xc}[n]$$
$$+ \int V_{\mathrm{ext}}\left(\mathbf{r};\mathbf{R}_1,\mathbf{R}_2,\cdots,\mathbf{R}_N\right)n(\mathbf{r})\mathrm{d}^3r$$

electron-nuclei electrostatic energy

positions of atomic nuclei

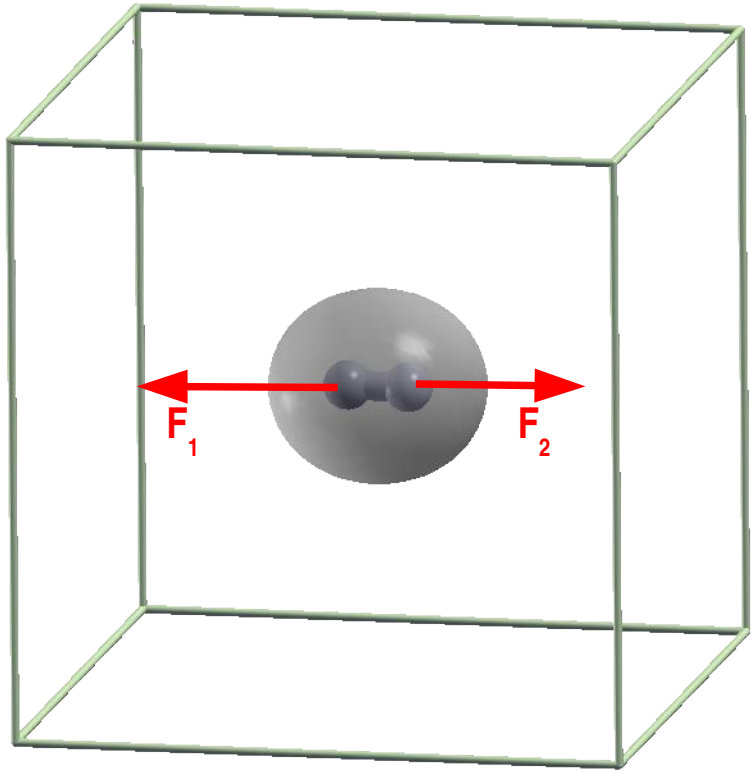
Simple Example: H_2 Molecule



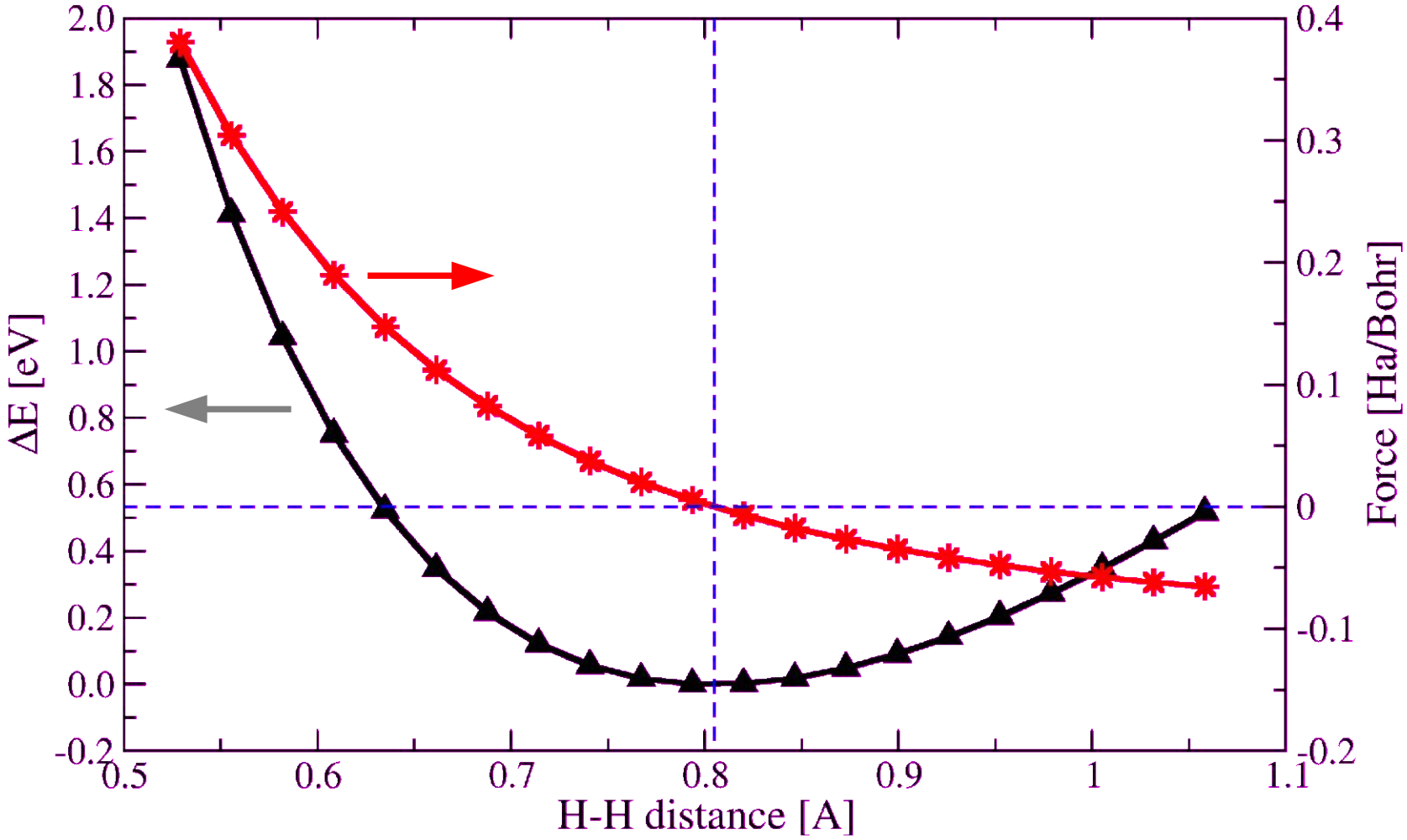
The Hellmann-Feynman Theorem

$$\mathbf{F}_I = -\frac{\partial}{\partial \mathbf{R}_I} E\left[\{\phi\}, \{\mathbf{R}\}\right]$$

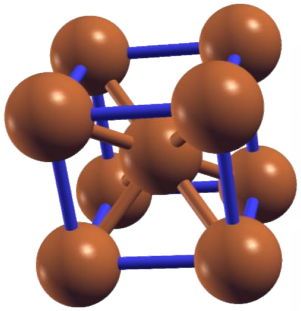
The force $\mathbf{F}_I$ *acting on the atom at position* $\mathbf{R}_I$ *can be calculated from the ground state energy and Kohn-Sham orbitals*

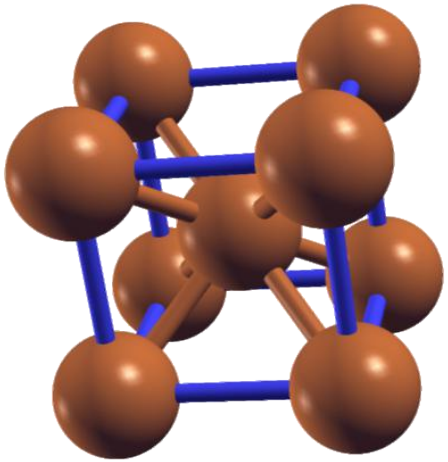


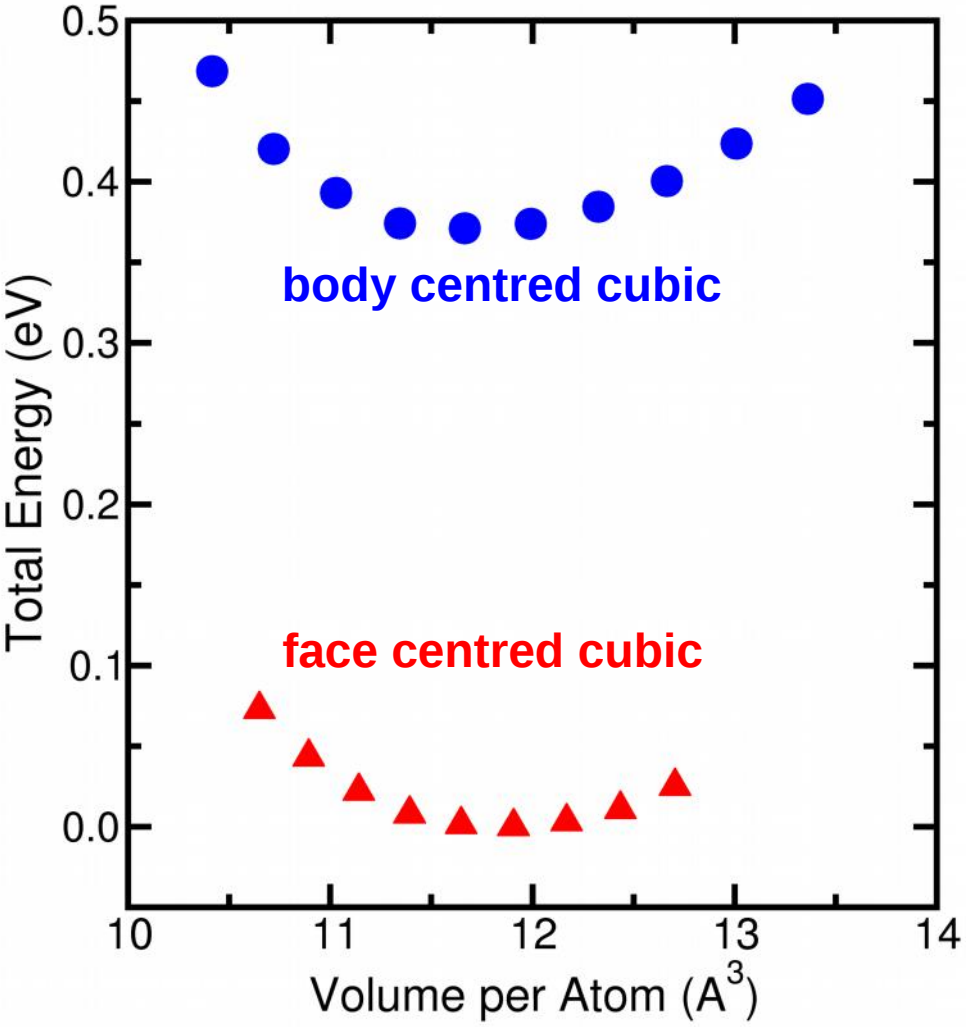
Simple Example: H_2 Molecule

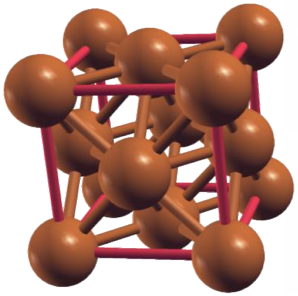


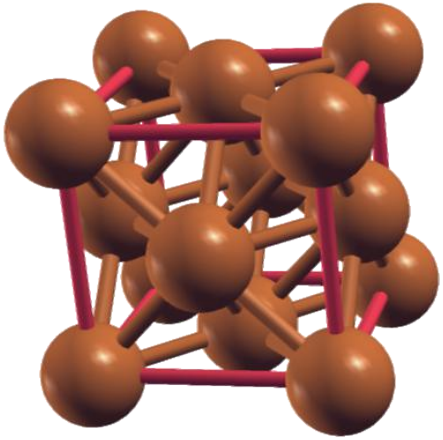
Elastic Properties: Bulk Modulus











Elastic Properties: Bulk Modulus

Definition:

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T$$

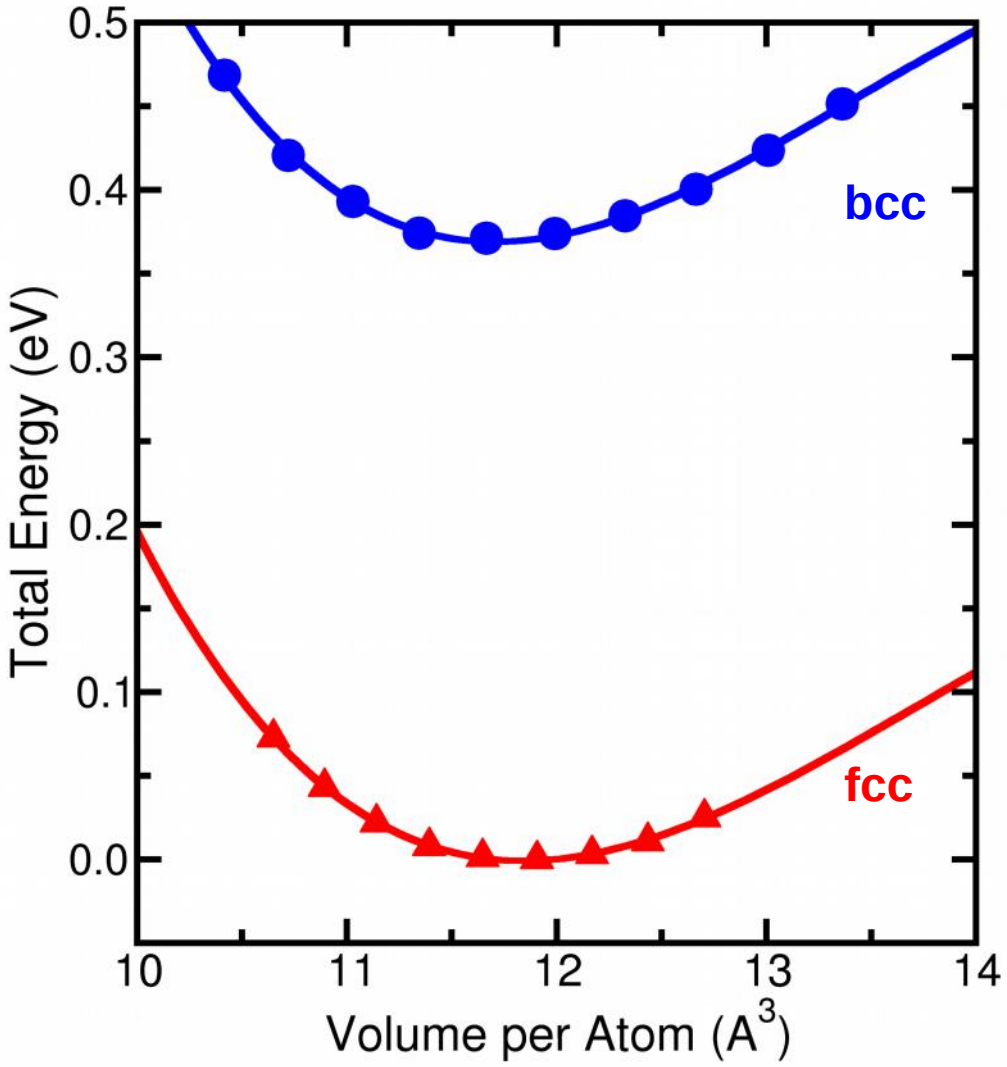
$$P = -\left(\frac{\partial E}{\partial V}\right)_S$$

Equation of State according to Murnaghan

$$B' = \left(\frac{\partial B}{\partial P}\right)_T \longrightarrow \textit{const.} \quad \Rightarrow \quad V(P) = V_0\left(1 + B_0' \frac{P}{B_0}\right)^{-1/B_0'}$$

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left(\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1\right) - \frac{B_0 V_0}{B_0' - 1}$$

Elastic Properties: Bulk Modulus



$$P = -\left(\frac{\partial E}{\partial V}\right)_S$$

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T$$

a_{exp} = 3.60 Å

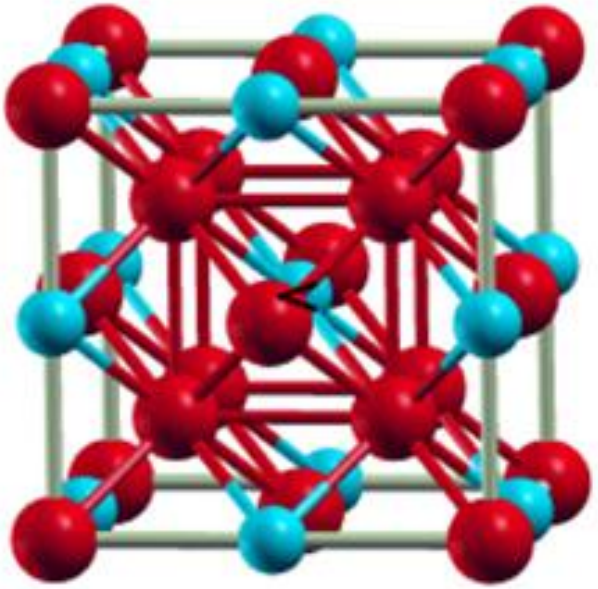
a_{DFT} = 3.63 Å

B_{exp} = 142 GPa

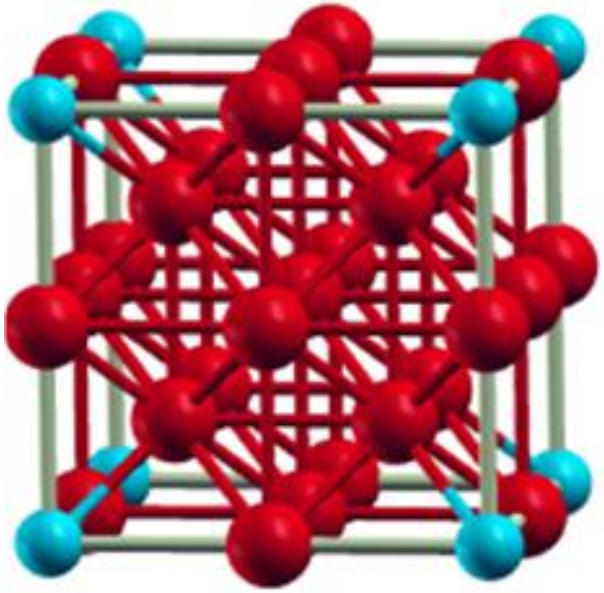
B_{DFT} = 139 GPa

Example: Fe-Si Alloy

Supercell Calculations:

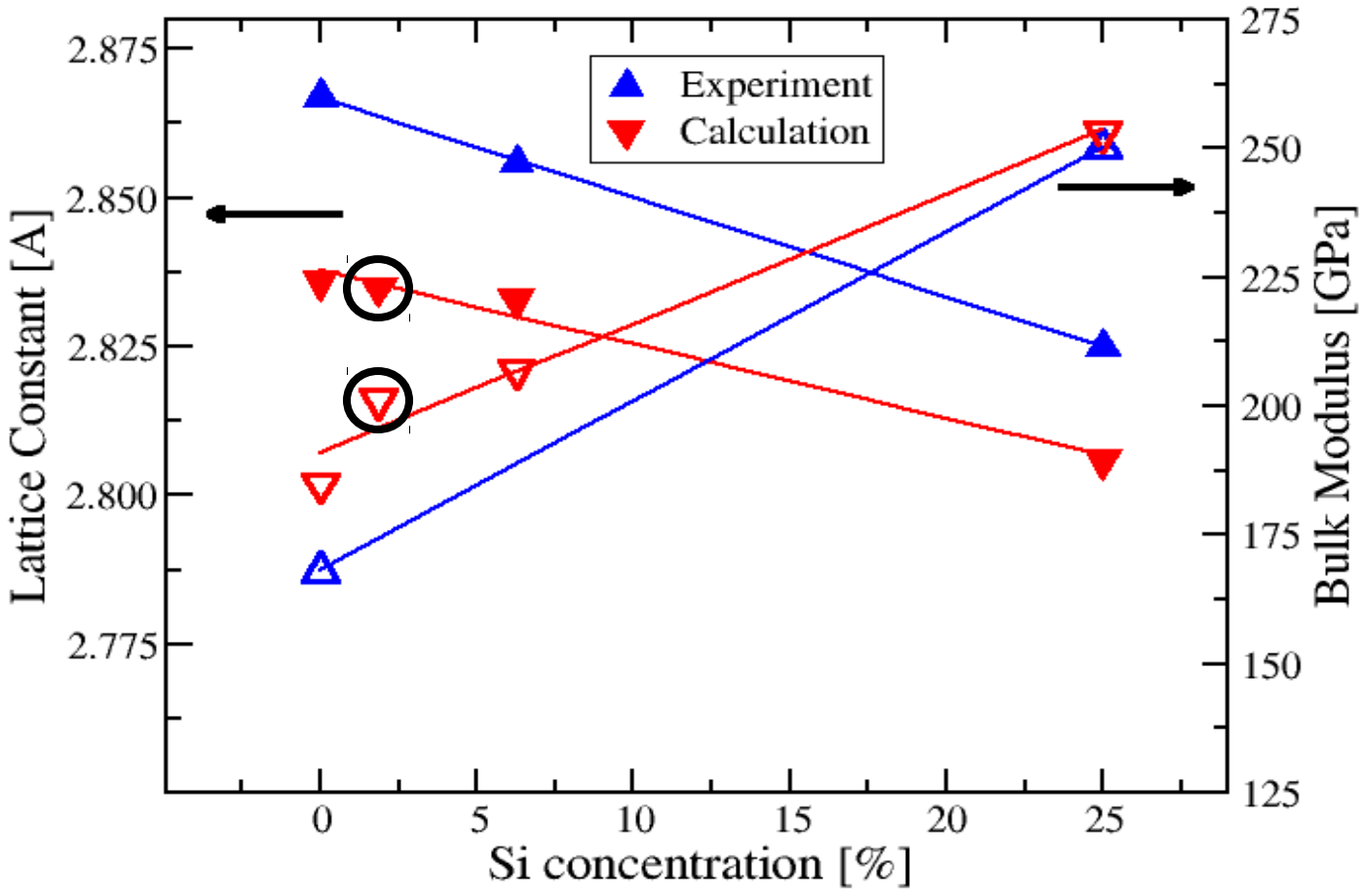


Fe_3Si

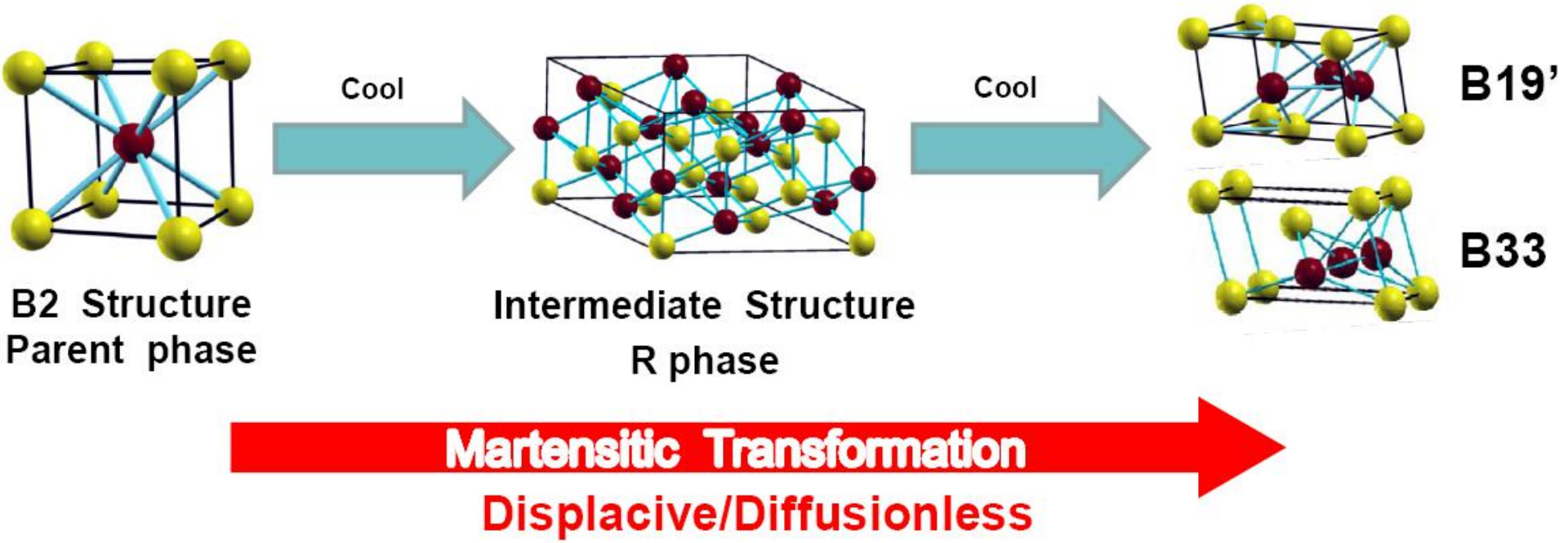


$Fe_{15}Si$

Example: Fe-Si Alloy



Example: NiTi Shape Memory Alloys



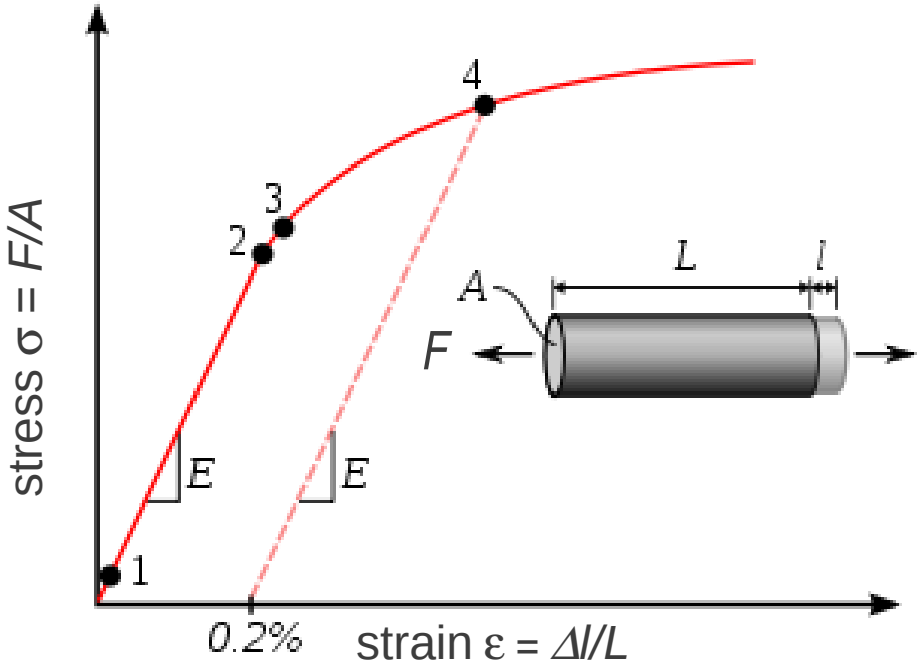
Elastic Constants

stress strain

Hooke's Law

$$\sigma_i = C_{ij}\varepsilon_j$$

„ut tensio sic vis“ (1678)



Elastic Constants

stress ↓ strain ↓

Hooke's Law

$$\sigma_i = C_{ij}\varepsilon_j$$

„ut tensio sic vis“ (1678)

Cubic Crystal

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{11} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix}$$

3 different components

Elastic Constants

stress → σ_i = C_{ij} ε_j ← strain

Hooke's Law

„ut tensio sic vis“ (1678)

Monoclinic Crystal

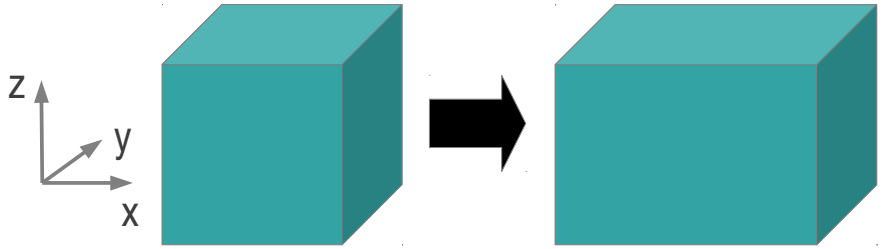
$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\ C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\ 0 & 0 & 0 & C_{44} & 0 & C_{46} \\ C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0 \\ 0 & 0 & 0 & C_{46} & 0 & C_{66} \end{pmatrix}$$

13 different components

How to Calculate Elastic Constants?

