Survey of Materials. Lecture 3

Electronic structure of materials

Andriy Zhugayevych

October 4, 2021

Outline

- Quantum mechanics and Schrodinger equation
- Electronic structure of materials
- Examples
- Complex bonding: hypervalent, secondary bonding, *d*-orbitals
- Atomic motions, vibrations, phonons
- Electron-phonon interaction, Jahn–Teller effect
- Electronic properties

Some slides of this lecture might require solid knowledge of quantum mechanics

Why do we need to know Quantum Mechanics

- mechanical
- thermal
- at macroscale

- electronic
- chemical
- anything at nanoscale

!!! In contrast to classical mechanics, many things are not intuitive in quantum world — if in doubt refer to solution of Schrodinger equation

Pragmatic approach to Quantum Mechanics

Let's start with a single particle

Particle position $\boldsymbol{r}(t) \rightarrow$ probability distribution $|\psi(\boldsymbol{r}, t)|^2$, where the wave-function ψ is the solution of Schrodinger equation:

$$\mathrm{i}\hbar\frac{\partial\psi}{\partial t} = \mathsf{H}\psi \equiv -\frac{\hbar^2}{2m}\Delta\psi + U(\boldsymbol{r}, t)\psi$$

Any observable can be calculated as follows:

$$A = \langle\psi|\mathsf{A}|\psi\rangle \equiv \int \overline{\psi(\boldsymbol{r}, t)}\,(\mathsf{A}\psi)\,(\boldsymbol{r}, t)\,\mathrm{d}V$$

For example, average position:

$$\bar{\boldsymbol{r}}(t) = \int \boldsymbol{r}|\psi(\boldsymbol{r}, t)|^2\,\mathrm{d}V$$

Example: particle in uniform field

Initial conditions (a particle at $\boldsymbol{r}_0$ with velocity $\hbar\boldsymbol{k}/m$):

$$\psi(\boldsymbol{r}, 0) = C \exp\left[\mathrm{i}\boldsymbol{k}\boldsymbol{r} - \frac{(\boldsymbol{r} - \boldsymbol{r}_0)^2}{a^2}\right]$$

If $U(\boldsymbol{r}, t) = -\boldsymbol{F}\boldsymbol{r}$ then

$$\psi(\boldsymbol{r}, t) \sim \exp\left[\mathrm{i}\left(\boldsymbol{k} + \frac{\boldsymbol{F}t}{\hbar}\right)\boldsymbol{r} - \frac{\left(\boldsymbol{r} - \boldsymbol{r}_0 - \frac{\hbar\boldsymbol{k}t}{m} - \frac{\boldsymbol{F}t^2}{2m}\right)^2}{a^2 + \mathrm{i}\frac{2\hbar t}{m}}\right]$$

$\Longrightarrow$ classical dynamics + gaussian broadening

Stationary Schrodinger equation

If the Hamiltonian is time-independent then the evolution can be written explicitly:

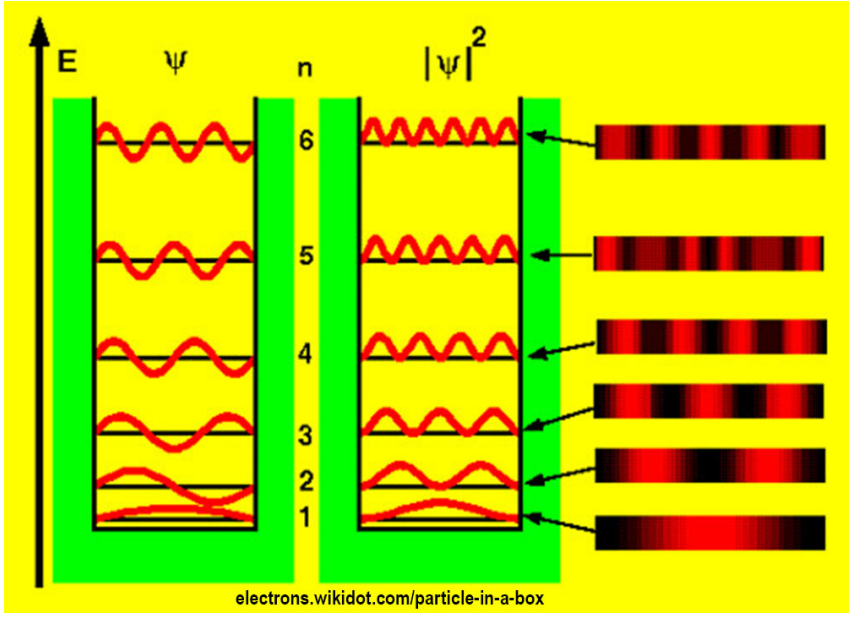
$$\psi(t) = \sum_n c_n \psi_n \mathrm{e}^{-\mathrm{i}\frac{E_n}{\hbar}t}, \quad c_n = \langle \psi_n | \psi(0) \rangle,$$