Special Strains

$$\overleftrightarrow{\varepsilon} = \begin{pmatrix} \varepsilon & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



Total Energy

$$E = E_0 + V_0 \left(\sigma_1 \varepsilon + \frac{1}{2} C_{11} \varepsilon^2 \right)$$

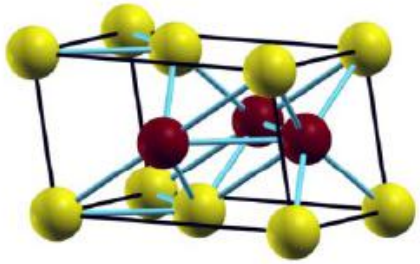
Monoclinic Crystal

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\ C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\ 0 & 0 & 0 & C_{44} & 0 & C_{46} \\ C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0 \\ 0 & 0 & 0 & C_{46} & 0 & C_{66} \end{pmatrix}$$

13 different components

Results for NiTi B19' Phase

B19′:



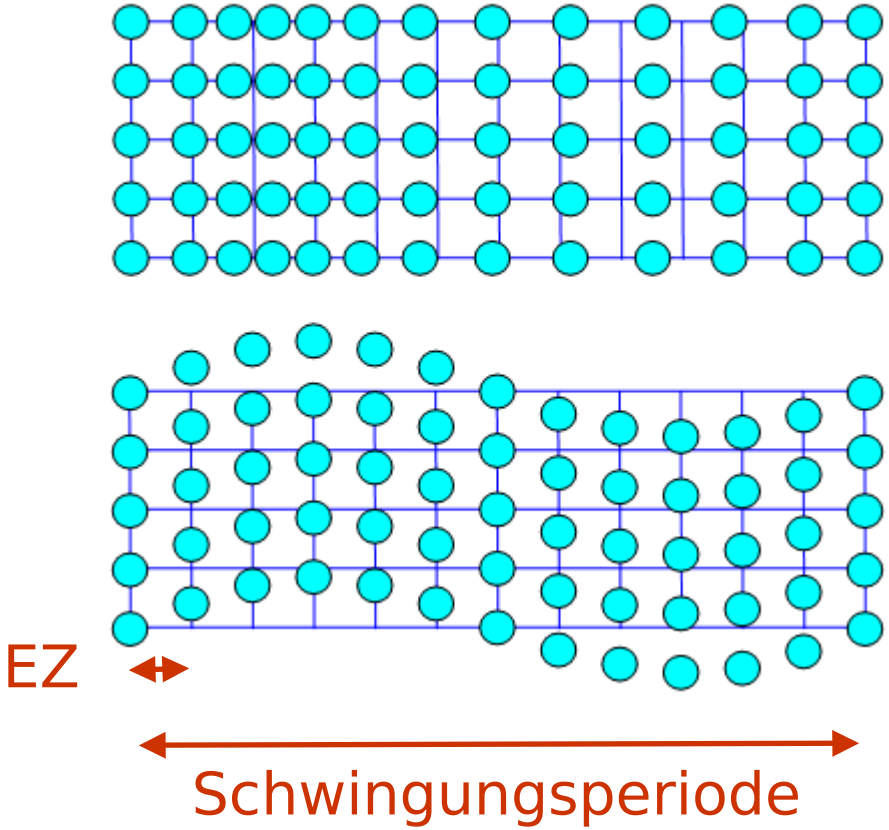
	a(a.u)	b(a.u)	c(a.u)	β
Experimental (3)	8.780	7.763	5.476	97.8
WIEN2k	8.910	7.668	5.557	100.6

[3] Acta MetallMater, 33, 2094, 1985

Elastic Constant (GPa)	C11	C12	C13	C15	C22	C23	C25	C33	C35	C44	C46	C55	C66
Elastic - WIEN2k	186	131	114	-3	239	121	-6	226	28	86	-3	23	80

Golesorkhtabar, Spitaler, Puschnig, Ambrosch-Draxl, *to be published*

Frozen Phonon Approach



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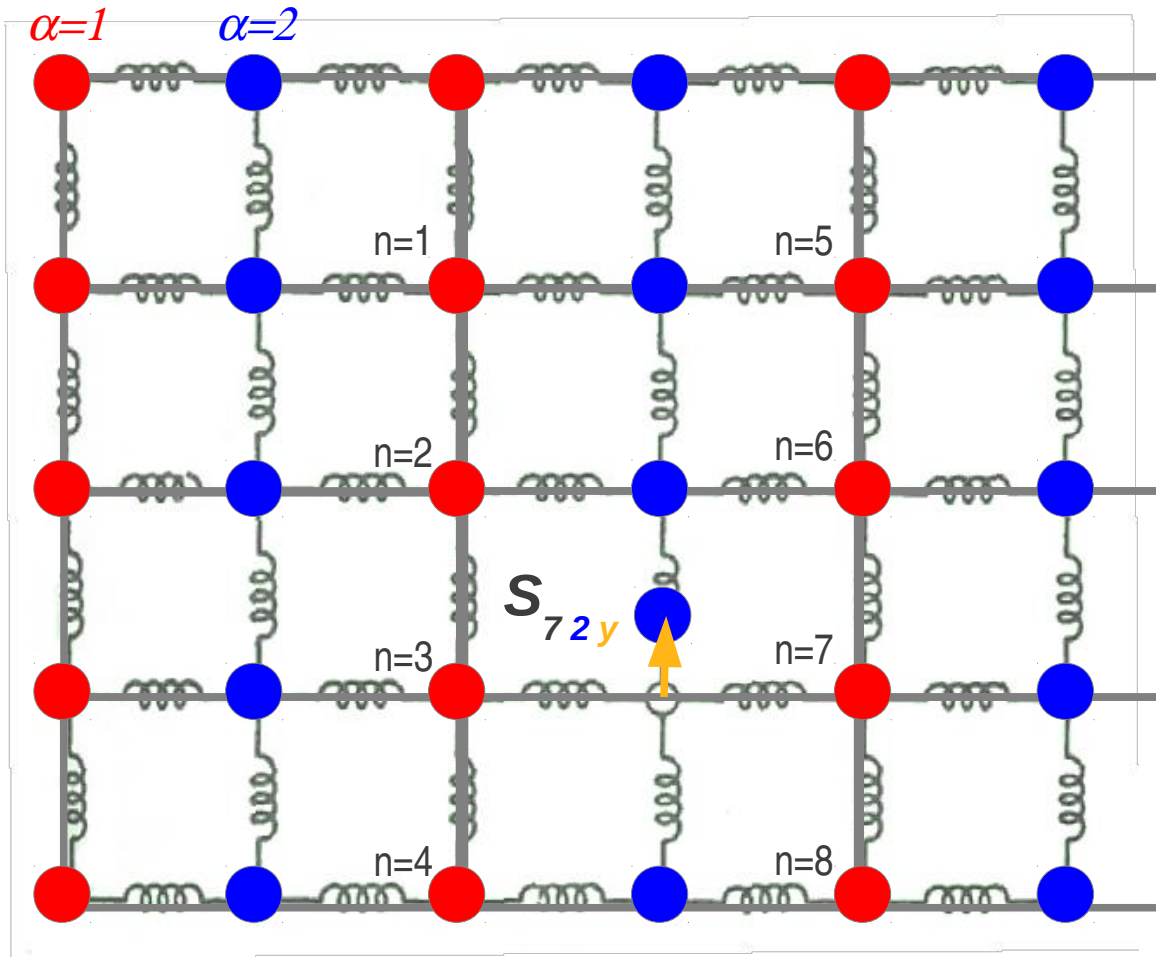
Super Cell Approach

Atom type A

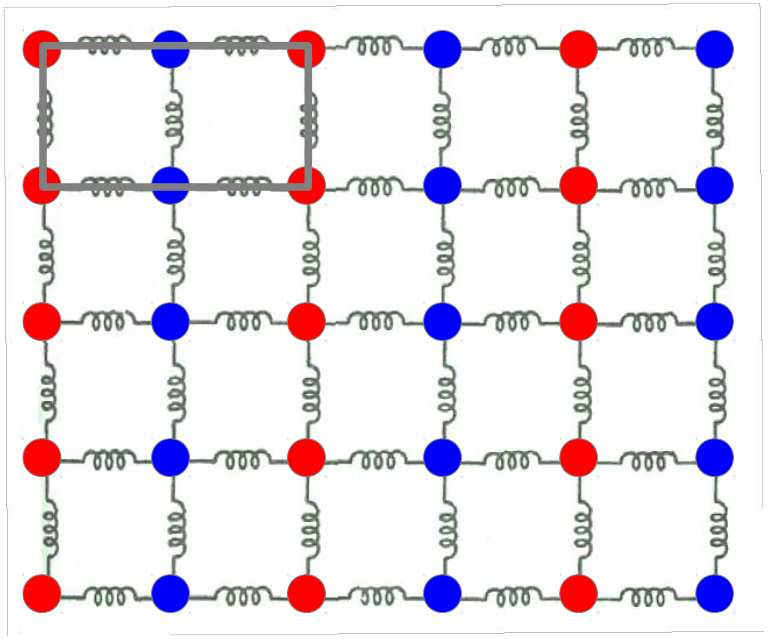
Atom type B

$s_{n\alpha i}$

displacement *s of*
atom type *a*
in unit cell *n*
in direction *i*



Equation of Motion



Kinetic Energy *T*

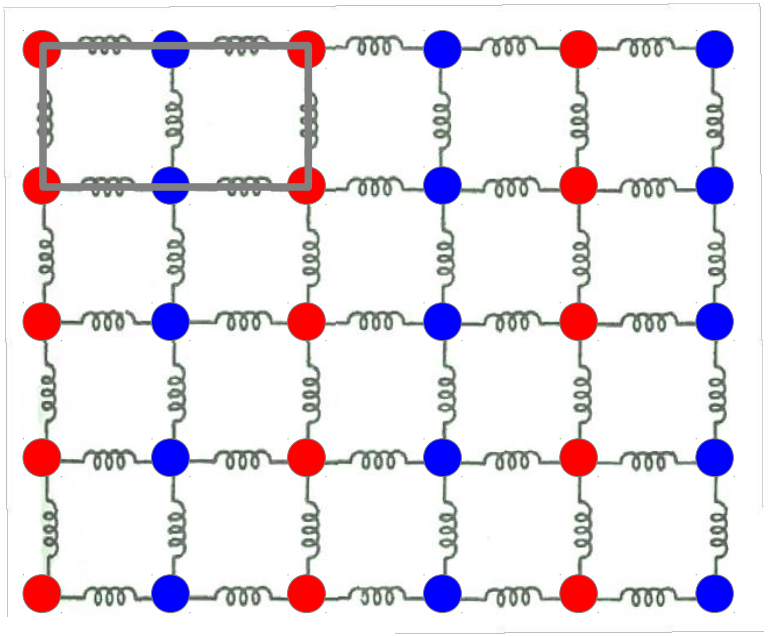
$$T = \sum_{n=1}^{N} \sum_{\alpha=1}^{r} \sum_{i=1}^{3} \frac{M_\alpha}{2} \left(\frac{ds_{n\alpha i}(t)}{dt} \right)^2$$

Potential Energy *W*

$$W = W(\mathbf{R}_{n\alpha}) + \sum_{n\alpha i} \underbrace{\left[\frac{\partial W(\mathbf{x})}{\partial s_{n\alpha i}} \right]_{\mathbf{x}=\mathbf{R}_{n\alpha}}}_{=0} s_{n\alpha i} +$$

$$+ \sum_{n\alpha i} \sum_{n'\alpha' i'} \underbrace{\left[\frac{\partial^2 W(\mathbf{x})}{\partial s_{n\alpha i} \partial s_{n'\alpha' i'}} \right]_{\mathbf{x}=\mathbf{R}_{n\alpha}}}_{=\Phi_{n\alpha i}^{n'\alpha' i'}} s_{n\alpha i}\, s_{n'\alpha' i'} + O(s^3)$$

Dynamical Matrix



Equation of motion

$$M_\alpha \frac{d^2 s_{n\alpha i}}{dt^2} = -\sum_{n'\alpha' i'} \Phi_{n\alpha i}^{n'\alpha' i'} s_{n'\alpha' i'}$$

Ansatz for solution

$$s_{n\alpha i}(t) = \frac{1}{\sqrt{M_\alpha}} u_{n\alpha i} e^{-i\omega t} \qquad u_{n\alpha i} = c_{\alpha i} e^{i\vec{q}\vec{R}_n}$$

Eigenvalue equation for phonon frequencies ω*(q)*

$$\omega^2 c_{\alpha i} = \sum_{\alpha' i'} \underbrace{\left[\sum_{n'} \frac{\Phi_{\alpha i}^{\alpha' i'}(n')}{\sqrt{M_\alpha M_{\alpha'}}} e^{i\vec{q}\vec{R}_{n'}} \right]}_{D_{\alpha i}^{\alpha' i'}(\vec{q})} c_{\alpha' i'}$$

Dynamical Matrix

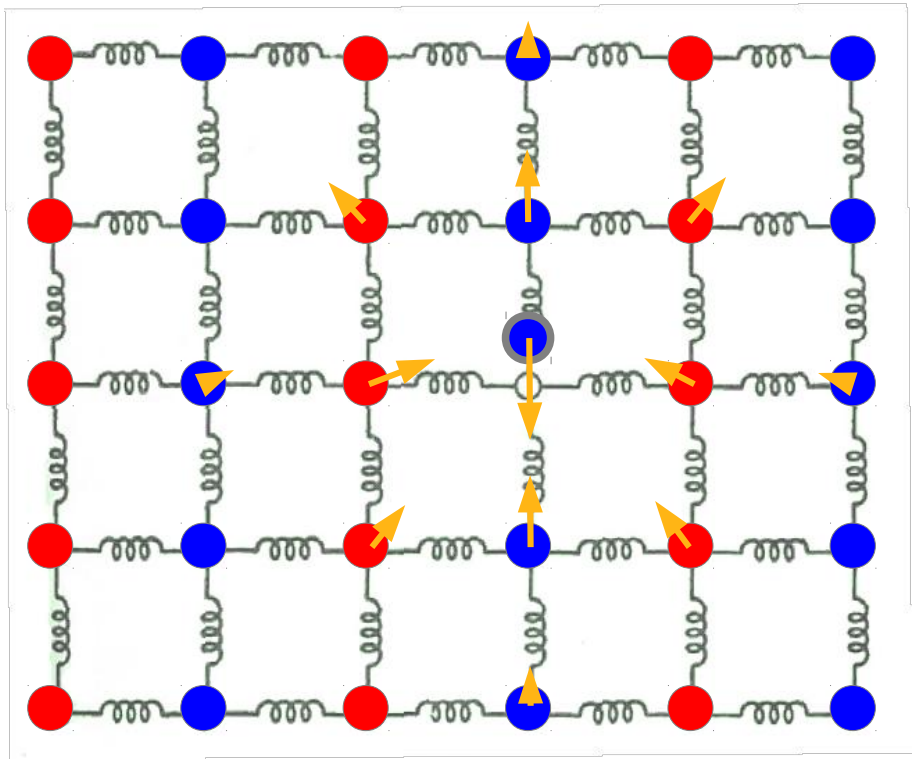
Hellmann-Feynman Theorem

$$\mathbf{F}_I = -\frac{\partial}{\partial \mathbf{R}_I} E\left[\{\phi\}, \{\mathbf{R}\}\right]$$

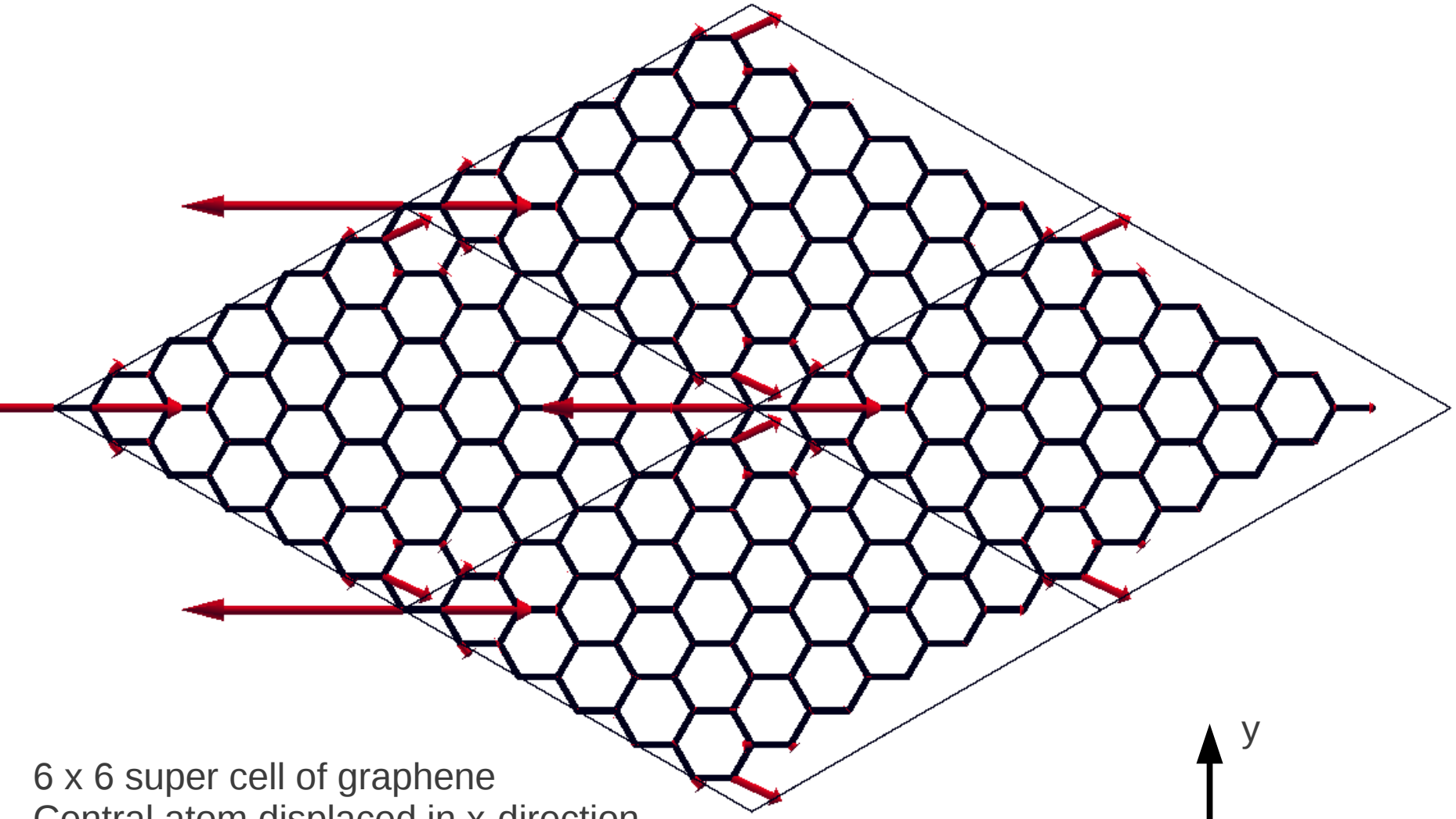
The force $\mathbf{F}_I$ *acting on the atom at position* $\mathbf{R}_I$ *can be calculated from the ground state energy and Kohn-Sham orbitals*

Force constant matrix

$$\Phi_{I\mu,\nu} = \frac{\partial^2 F^{\mathrm{el}}}{\partial u_{I\mu} \partial u_\nu} = \frac{\partial \widetilde{F}^{\mathrm{HF}}_{I\mu}}{\partial u_\nu}$$

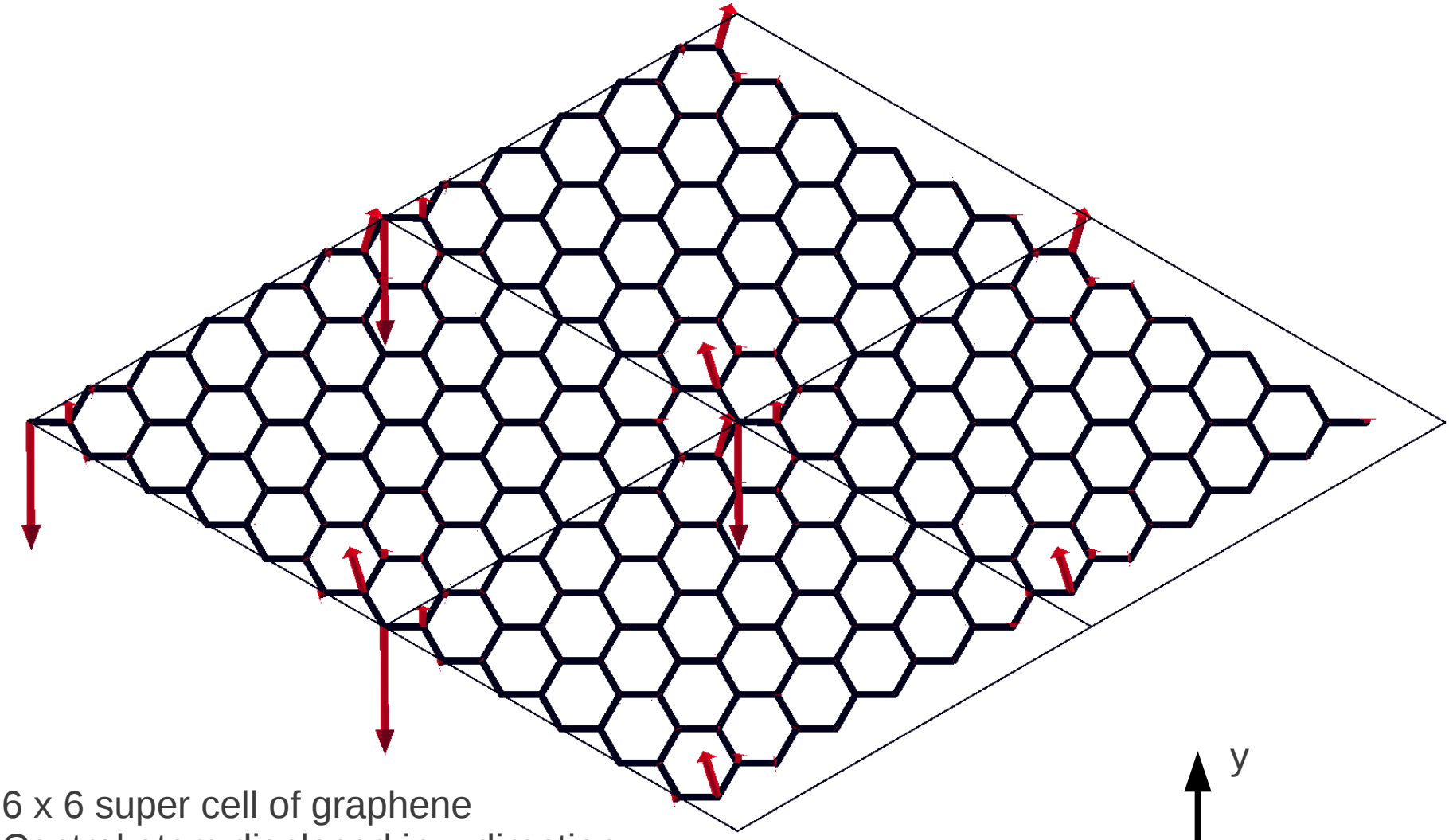


Force Constants in Graphene



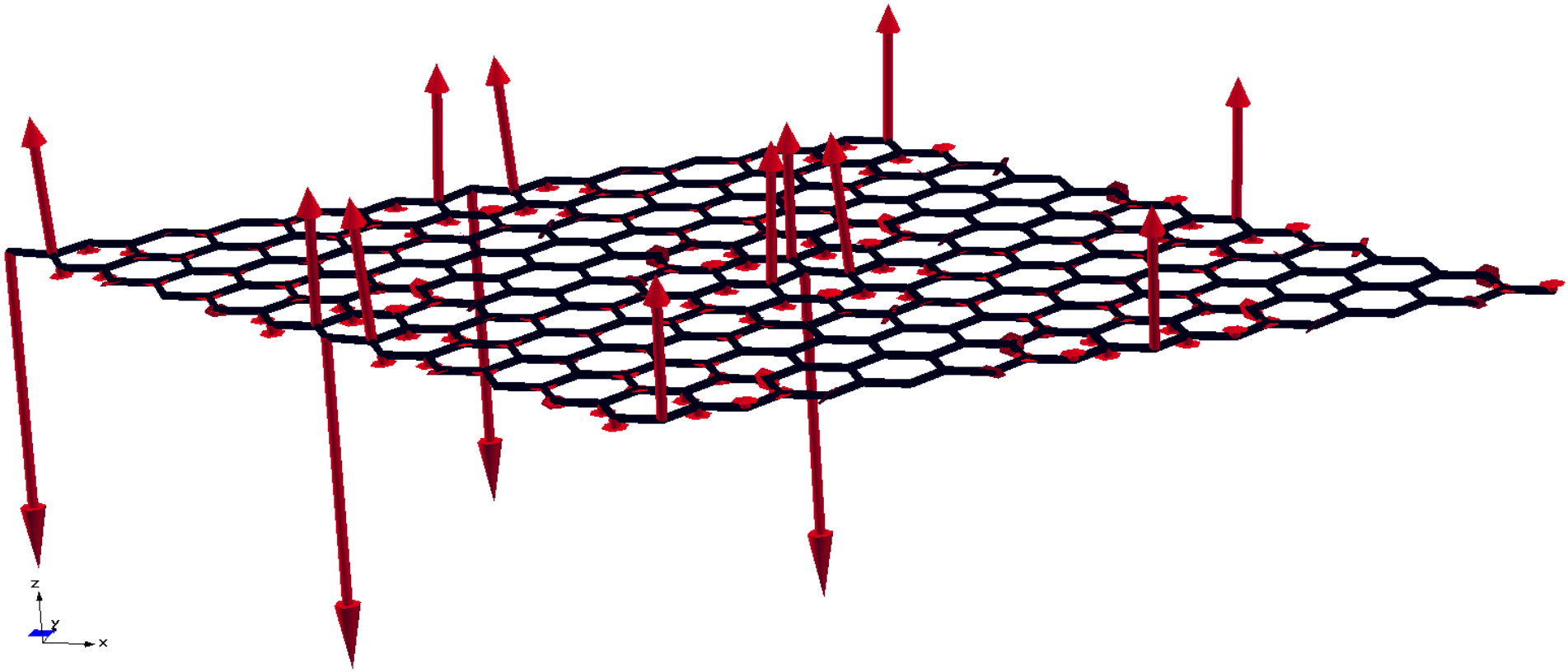
6 x 6 super cell of graphene
Central atom displaced in x-direction
GGA-DFT forces indicated by red arrows

Force Constants in Graphene



6 x 6 super cell of graphene
Central atom displaced in y-direction
GGA-DFT forces indicated by red arrows

Force Constants in Graphene

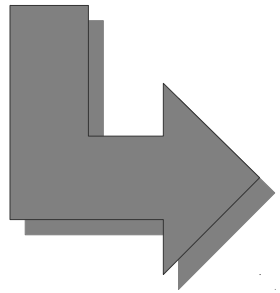


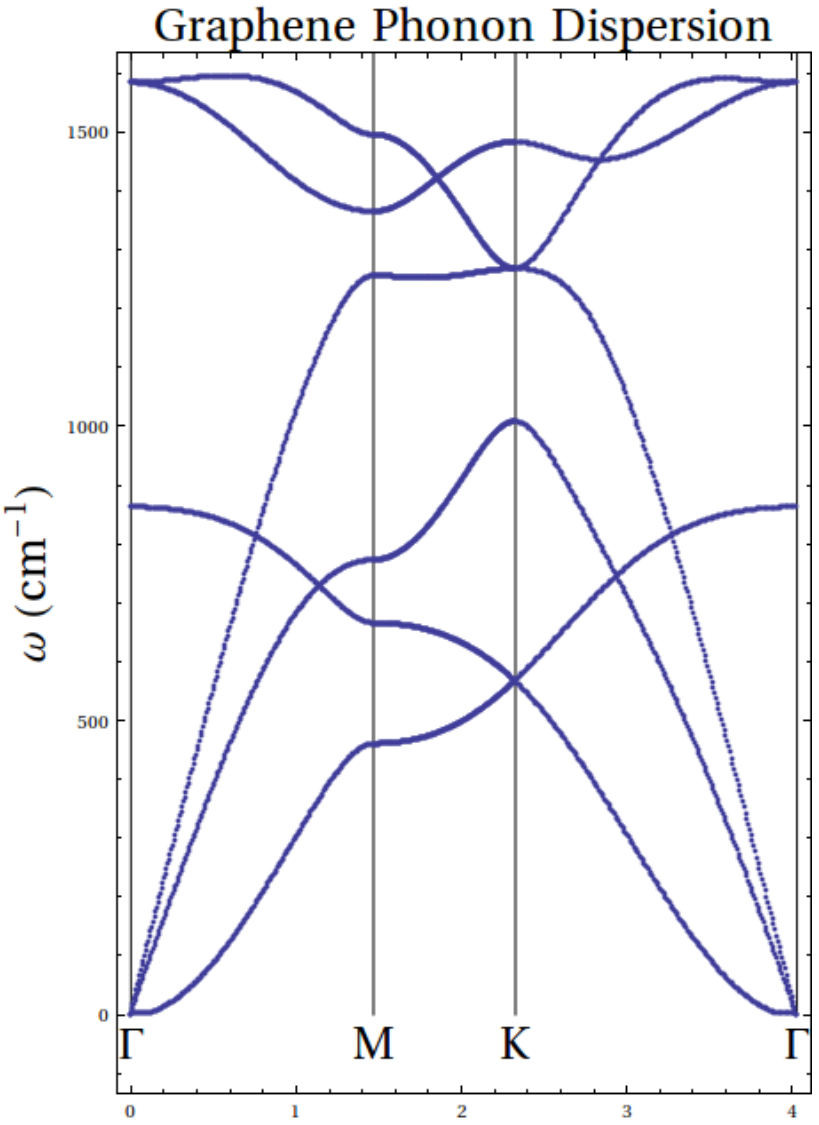
6 x 6 super cell of graphene
Central atom displaced in z-direction
GGA-DFT forces indicated by red arrows

Phonon Dispersion in Graphene

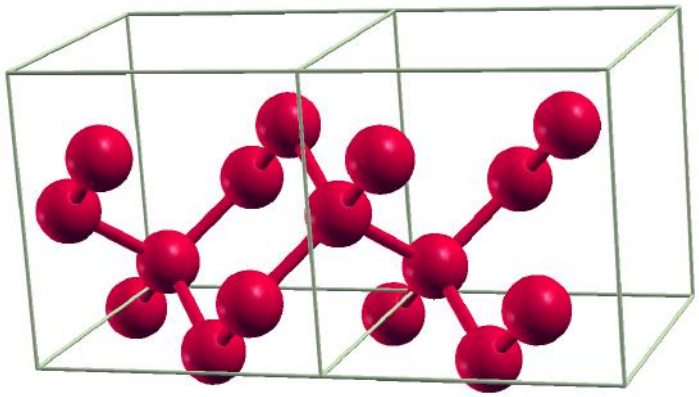
The force constants are used to set up
the dynamical matrix D(q) whose eigenvalues
Are the squares of the phonon frequencies ω(q)

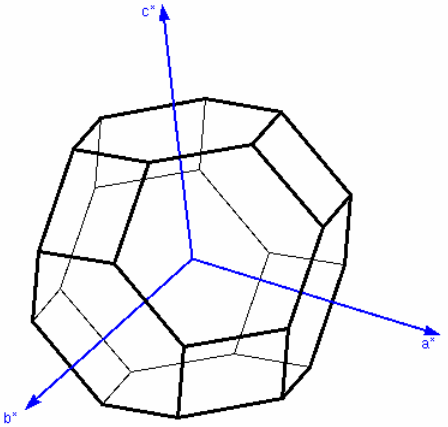
$$\omega^2 c_{\alpha i} = \sum_{\alpha' i'} \underbrace{\left[\sum_{n'} \frac{\Phi_{\alpha i}^{\alpha' i'}(n')}{\sqrt{M_\alpha M_{\alpha'}}} e^{i\vec{q}\vec{R}_{n'}} \right]}_{D_{\alpha i}^{\alpha' i'}(\vec{q})} c_{\alpha' i'}$$

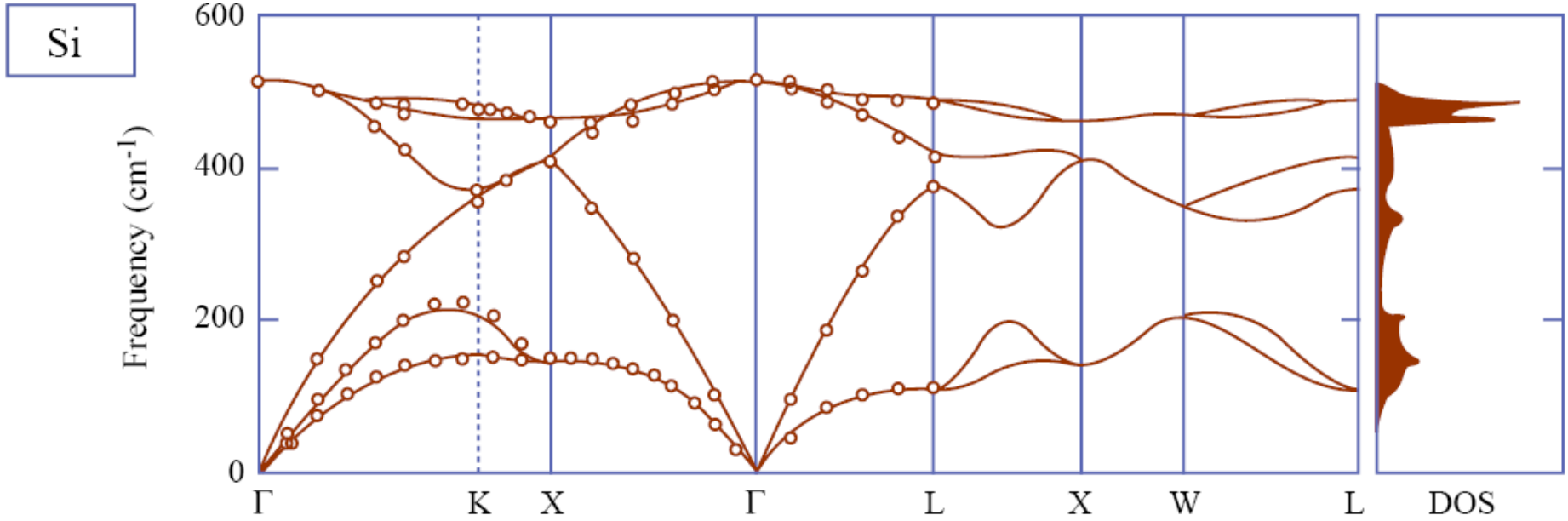




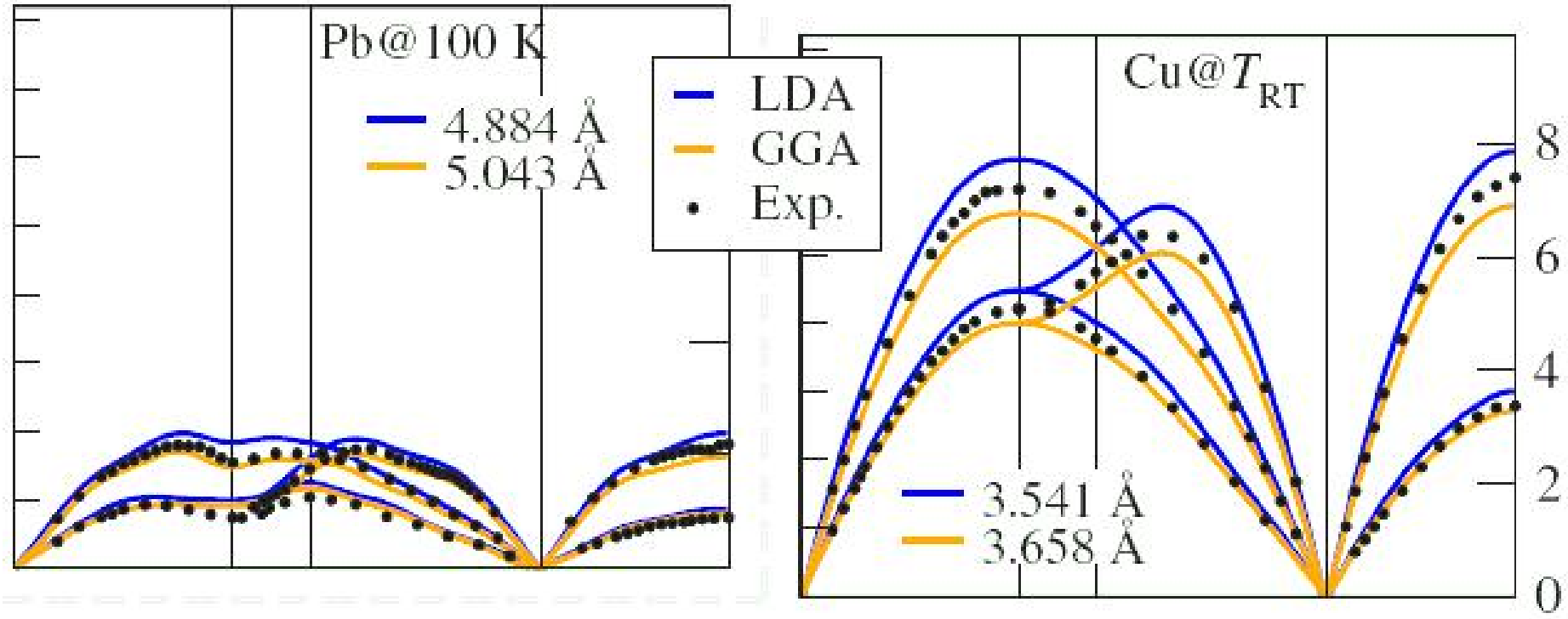
Phonon Dispersion in Silicon







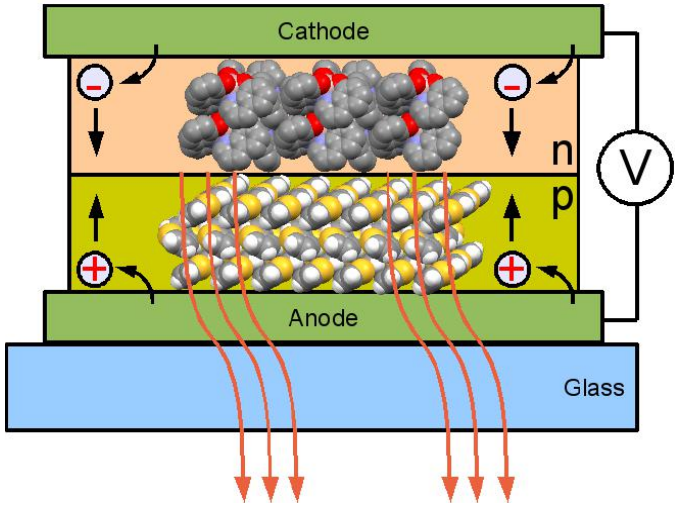
Phonon Band Structure of fcc-Metals

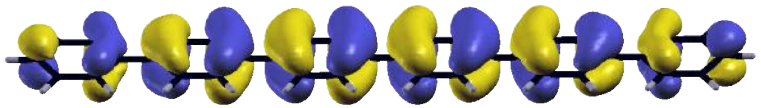


DFT-calculated phonon dispersion in Pb (left) and Cu (right) compared to experiment (dots)

Graphs are taken from Grabowski et al, *Phys. Rev. B* ***76****, 024309 (2007).*

Organic-LED



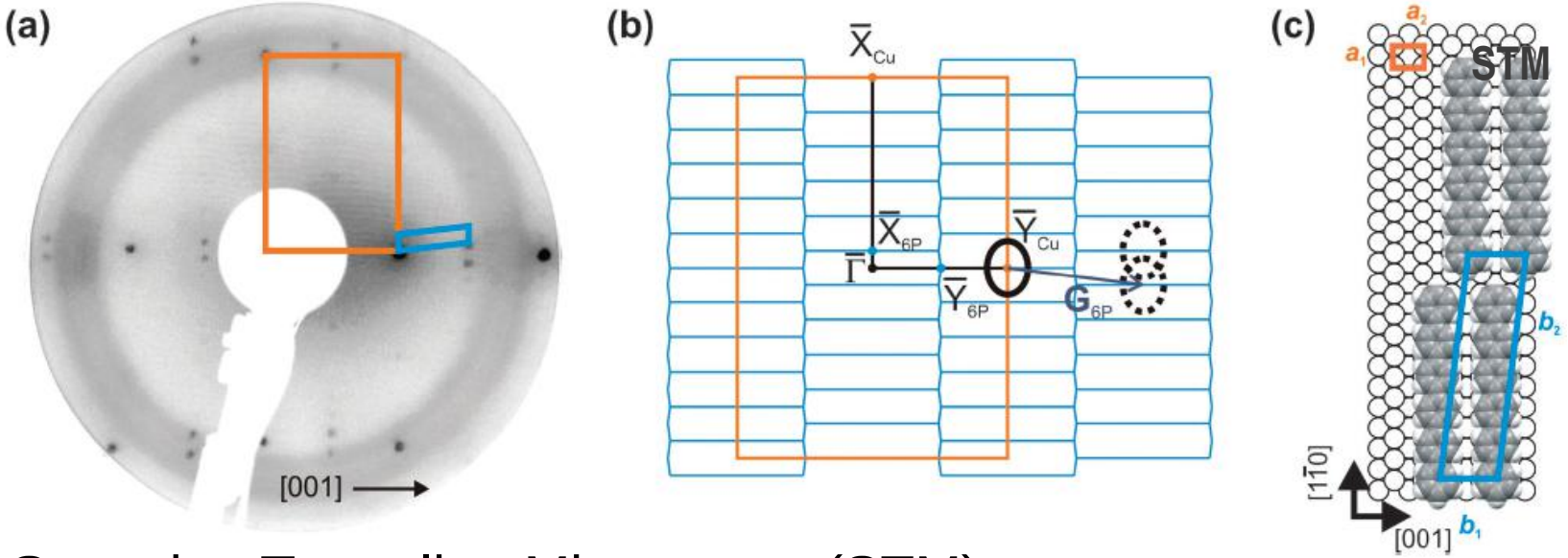


Highest Molecular Orbital (HOMO)
of para-Sexiphenyl (6P) ($C_{36}H_{26}$)

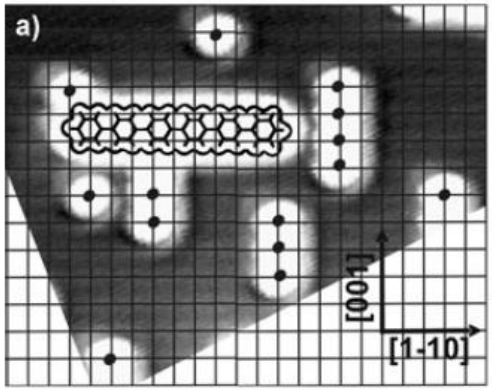
Monolayer 6P/Cu(110)

Experimental Evidence

Low **E**nergy **E**lectron **D**iffraction (LEED)

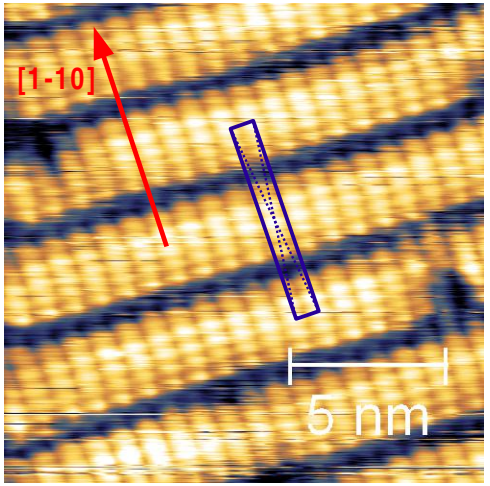


Scanning **T**unneling Microscopy (STM)

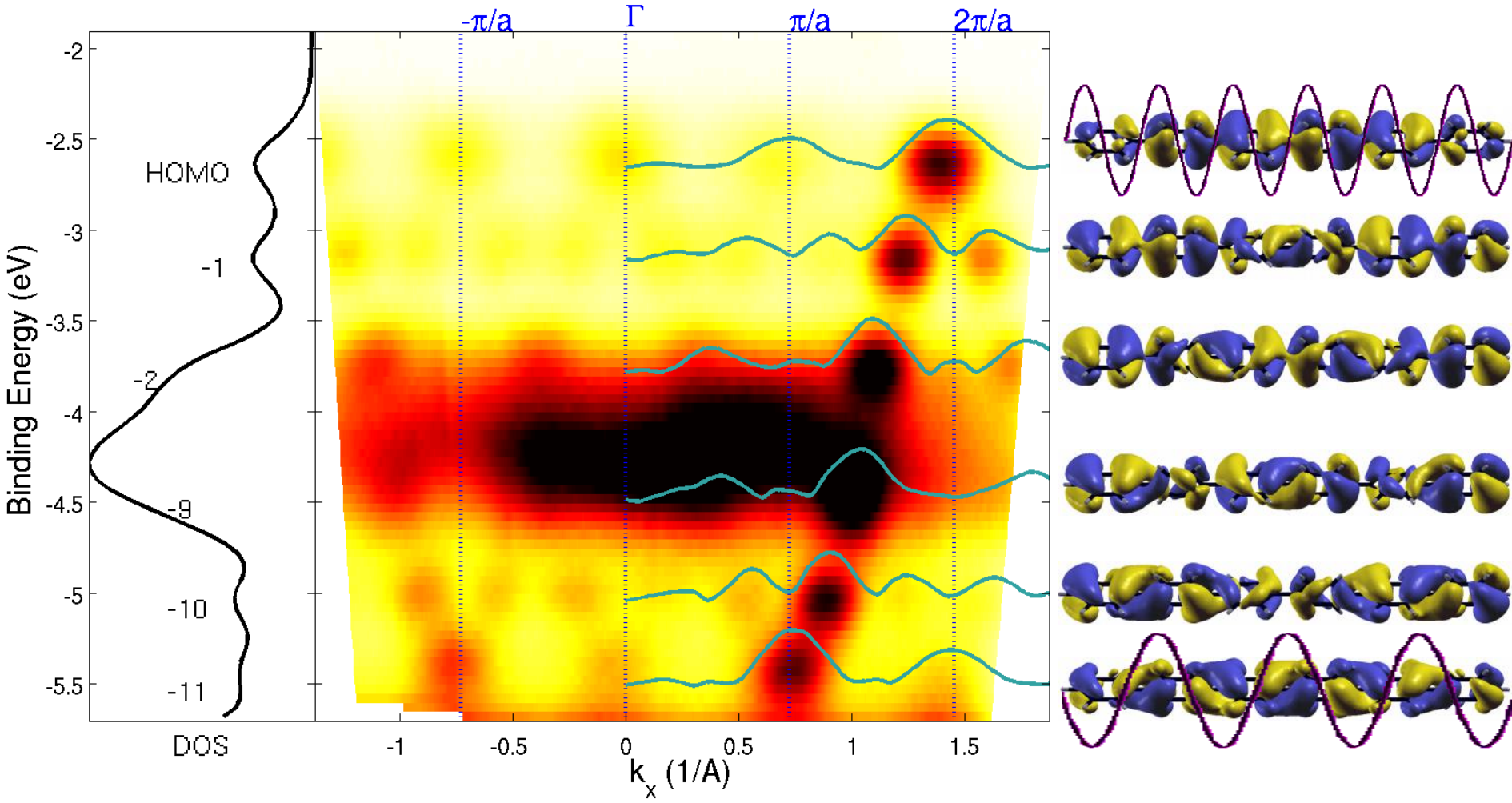


Berkebile et al.,
Phys. Chem. Chem. Phys.,
13, 3604–3611 (2011).

M. Oehzelt et al.,
ChemPhysChem 8,
1707 – 1712 (2007).



Angle-Resolved Photoemission: Multilayer

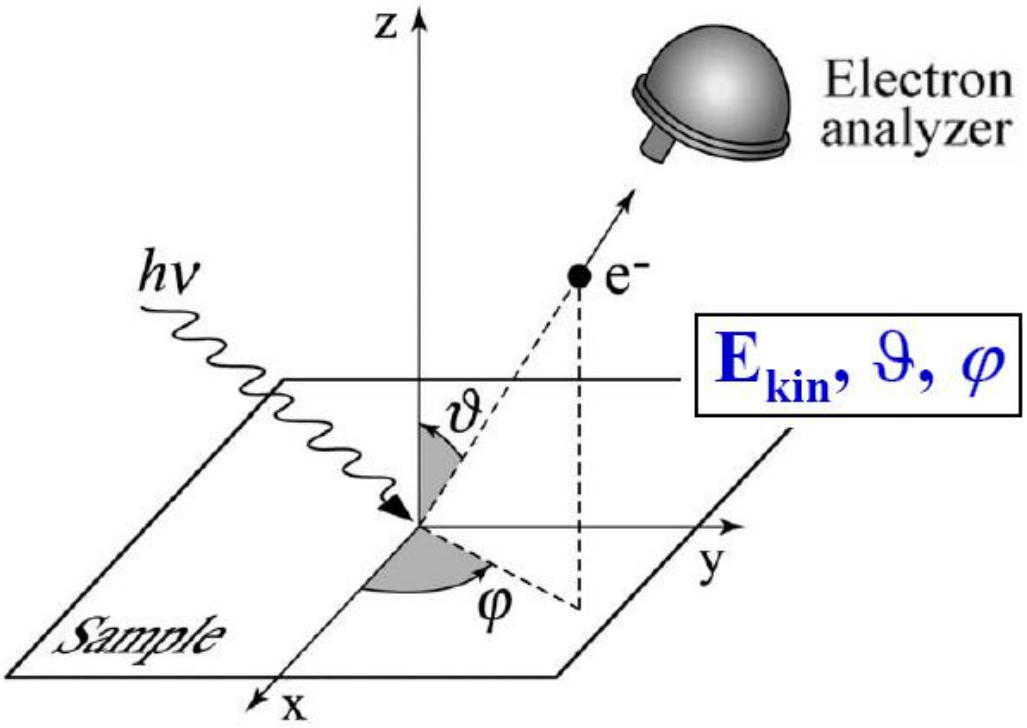


G. Koller et al., *Science* ***317****, 351 (2007).*

Photoemission Intensity

One Step Model

$$I(\theta, \phi; E_{\mathrm{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\mathrm{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta\left(E_i + \Phi + E_{\mathrm{kin}} - \hbar\omega\right)$$

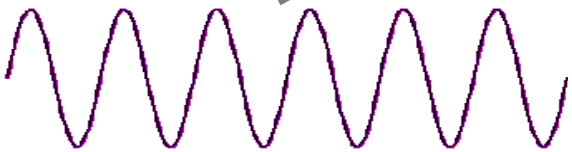


$I(\theta, \phi; E_{\mathrm{kin}})$

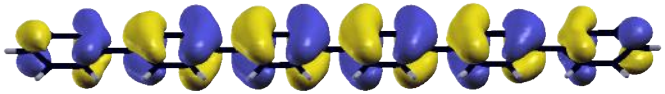
Photoemission Intensity

One Step Model

$$I(\theta, \phi; E_{\text{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\text{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta\left(E_i + \Phi + E_{\text{kin}} - \hbar\omega\right)$$



plane wave $e^{i\,k\,r}$



molecular orbital

Approximation: final state = plane wave

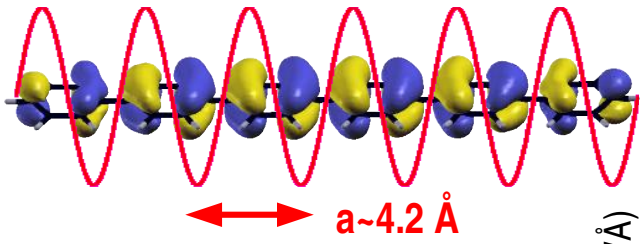
$$I_i(\theta, \phi) \propto \left|(\mathbf{A} \cdot \mathbf{k})\right|^2 \times \left|\tilde{\psi}_i(\mathbf{k})\right|^2$$

Fourier Transform of Initial State Orbital

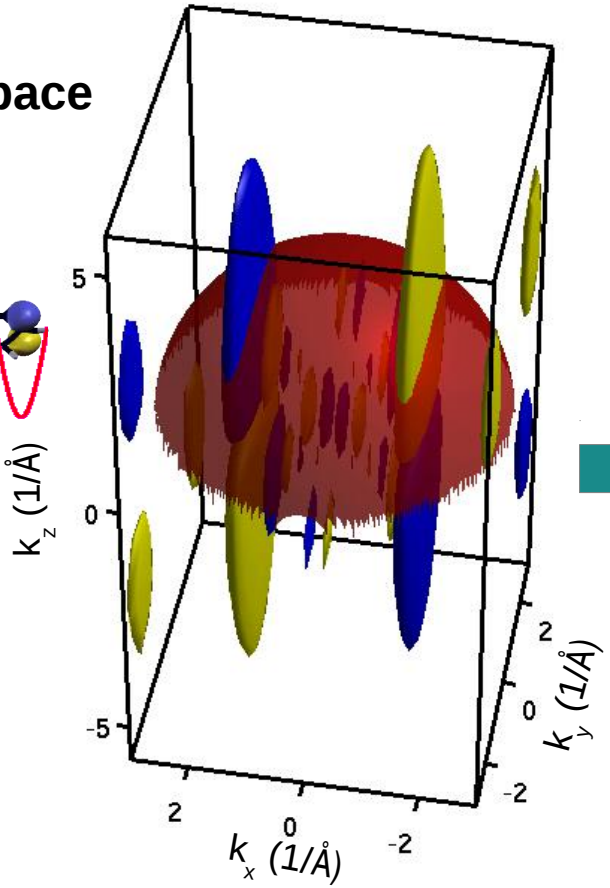
[Feibelman and Eastman, *Phys. Rev. B* **10**, 4932 (1974).]

Photoemission Intensity

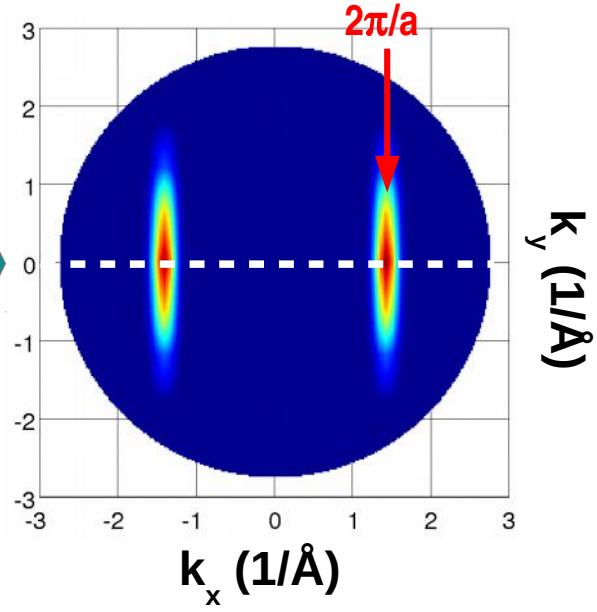
Molecular Orbital in Real Space



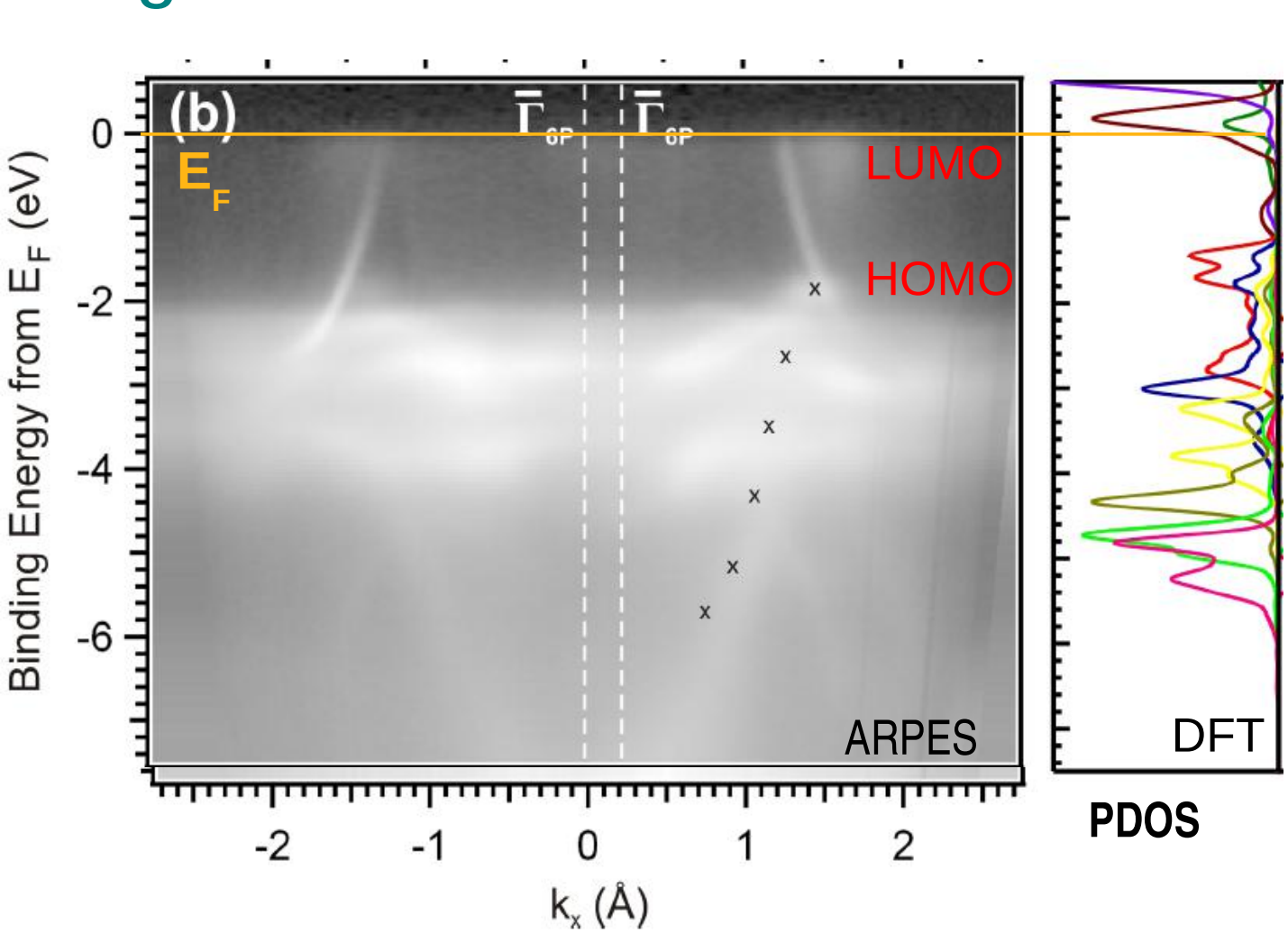
Calculation of the Fourier Transform

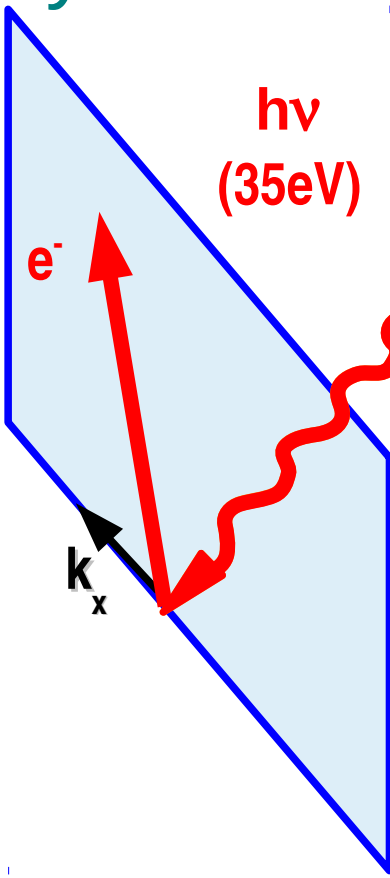


Hemispherical Cut Through 3D Fourier Transform



Angle-Resolved Photoemission: Monolayer

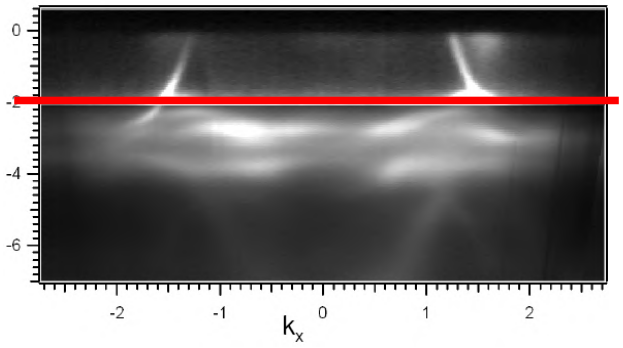


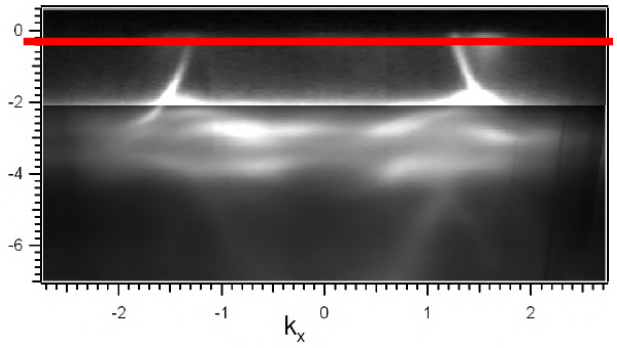


Berkebile et al., PCCP 13, 3604 (2011)

2D-Momentum Maps

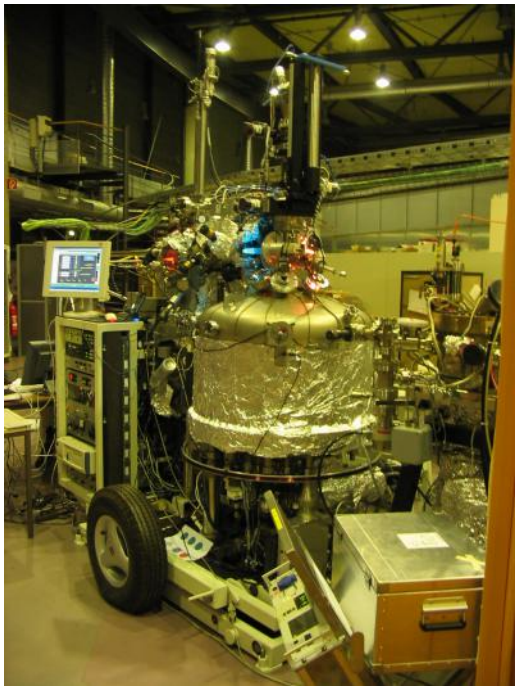
HOMO

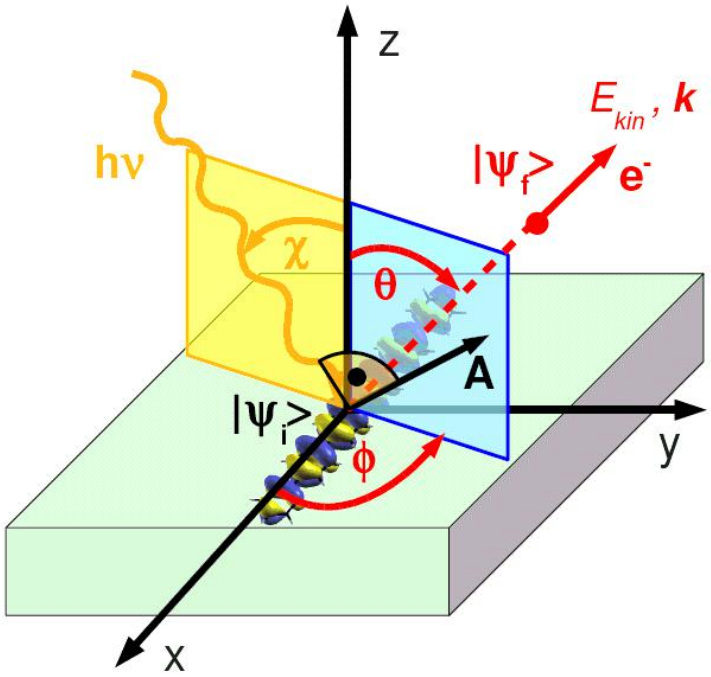




filled LUMO

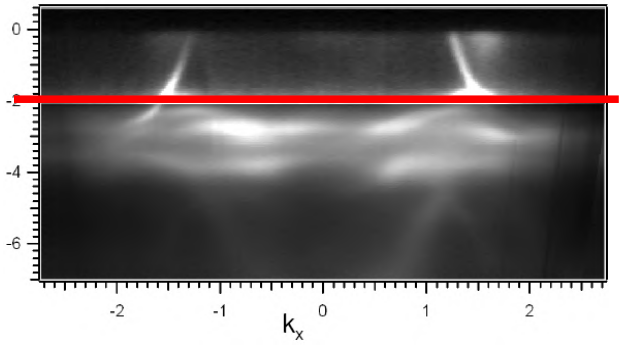
The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II

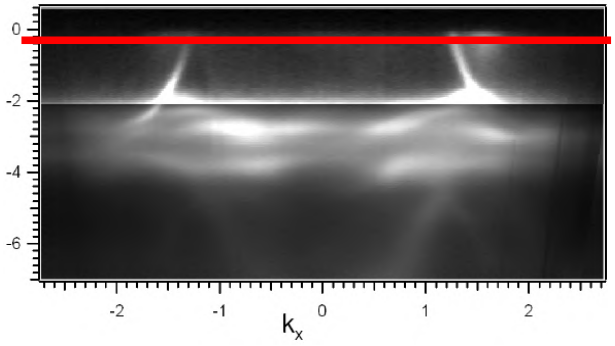




2D-Momentum Maps

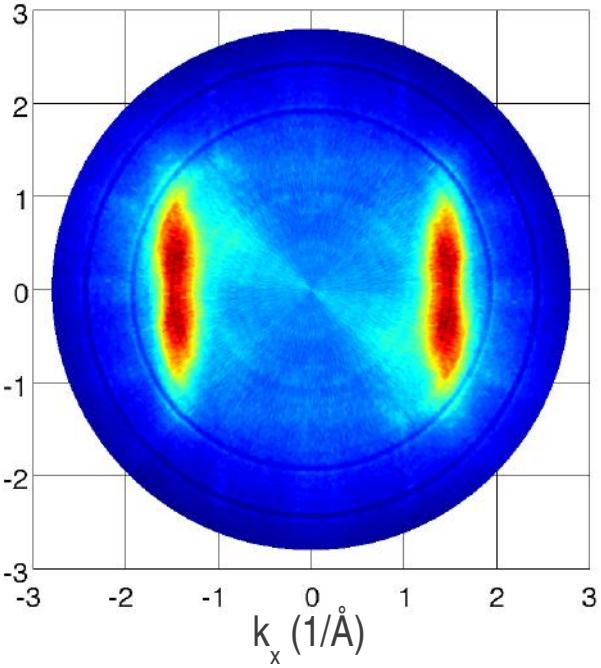
HOMO

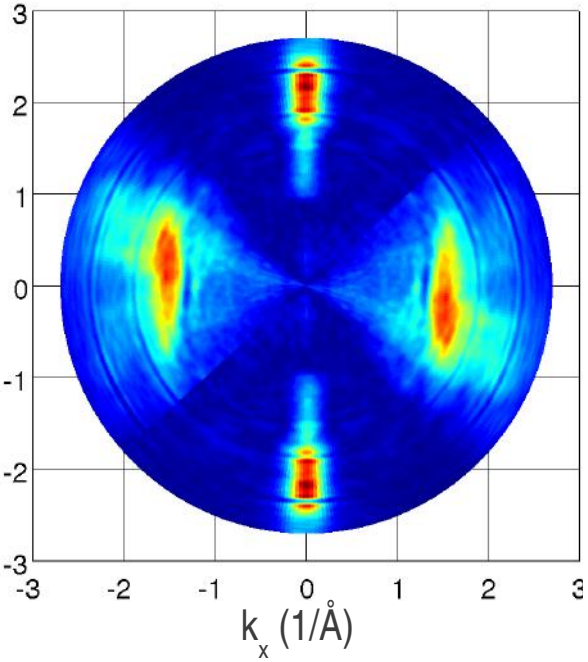




filled LUMO

ARPES data for a monolayer of 6P / Cu(110)

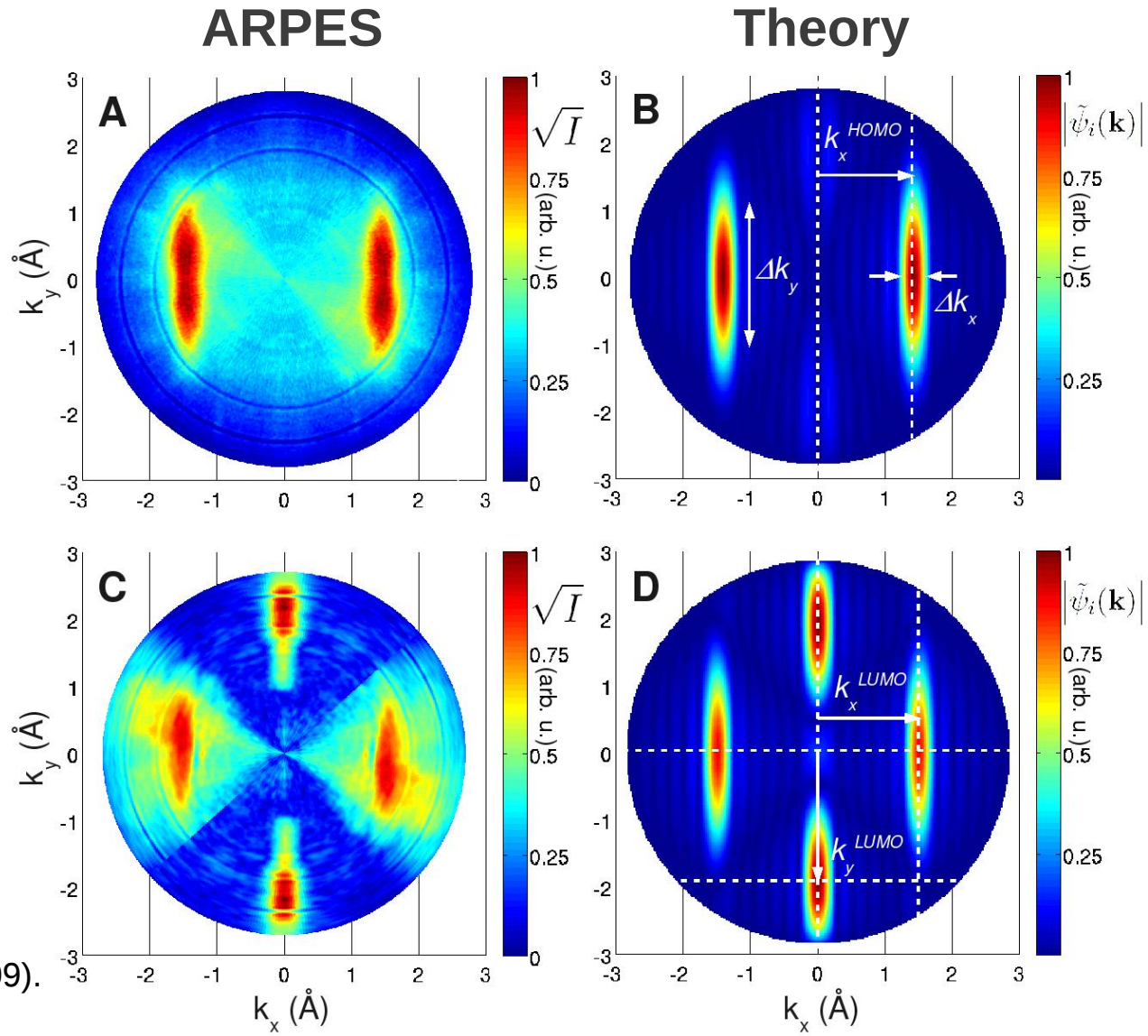




2D-Momentum Maps

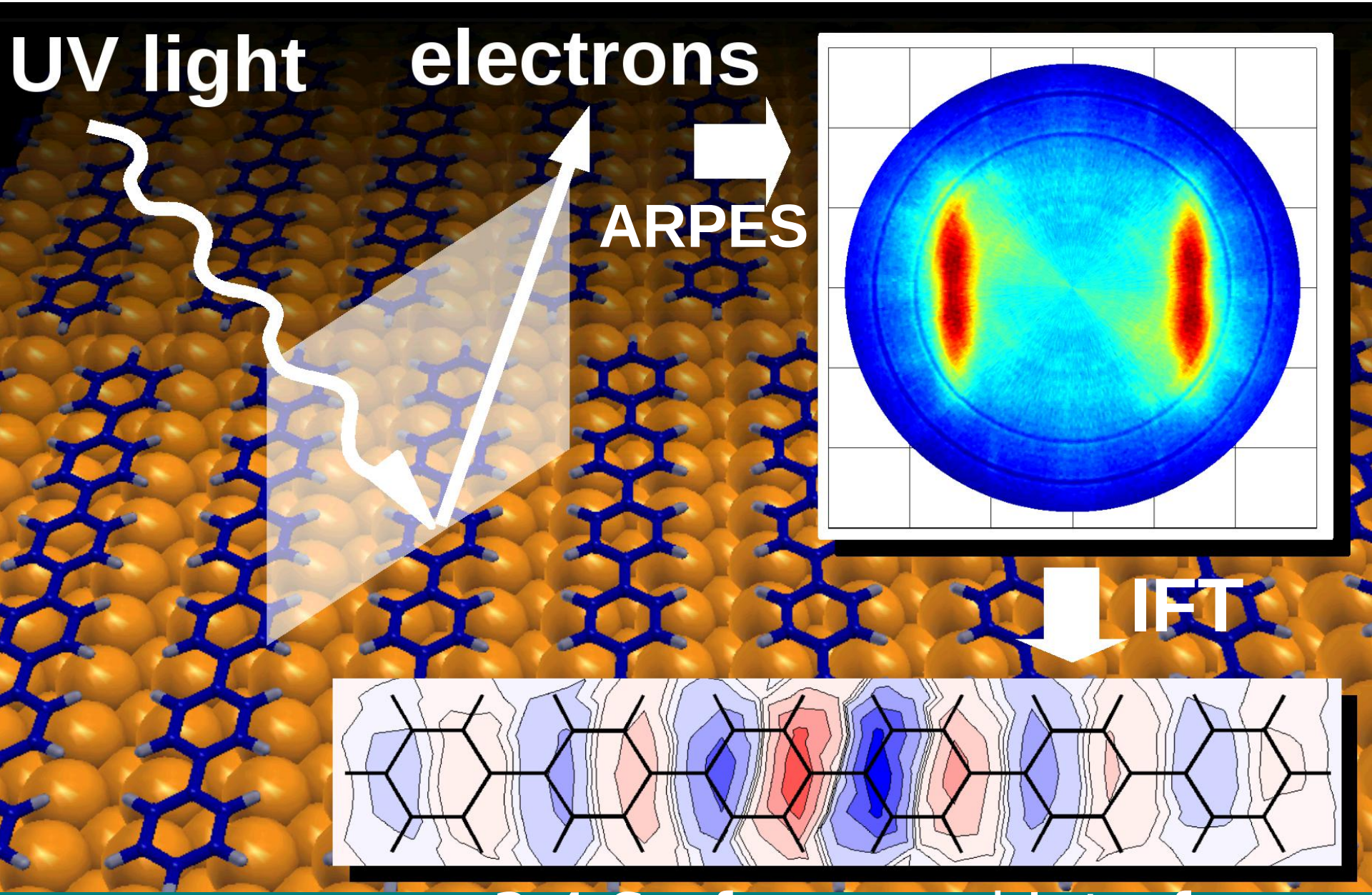
HOMO

LUMO



Puschnig et al.,
Science **326**, 702 (2009).

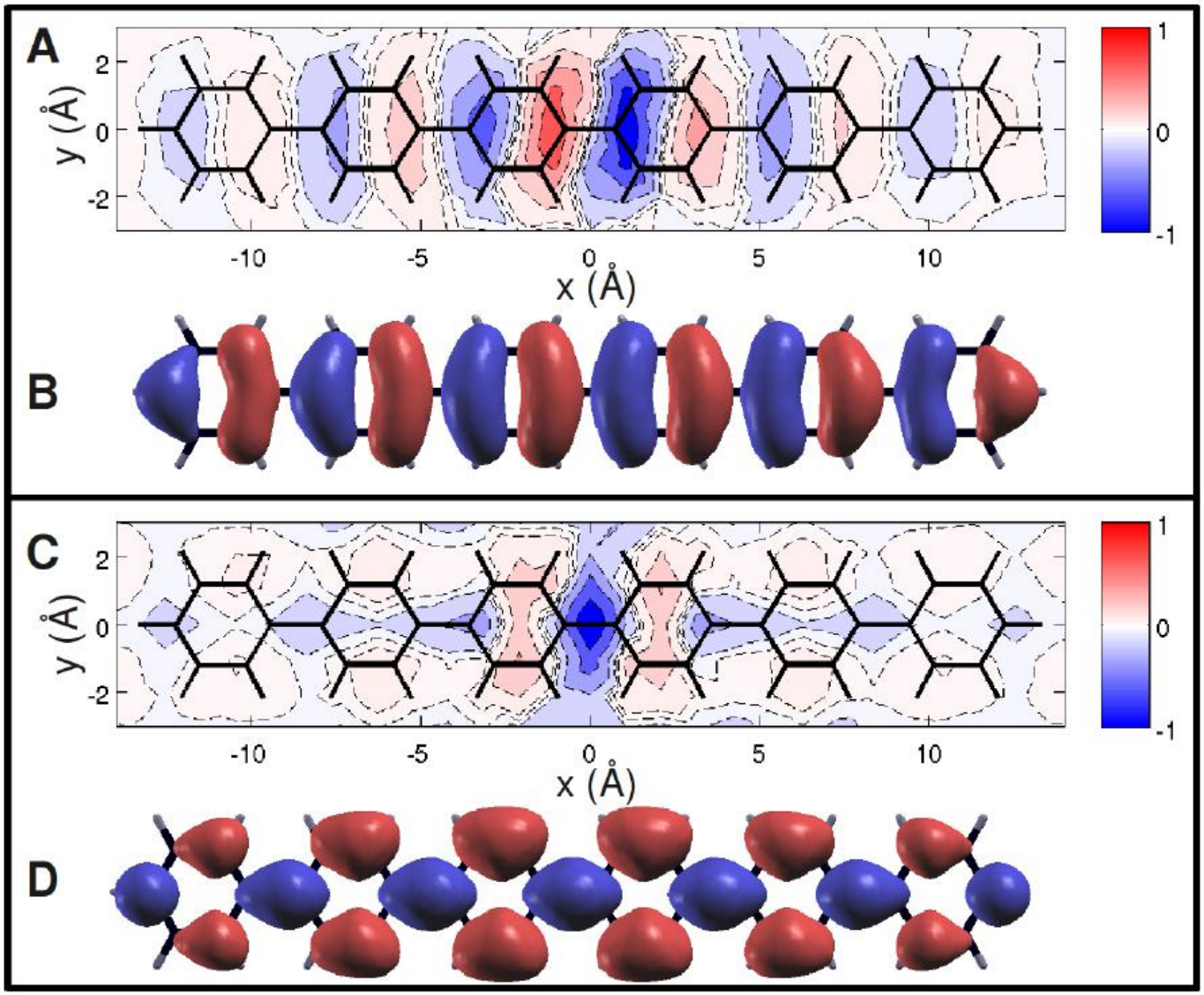
Reconstruction of Orbitals



Reconstruction of Orbitals

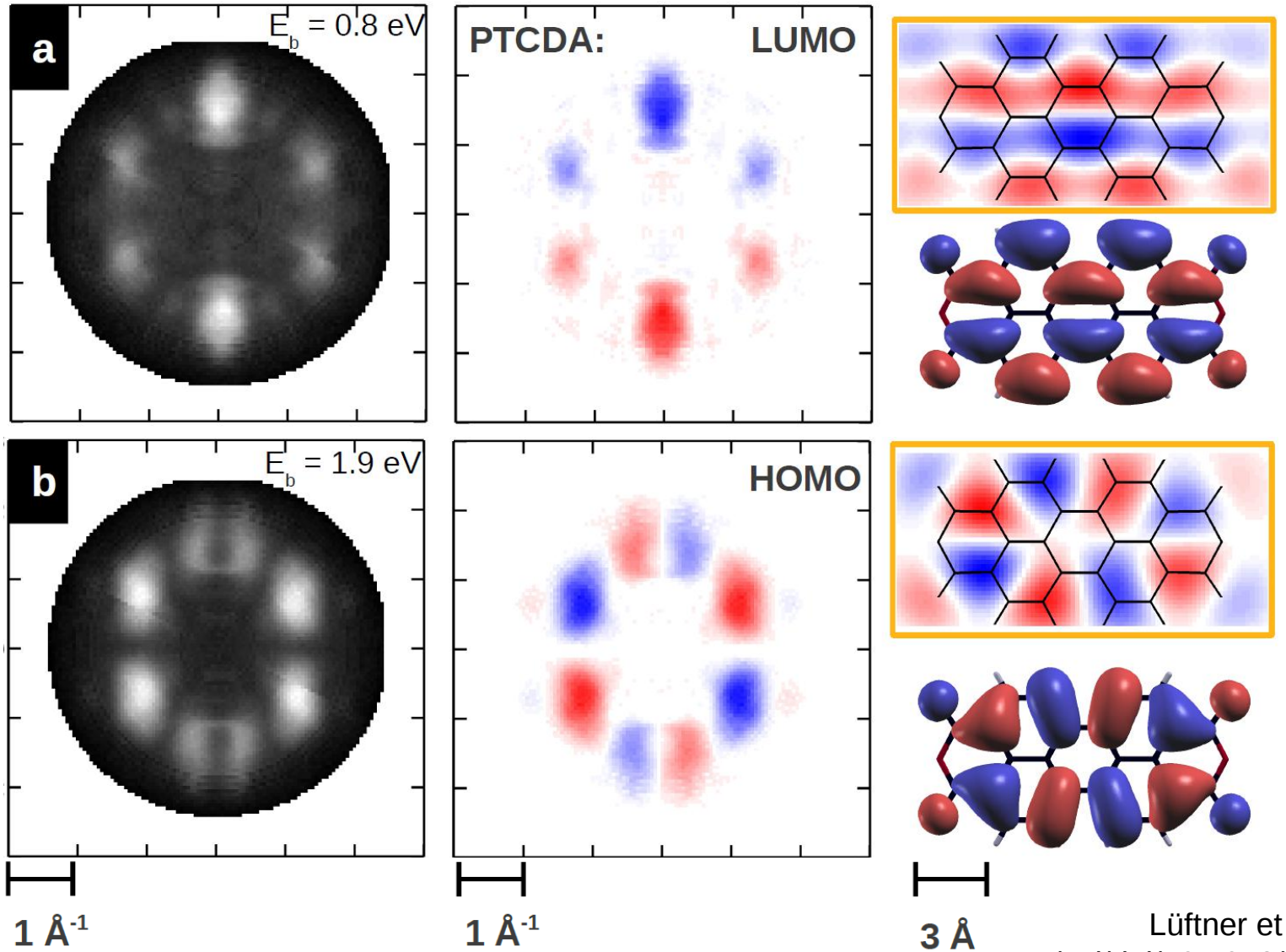
HOMO

LUMO



Puschnig et al.,
Science **326**, 702 (2009).

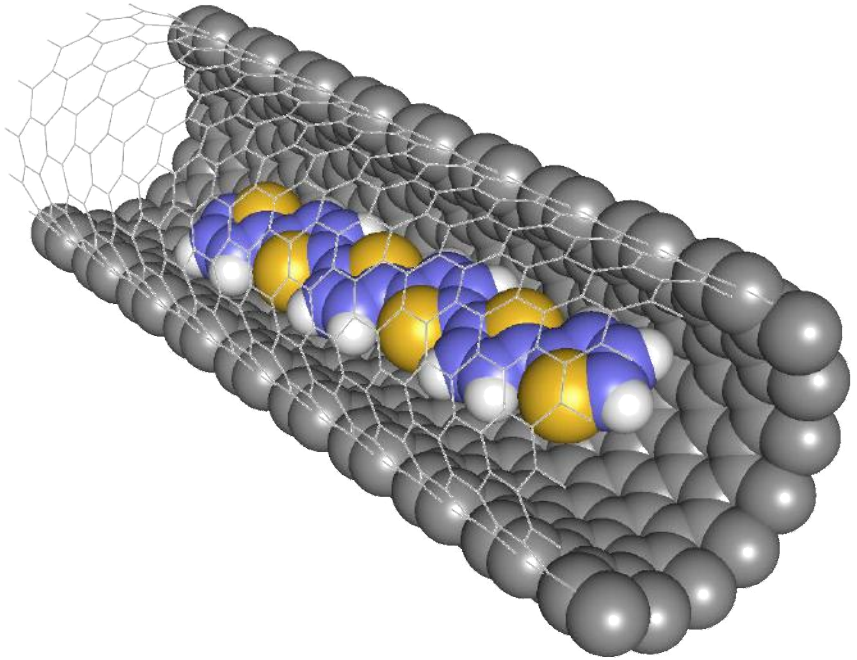
Reconstruction of Orbitals



Lüftner et al., *PNAS (2013)*, www.pnas.org/cgi/doi/10.1073/pnas.1315716110

Example: Nano-Peapods

peas in a pod



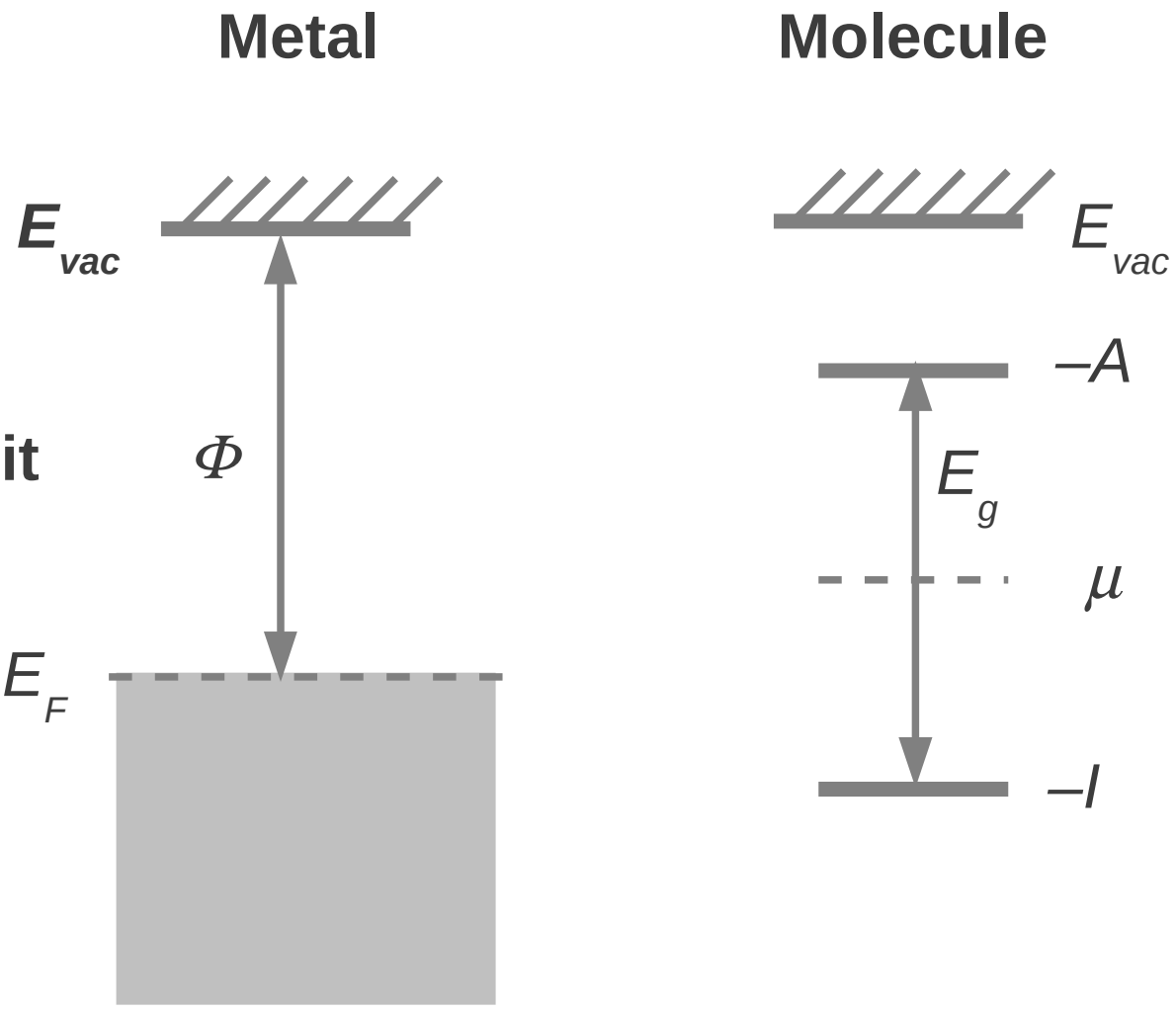
organic molecules in a carbon nanotube

EU-project
Nano-Hybrids for **Pho**tonic **D**evices

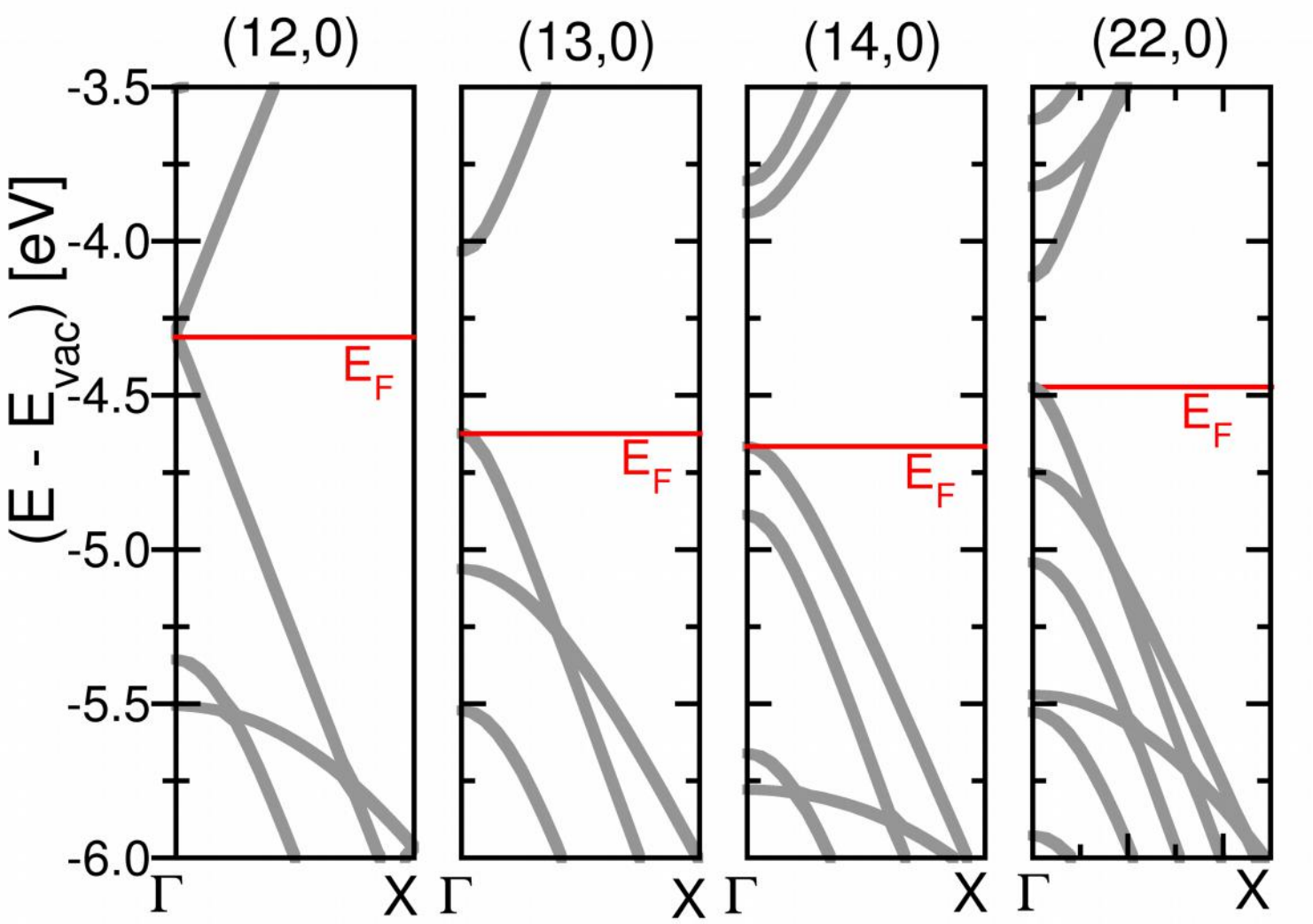
Level Alignment

Weak interaction
(physisorption)

Vacuum Level Alignment
= Schottky-Mott Limit



Band Structure: CNT



Single-Wall Carbon Nanotubes

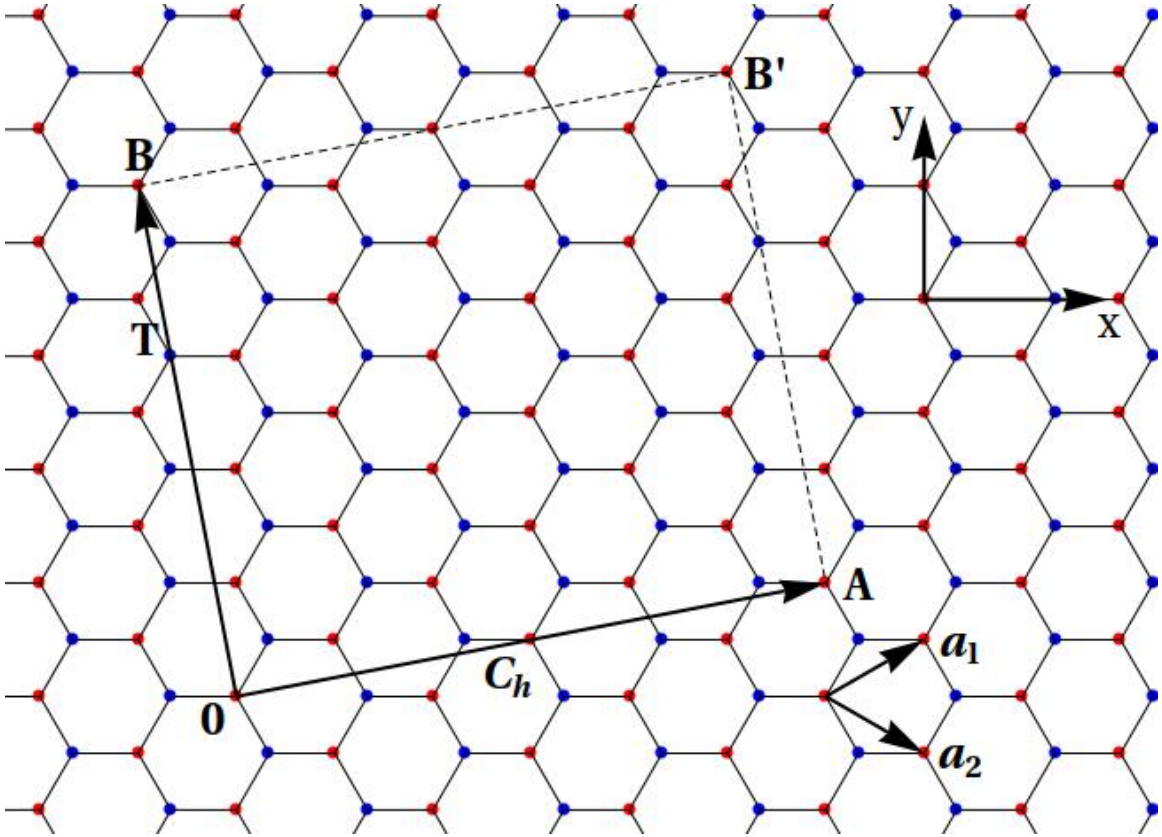
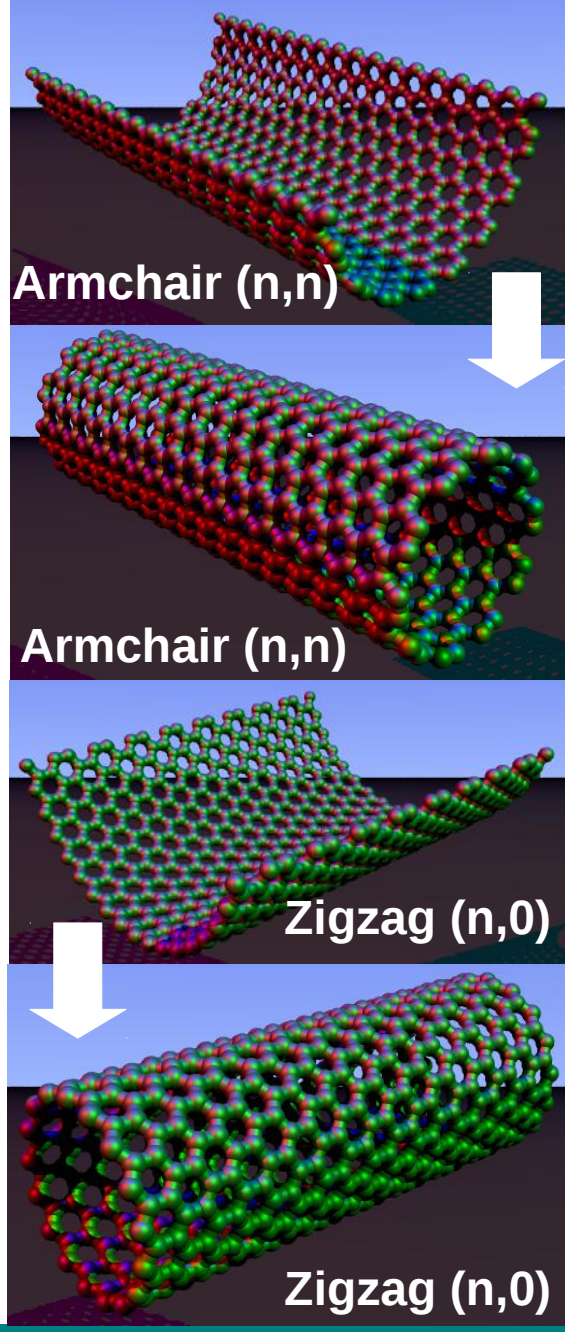
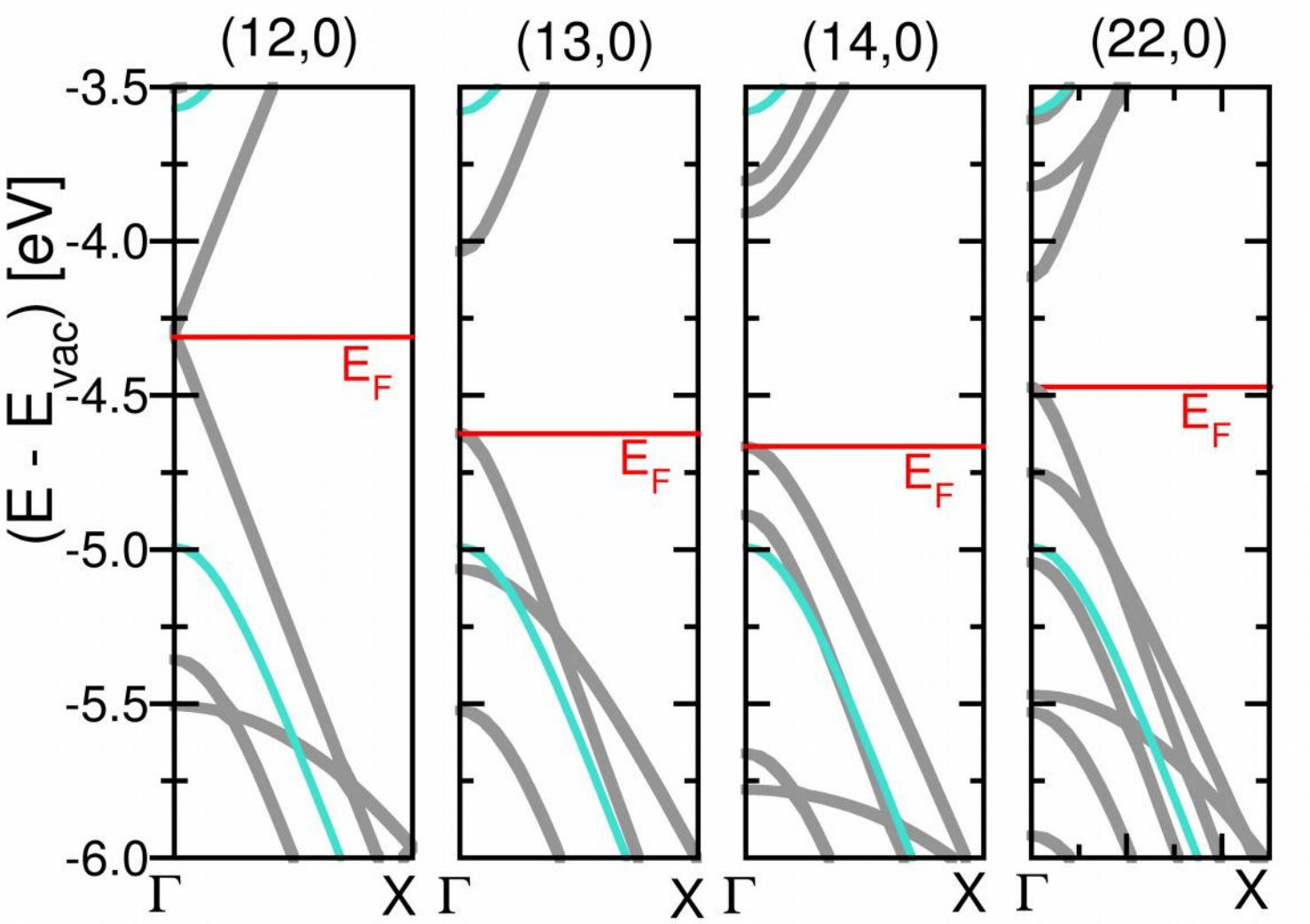
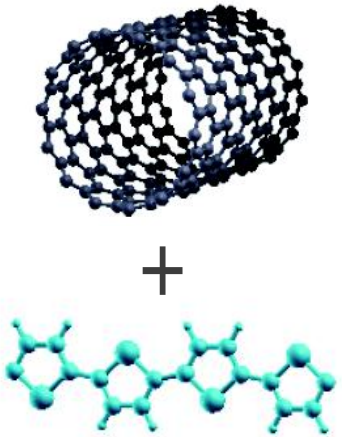


Figure 1: Aufrollen des Graphengitters zu einer Kohlenstoffnanoröhre (CNT). Das Rechteck $\mathbf{0AB'B}$ definiert die Einheitszelle der CNT, die durch Verbinden der Punkte $\mathbf{0}$ und $\mathbf{A}$ sowie $\mathbf{B}$ und $\mathbf{B'}$ entsteht. Der chirale Vektor $\mathbf{C}_h$ beschreibt dabei den Umfang der CNT, und der Vektor $\mathbf{T}$ definert den Translationsvektor entlang der CNT-Achse. Die in der Figur gezeichnete CNT entspricht $\mathbf{C}_h = (4, 2)$ und $\mathbf{T} = (4, -5)$.

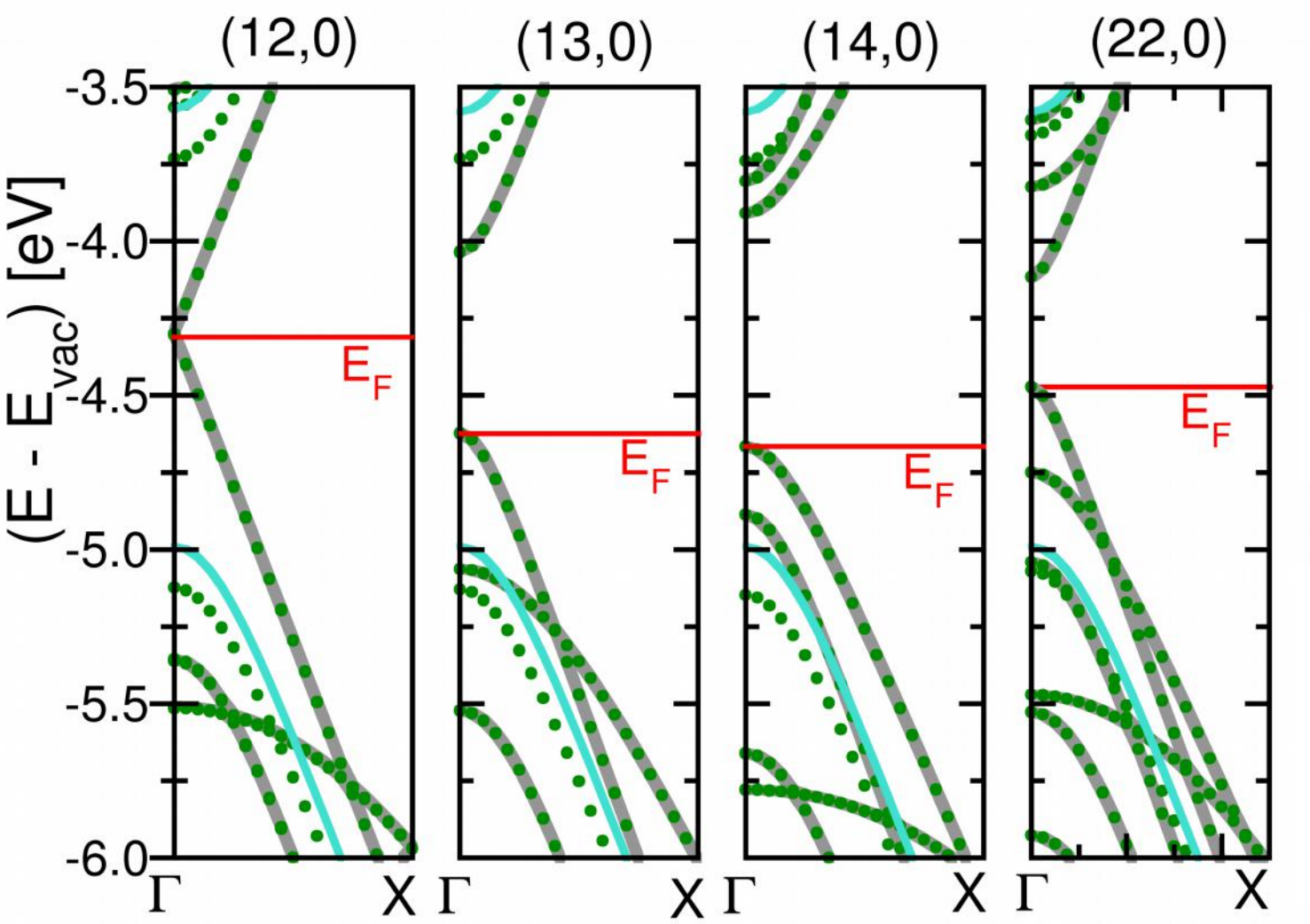


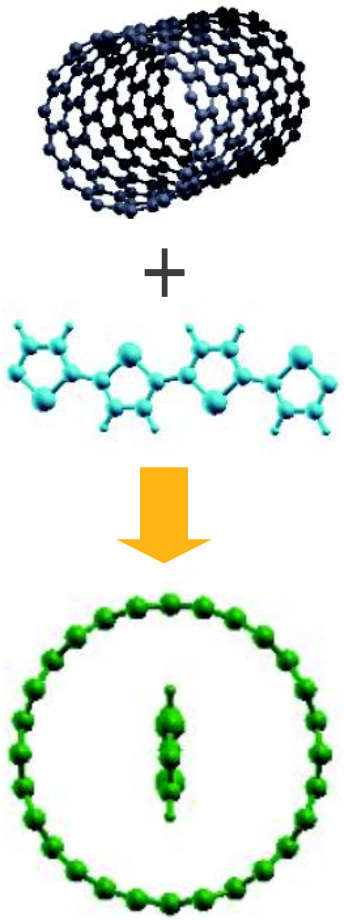
Band Structure: CNT + Polymer



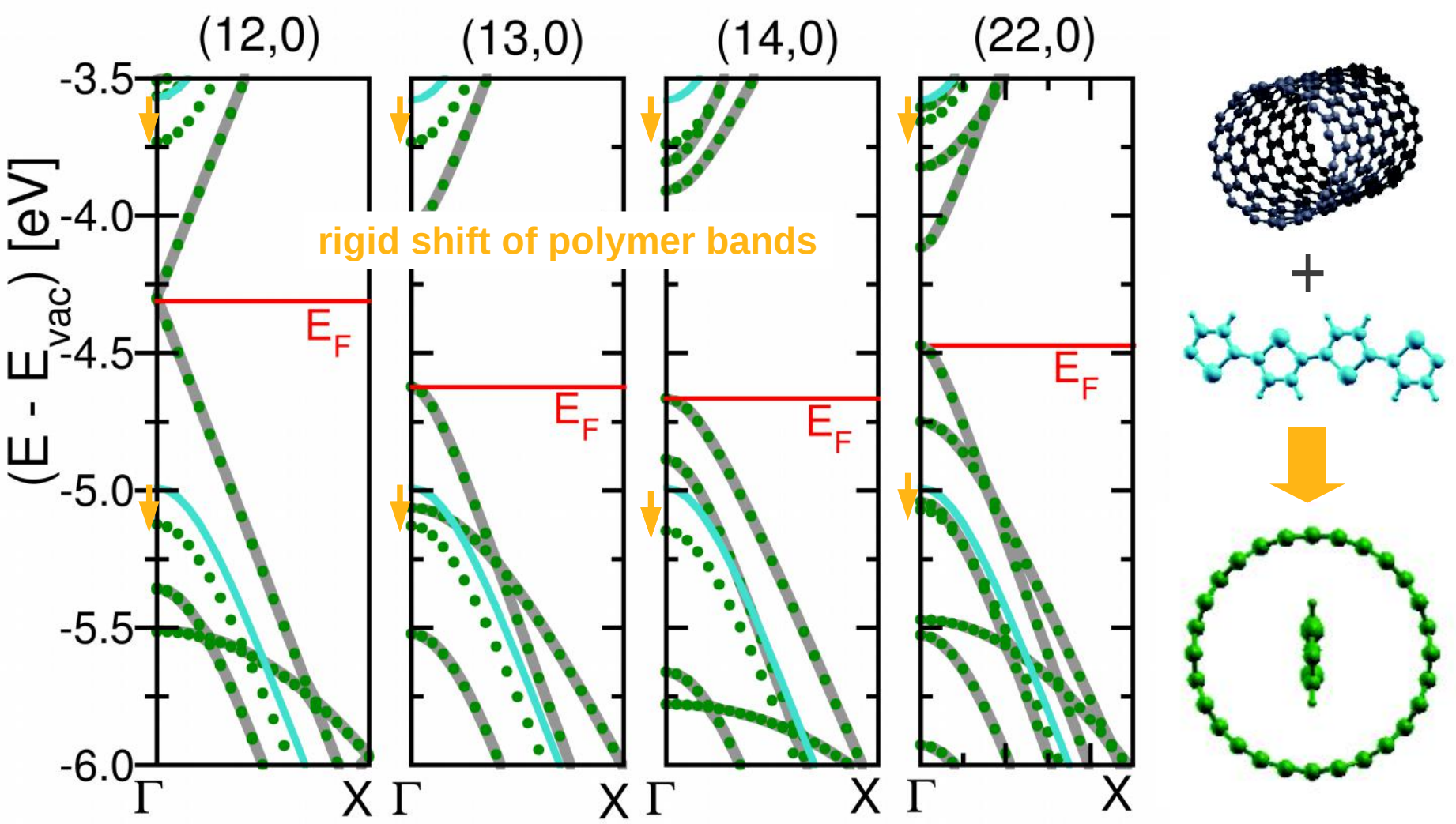


Band Structure: Peapod

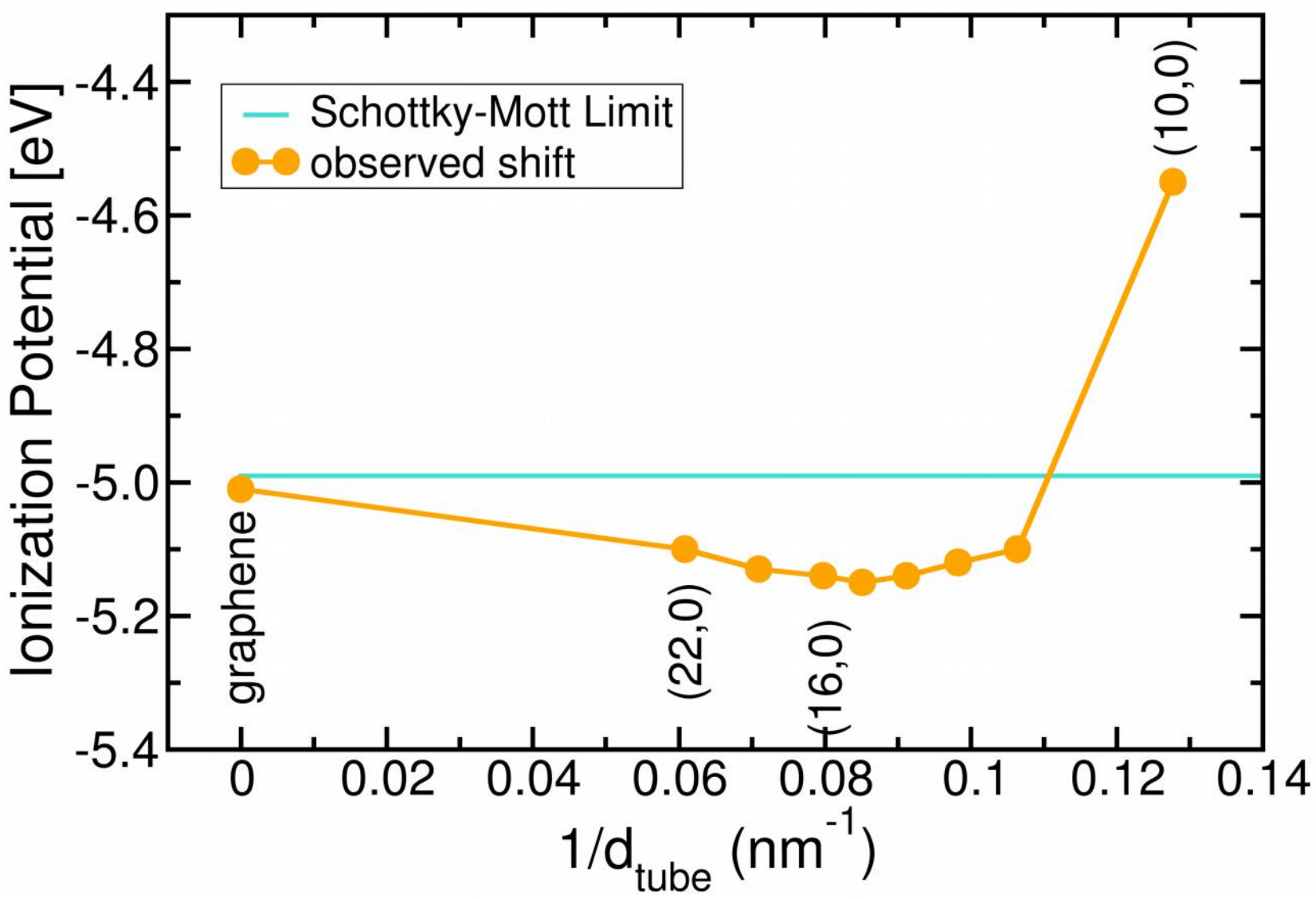




Band Structure: Level Alignment

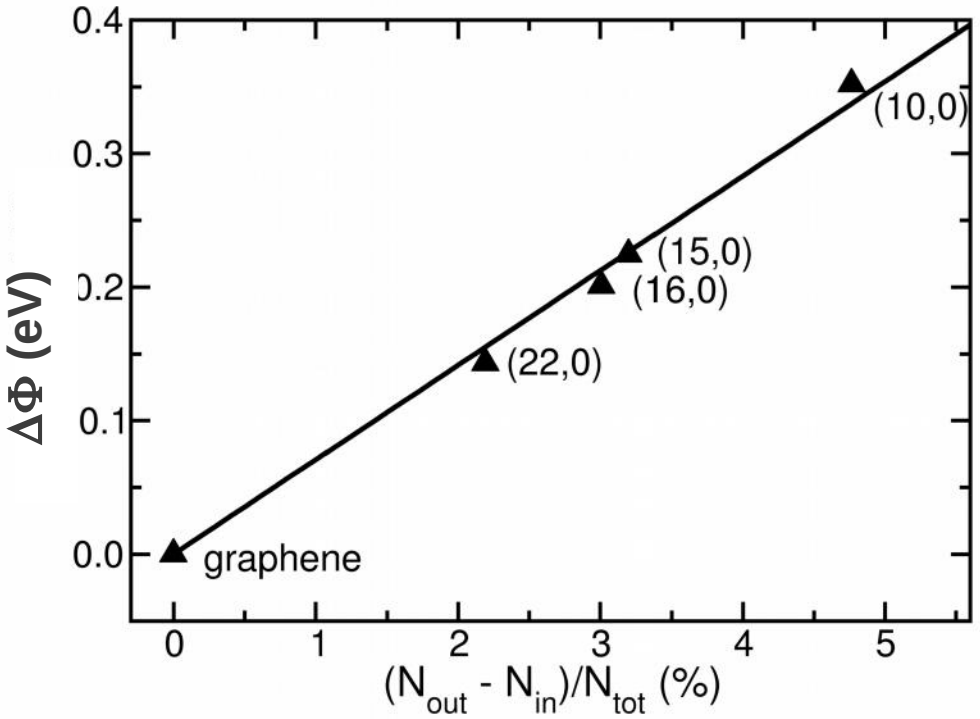


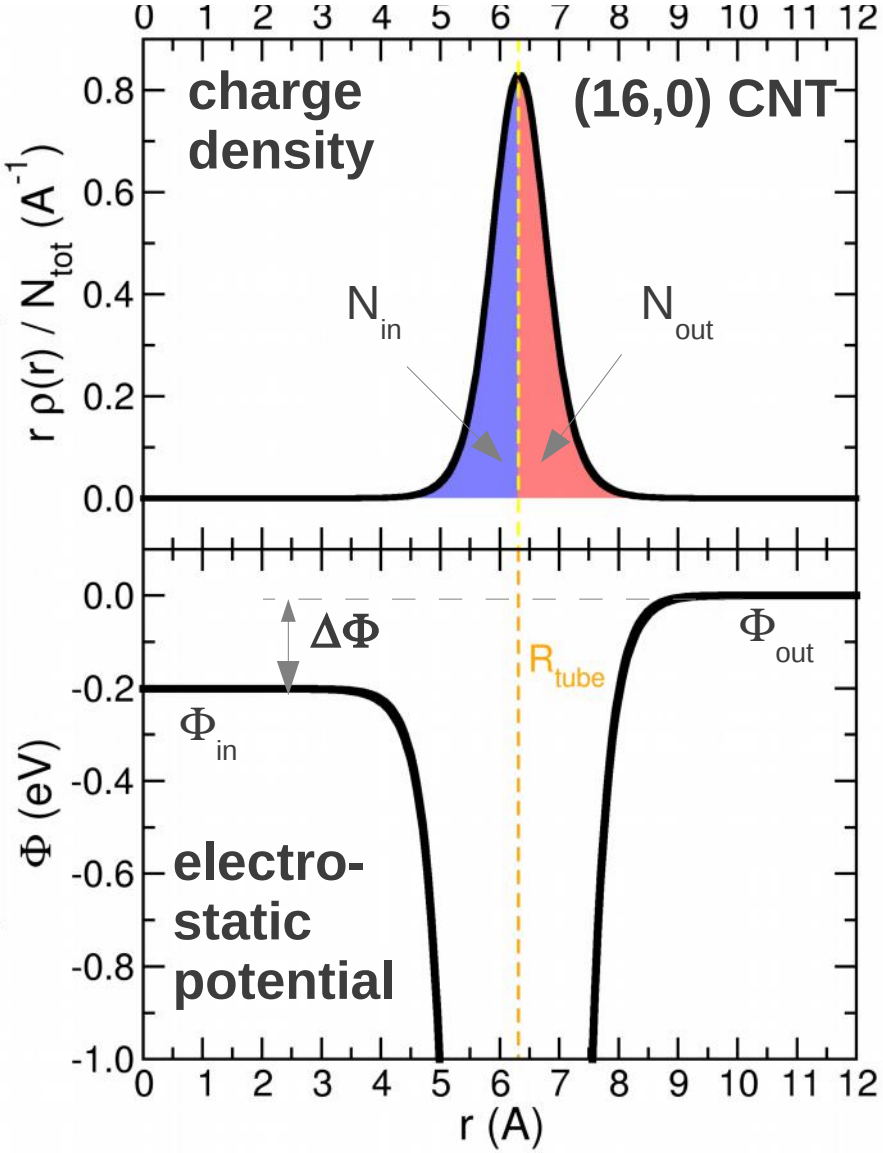
Ionization Potential of Polymer



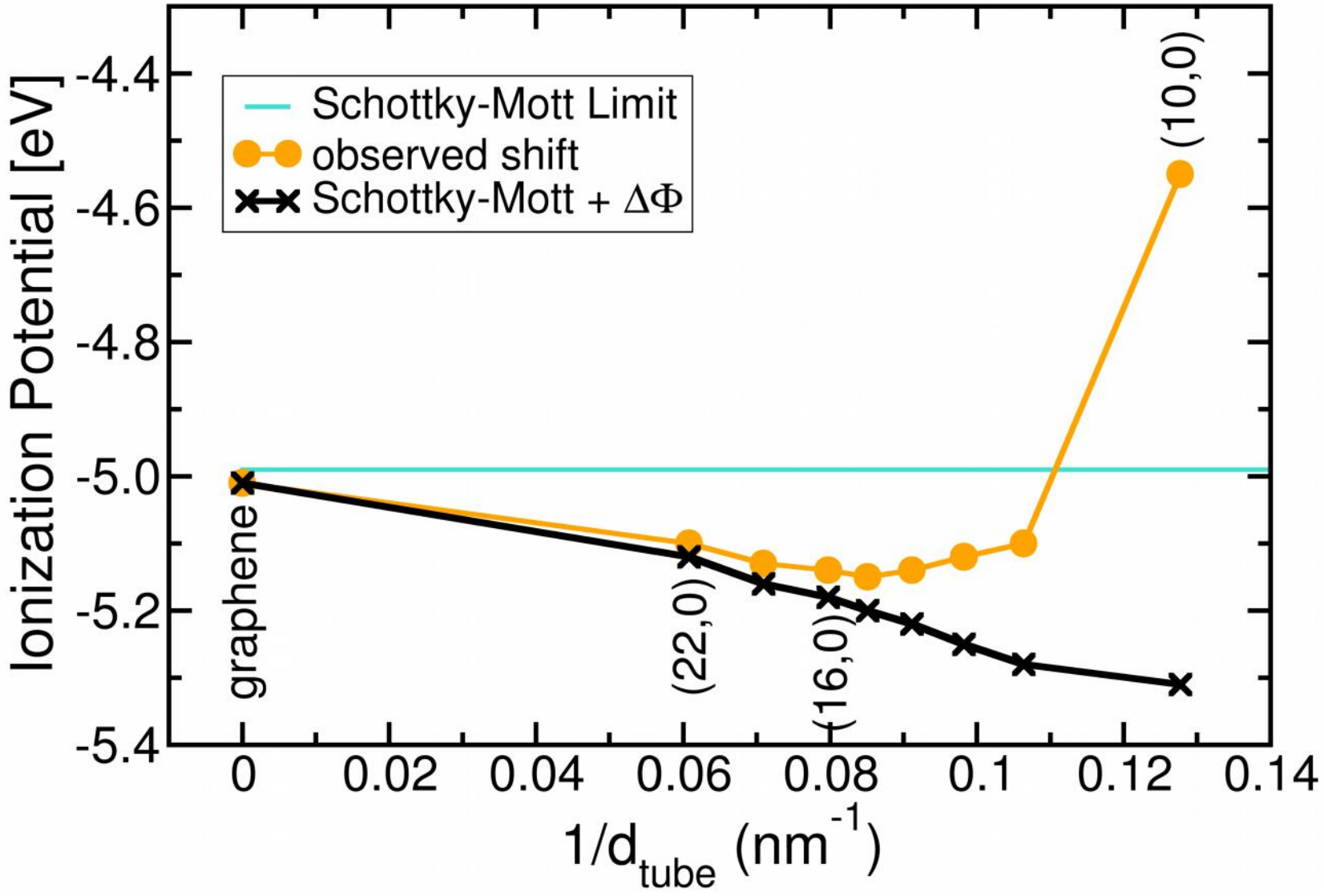
Ionization Potential of Polymer

1. Charge asymmetry in CNTs
→ ΔΦ





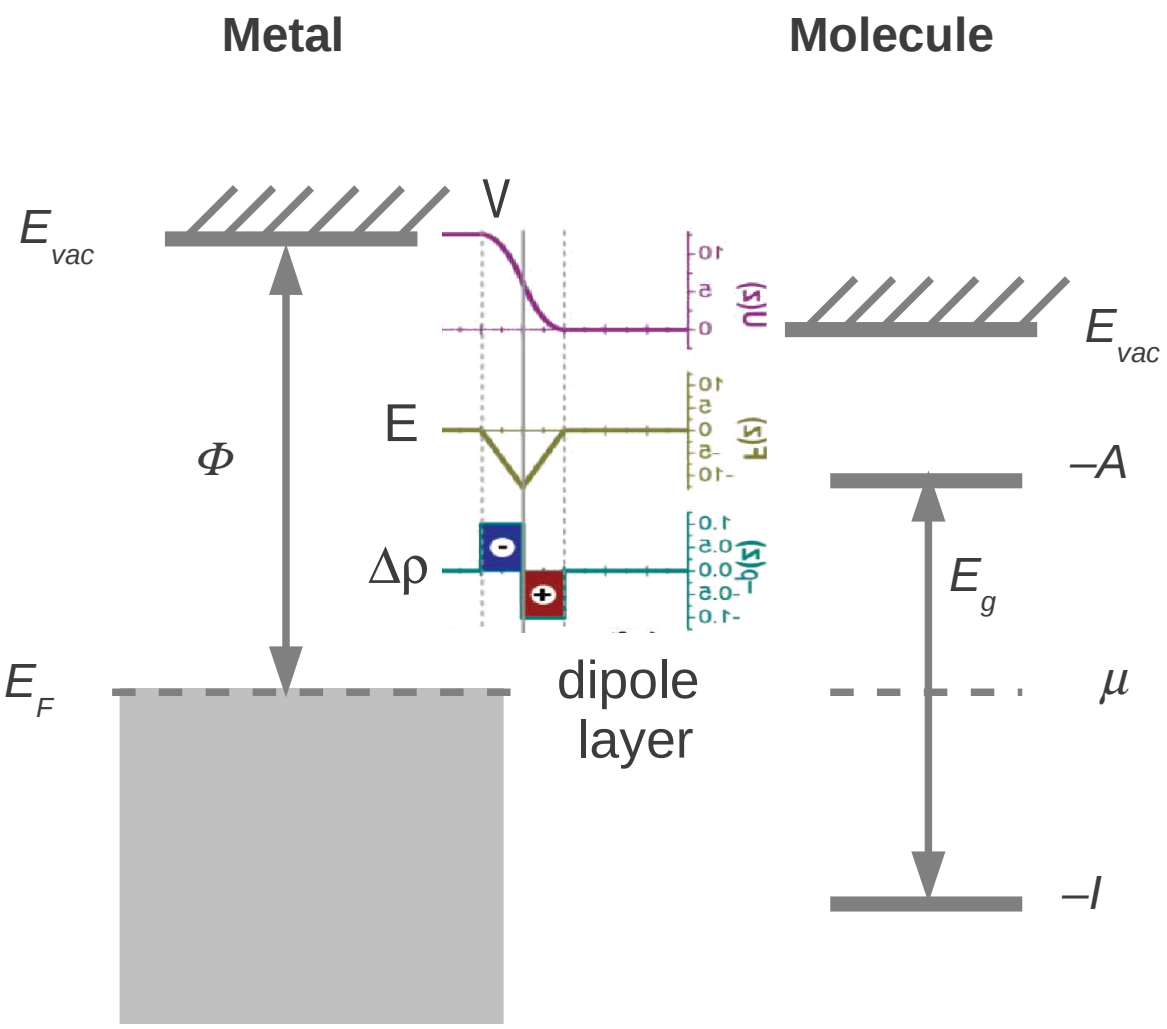
Level Alignment



Level Alignment

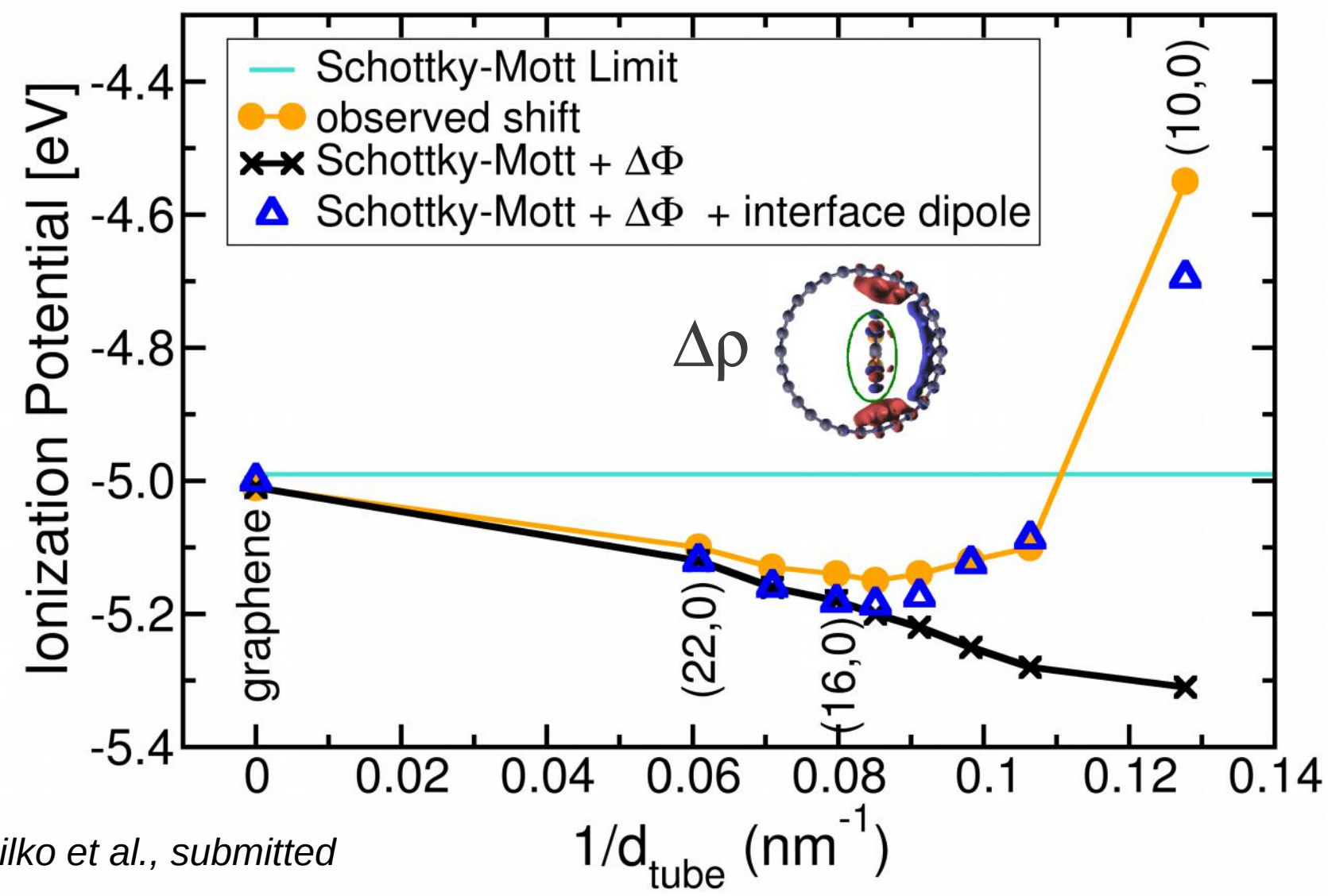
Weak interaction
(physisorption)

2. Interface dipole
(push-back effect)



See for instance: Heimel et al., *Acc. Chem. Res.* **41**, 721-729 (2008).

Level Alignment



Milko et al., submitted

Free Energy from Statistical Physics

$$H \rightarrow E_r(V,N) \rightarrow Z(T,V,N) \rightarrow F(T,V,N)$$

Microscopic Hamiltonoperator

$$H|\Psi\rangle = E_r|\Psi\rangle$$

Partition Function for canonical ensemble

$$Z(T,V,N) = \sum_r \exp\left[-\beta E_r(V,N)\right]$$

Free Energy

$$F(T,V,N) = -k_B T \ln\left[Z(T,V,N)\right]$$

Coarse-Graining Procedure

$$H|\Psi\rangle = E_r|\Psi\rangle$$

Should contain all electronic, magnetic, vibrational and configurational degrees of freedom!
Unfortunately, this is an extremely challengling – if not impossible – task :-(

But we can make use of different time-scales of excitations

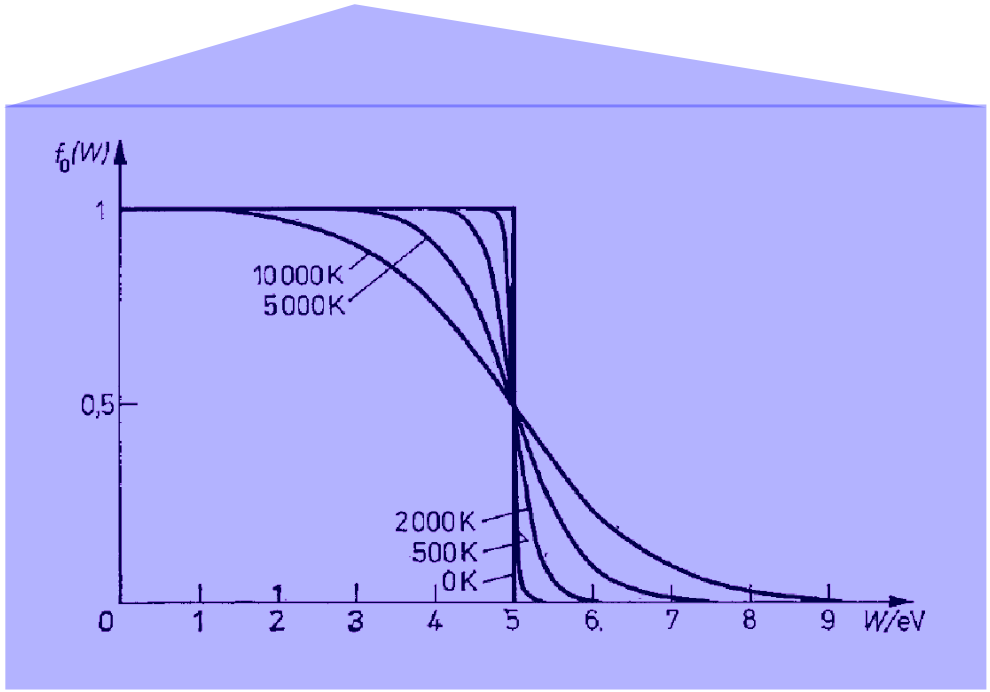
- Electronic : 10^{-15} sec
- Magnetic : 10^{-13} sec
- Vibrational : 10^{-12} sec
- Configurational : $>10^{-10}$ sec

→ **Can be calculated separately**

Entropy Contributions

$$F(T,V,N) = E_0(V,N) - TS$$

$$S_{el} + S_{mag} + S_{vib} + S_{conf}$$



Entropy Contributions

$$F(T,V,N) = E_0(V,N) - TS$$

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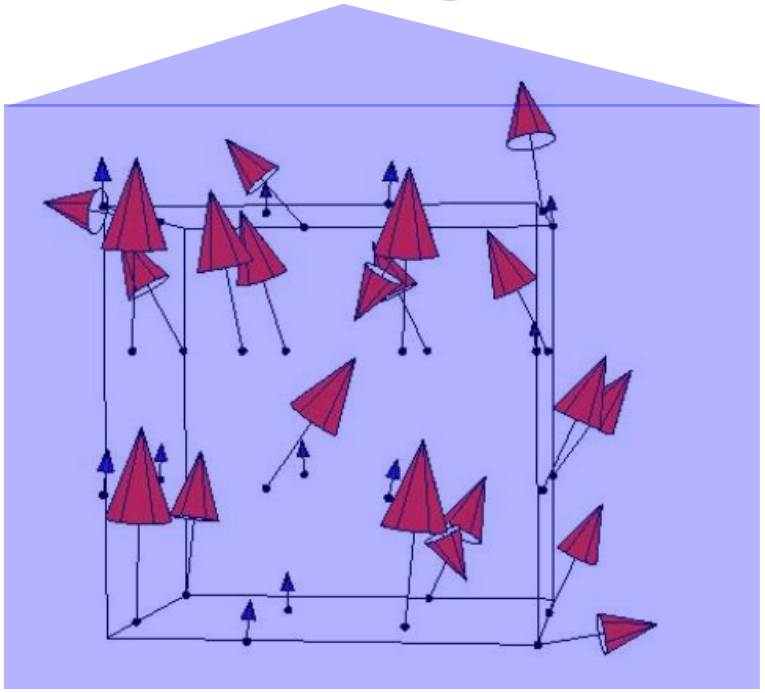

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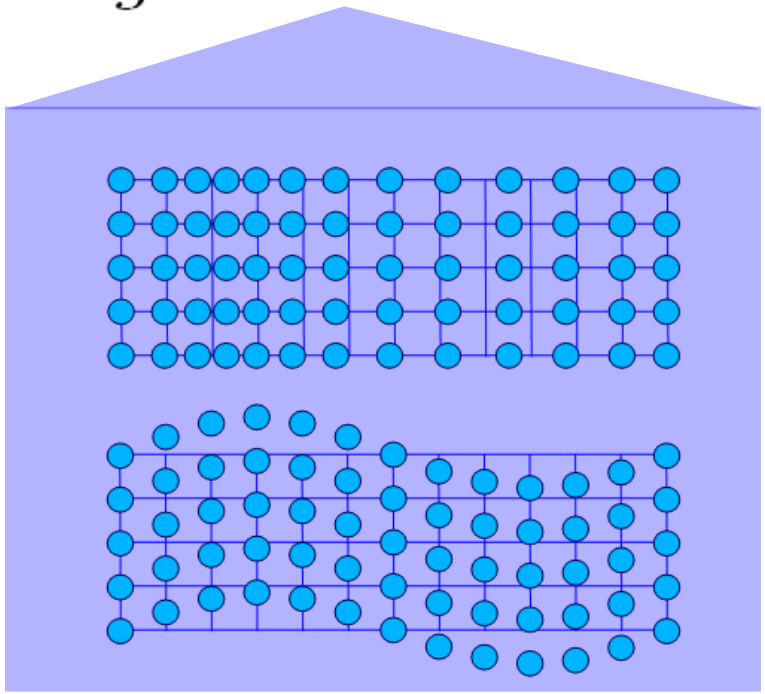

Entropy Contributions

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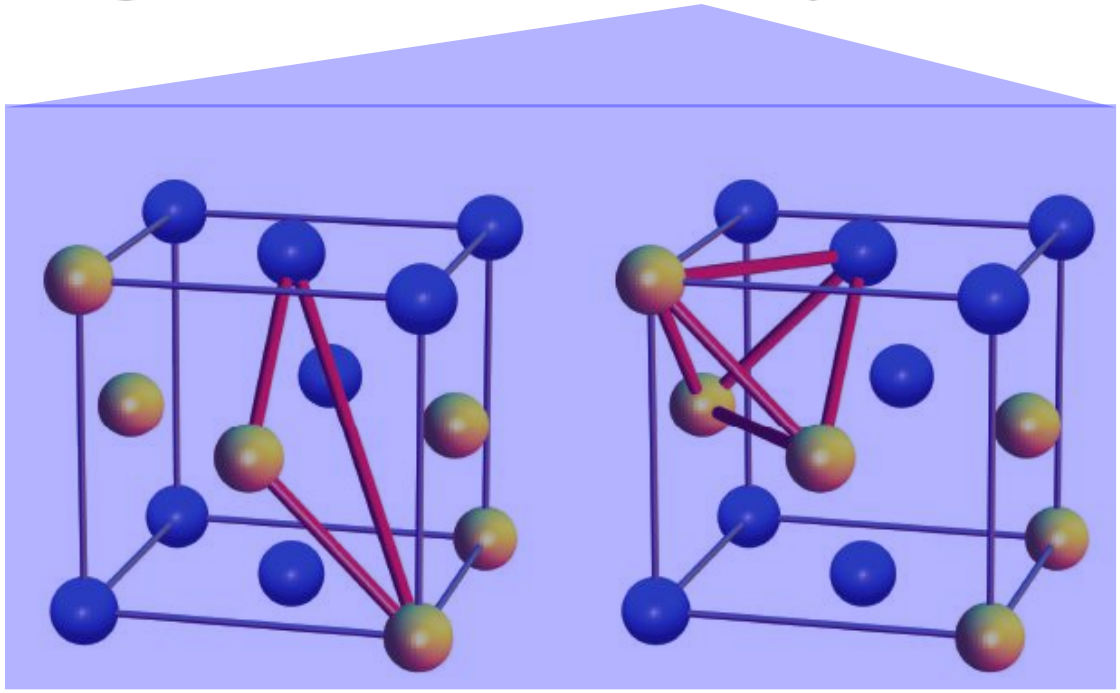


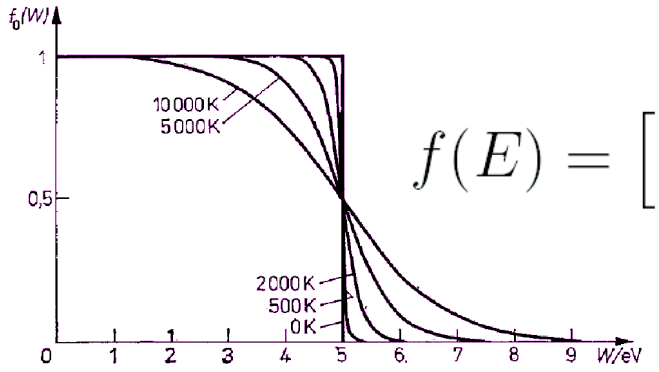
Electronic Entropy

Electronic entropy: easy to evaluate from DFT, but usually small contribution to the free energy

$$F^{\mathrm{el}} = E^{\mathrm{tot}}(T) - TS^{\mathrm{el}}$$

$$S_{el} = -\int dE N(E) \left[f(E) \ln f(E) + (1 - f(E)) \ln(1 - f(E)) \right]$$

Density of States (DOS)



$$f(E) = \left[1 + e^{\beta(E-\mu)} \right]^{-1}$$

Vibrational Entropy

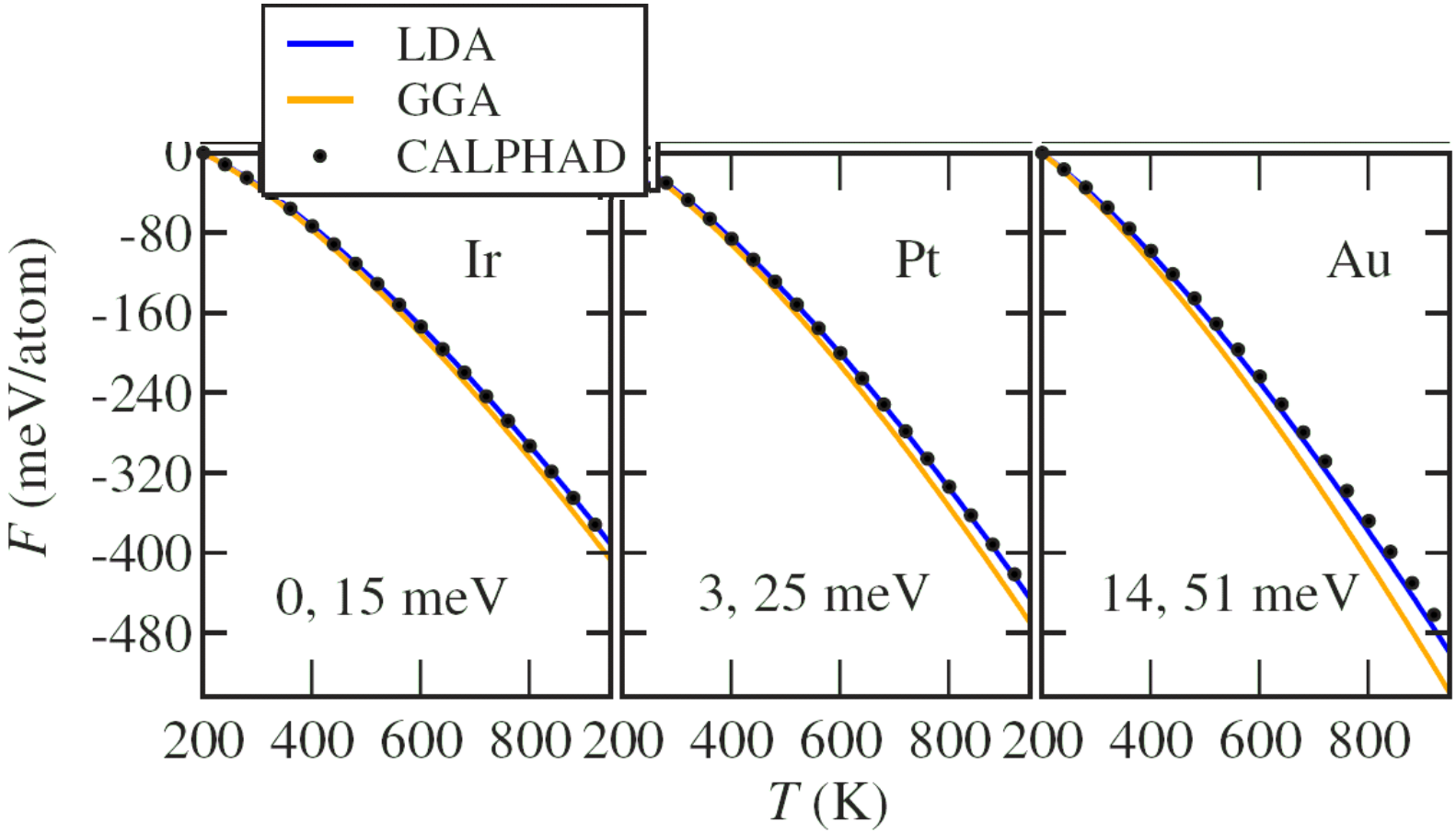
Vibrational entropy: Phonon density of states is required which is usually evaluated with the quasi-harmonic approximation. Important for thermal expansion and phase equilibria.

$$F^{\mathrm{vib}} = \frac{1}{N}\sum_{i}^{3N}\left\{\frac{1}{2}\hbar\omega_i + k_B T \ln\left[1 - \exp\left(-\frac{\hbar\omega_i}{k_B T}\right)\right]\right\}$$

sum over all degrees of freedom

phonon frequencies

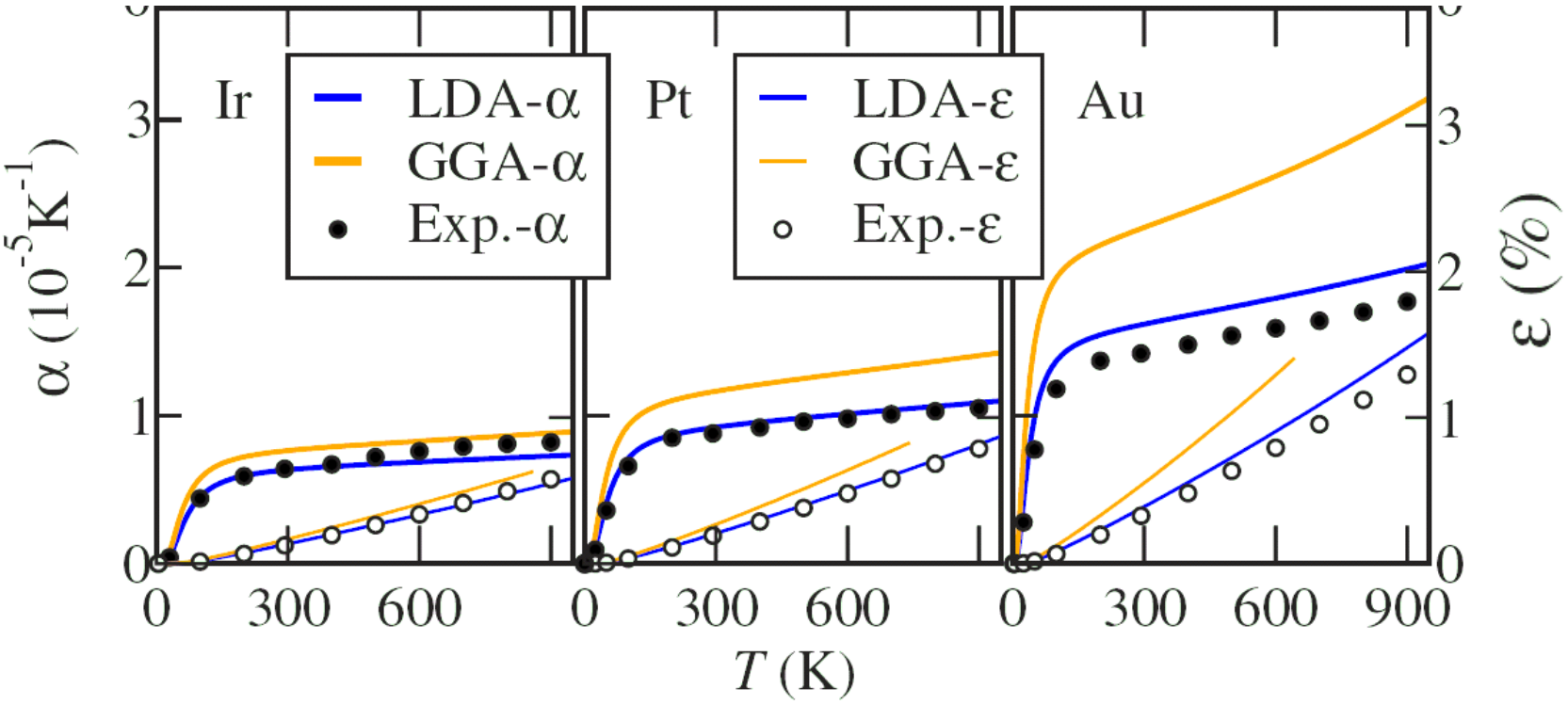
Free Energy



DFT-calculated free energy *F* for Ir, Pt, Au

Graphs are taken from Grabowski et al, *Phys. Rev. B* ***76****, 024309 (2007).*

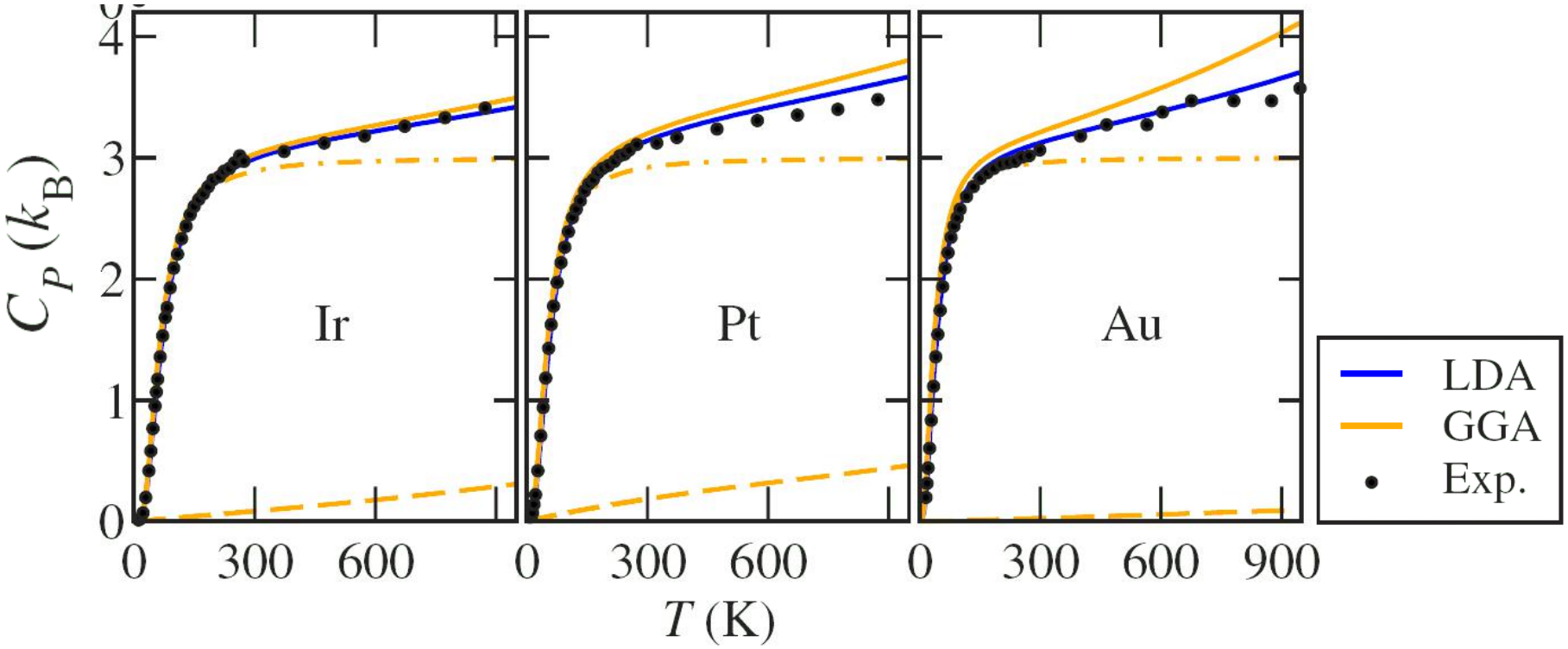
Thermal Expansion



DFT-calculated linear thermal expansion, e, and the thermal expansion coefficient, a, for Ir, Pt, Au

Graphs are taken from Grabowski et al, *Phys. Rev. B **76**, 024309 (2007).*

Heat Capacity



DFT-calculated specific heat capacity C_p for Ir, Pt, Au

Graphs are taken from Grabowski et al, *Phys. Rev. B* ***76****, 024309 (2007).*

What can go wrong?

I. Total Energy Related:

a) Typical error in equilibrium geometries: 2-5% (GGA) or 5-10% in LDA

b) No Van-der-Waals Bonding in LDA or GGA

II. Band Structure Related:

a) Band Gaps of Semiconductors / Insulators are too small (50 %)

b) Band width of localized states (e.g. d- or f-bands) too large in LDA / GGA

c) Wrong relative order of electronic states

d) LDA or GGA yield metallic state although real material is insulator

Van der Waals Forces

Van der Waals force is the sum of the attractive or repulsive forces between molecules other than those due to covalent bonds, the hydrogen bonds, or the electrostatic interaction of ions with one another or with neutral molecules. It includes:

(1) force between two permanent dipoles (ok in LDA/GGA)

(2) force between a permanent dipole and a corresponding induced dipole (ok in LDA/GGA)

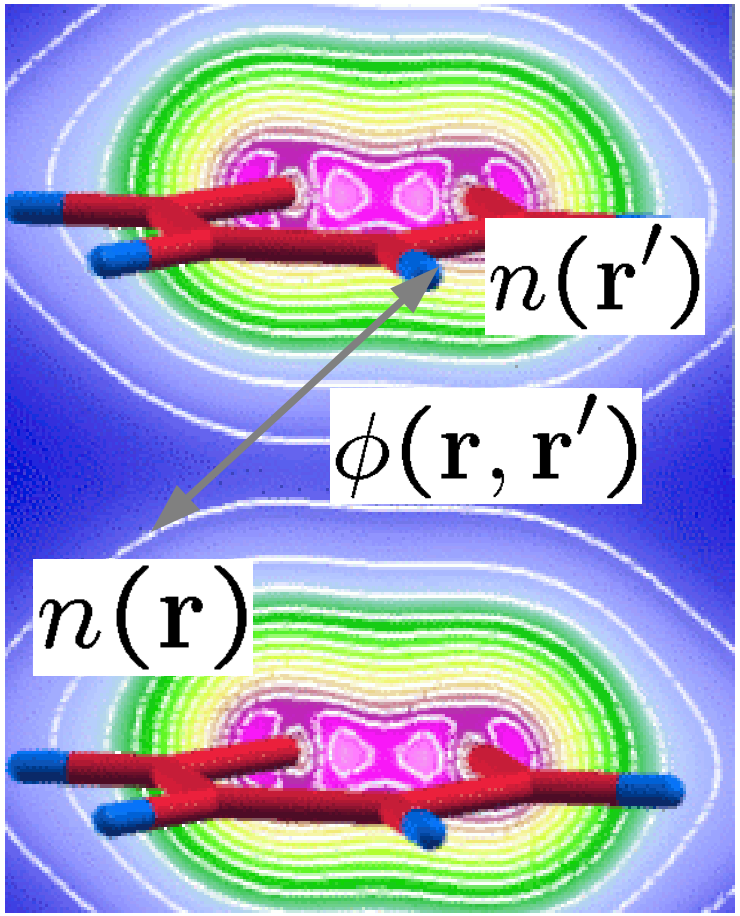
(3) force between two instantaneously induced dipoles (London dispersion force)

It is also sometimes used loosely as a synonym for the totality of intermolecular forces. Van der Waals forces are relatively weak compared to covalent bonds, but play a fundamental role in fields as diverse as supramolecular chemistry, structural biology, polymer science, nanotechnology, surface science, and condensed matter physics.

How Geckos Stick on der Waals:
http://news.sciencemag.org/sciencenow/2002/08/27-02.html

Non-overlapping densities:

Dispersion forces arise from a truly non-local correlation effect



Van-der-Waals Density Functional

Total energy in DFT:

$$E[n] = T_s[n] + V_{ee}[n] + V_{ion}[n] + E_{xc}[n]$$

Exchange-Correlation in vdW-DF according to Langreth-Lundqvist (Phys. Rev. Lett. 92, 246401 (2004).

Exchange in GGA

$$E_{xc}[n] = E_x^{GGA}[n] + E_c^{new}[n]$$

Correlation split into local and non-local part (nl)

$$E_c[n] = E_c^{o}[n] + E_c^{nl}[n]$$

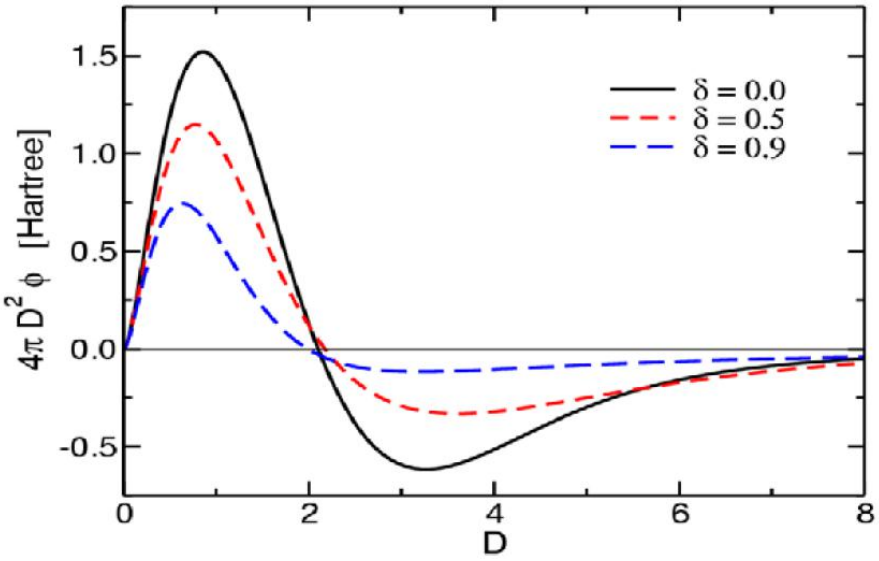
Non-Local Correlation Energy:

$$E_c^{nl} = \frac{1}{2}\int d^3r \int d^3r'\, n(\boldsymbol{r})\Phi(\boldsymbol{r},\boldsymbol{r}')n(\boldsymbol{r}')$$

where $\Phi(\boldsymbol{r},\boldsymbol{r}') = \Phi(q(\boldsymbol{r}), q(\boldsymbol{r}'))$. The interaction kernel depends on the density and its gradient, $q(\boldsymbol{r}) = q(n(\boldsymbol{r}), \nabla n(\boldsymbol{r}))$, and can be given a scalable form via

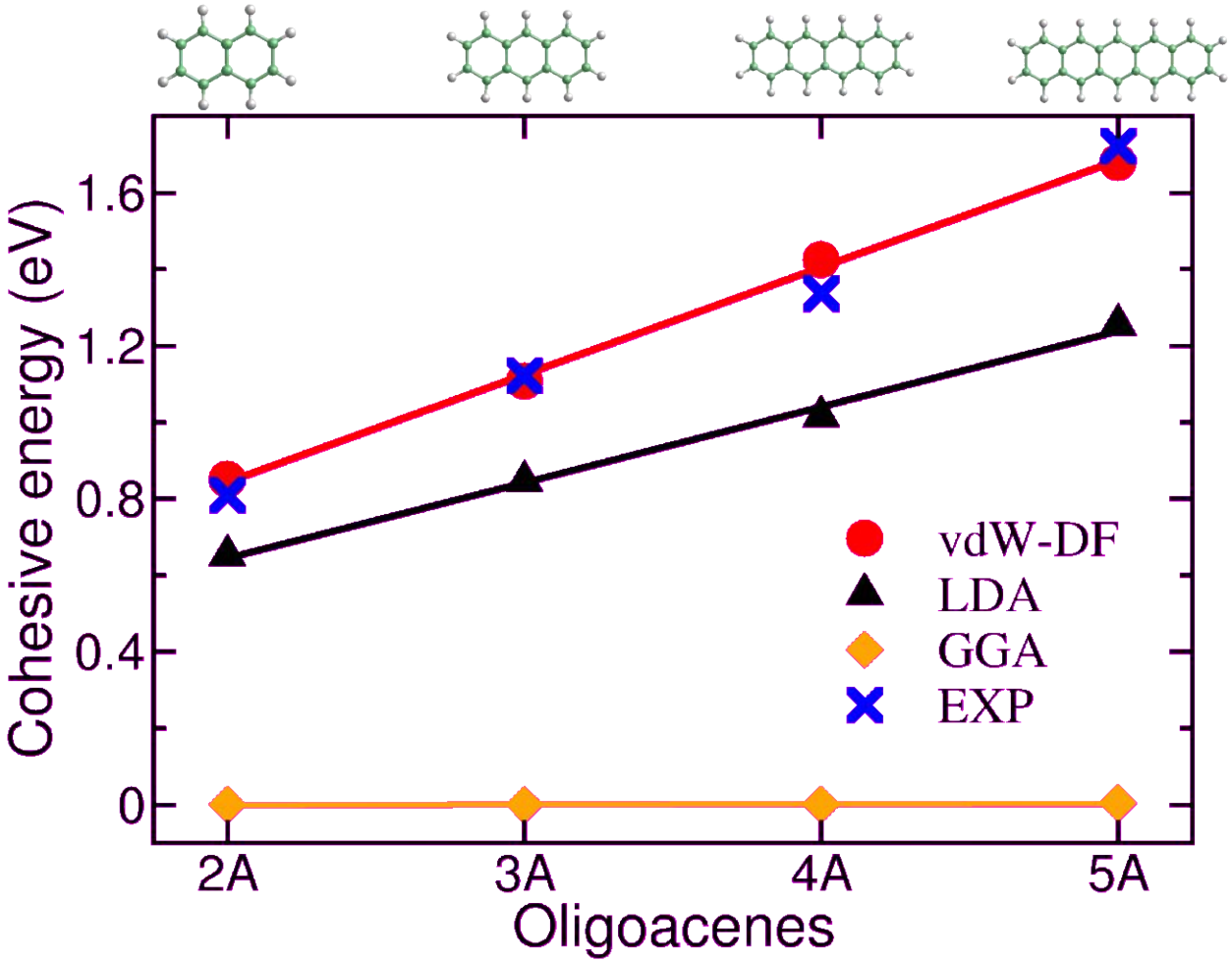
$$D = \frac{q+q'}{2}|\boldsymbol{r}-\boldsymbol{r}'|, \qquad \delta = \frac{1}{2}\frac{q-q'}{q+q'},$$

$$q = q(\boldsymbol{r}), \qquad q' = q(\boldsymbol{r}').$$



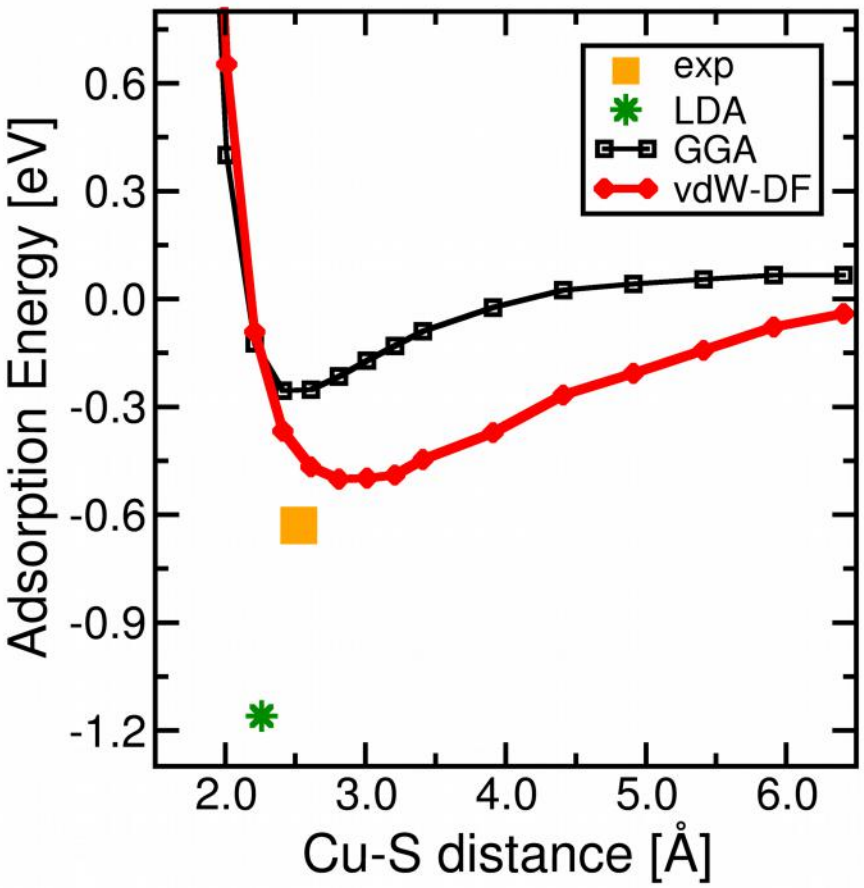
Langreth et al., A density functional for sparse matter J. Phys.: Condens. Matte 21, 084203 (2009).

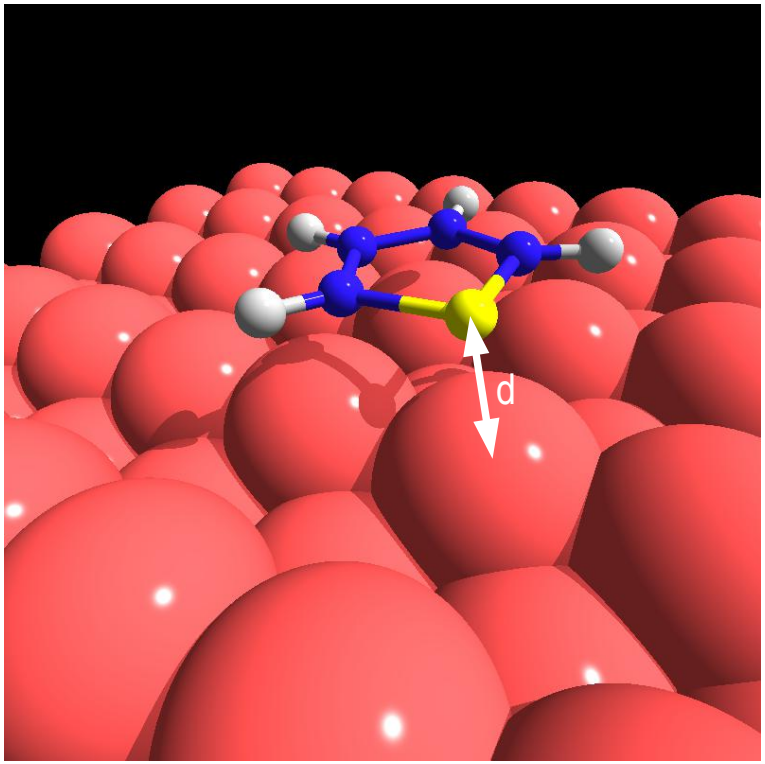
Cohesive Energy of Molecular Crystals



Nabok, Puschnig, Ambrosch-Draxl, *Phys. Rev. B* ***77****, 245316 (2008).*

Thiophene Molecule / Cu(110)





Thiophene@Cu(110): Sony, Puschnig, Nabok, Ambrosch-Draxl, *Phys. Rev. Lett.* ***99****, 176401 (2007).*

PTCDA@Cu,Ag,Au(111): Romaner et al., New. J. Phys. ***11****, 053010 (2009).*

Alternative Approaches

Ab-initio vdW-Density Functional

Theory

Dion et al, *Phys. Rev. Lett.* ***92****, 246401 (2004).*
Thonhauser *et al., Phys. Rev. B,* ***76****, 125112 (2007)*
Vydrov *et al., Phys. Rev. Lett.,* ***103****, 063004 (2009)*
Lee *et al. Phys. Rev. B* ***82****, 081101 (2010)*

Efficient Implementations

Roman-Perez *et al. Phys. Rev. Lett.* ***103****, 096102 (2009).*
Vydrov *et al., J. Chem. Phys.* ***132****, 164113 (2010).*
Lazic *et al. Comp. Phys. Commun.* ***181****, 371 – 379 (2010).*
Nabok *et al. Comp. Phys. Commun.* ***182****, 1657-1662 (2011).*

Applications

… huge number …

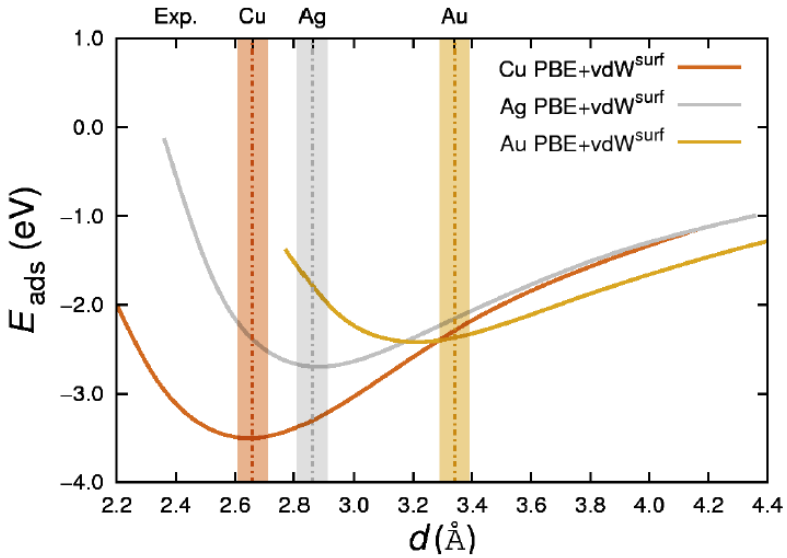
Brief Review see e.g.:
Langreth *et al., J. Phys.: CM* ***21****, 084203 (2009)*

Semi-Empirical Correction

Grimme, *J. Comput. Chem.,* ***25****, 1463 (2004).*
Grimme, *J. Comput. Chem.,* ***27****, 1787 (2006).*
Tkatchenko *et al. PRL* ***102****, 073005 (2009).*

Ruiz *et al. PRL* ***108****, 146103 (2012):*

PTCDA / Coinage-Metal(111)-Surfaces



Alternative Approaches

Adiabatic Connection Fluctuation-Dissipation (ACFD)

Theory