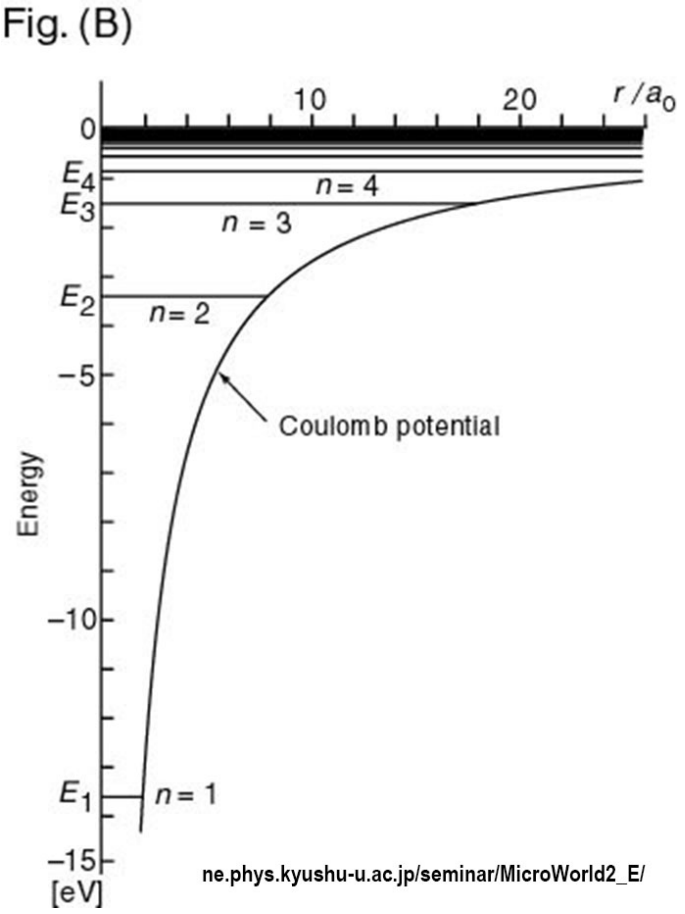
here (E_n, ψ_n) are eigenvalues and eigenfunctions of the stationary Schrodinger equation:

$$\mathrm{H}\psi = E\psi$$

Quantum effects: quantization

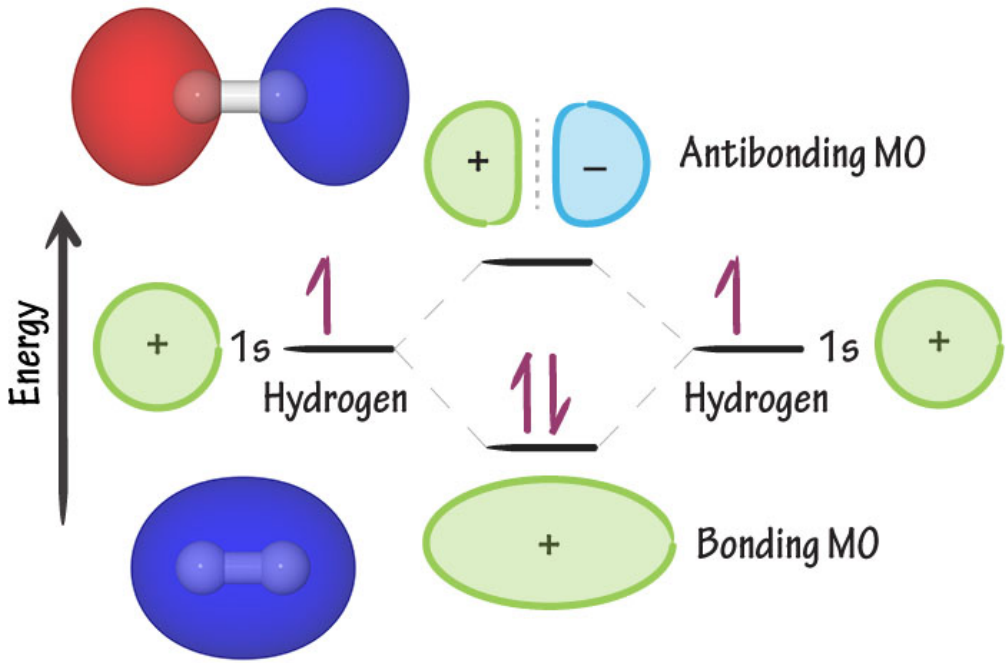
(Materials Science examples)





Quantum effects: interference

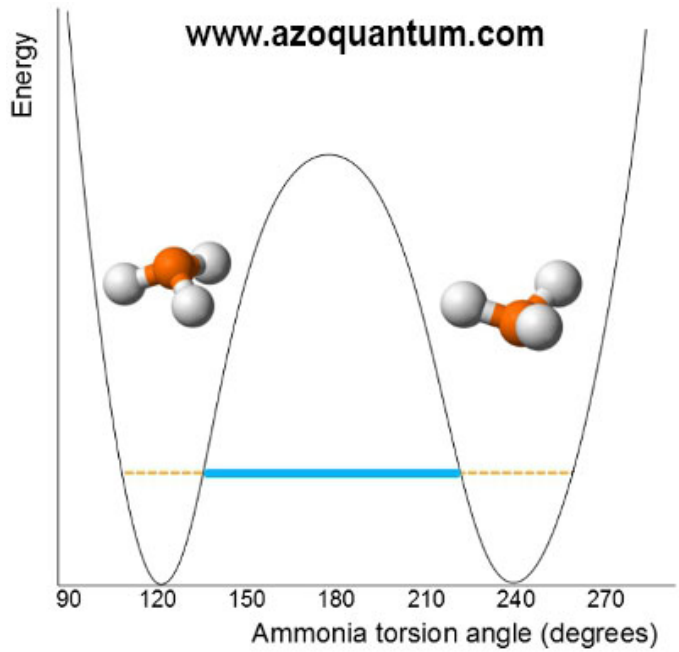
(Materials Science examples)



Quantum effects: tunneling

(Materials Science examples)

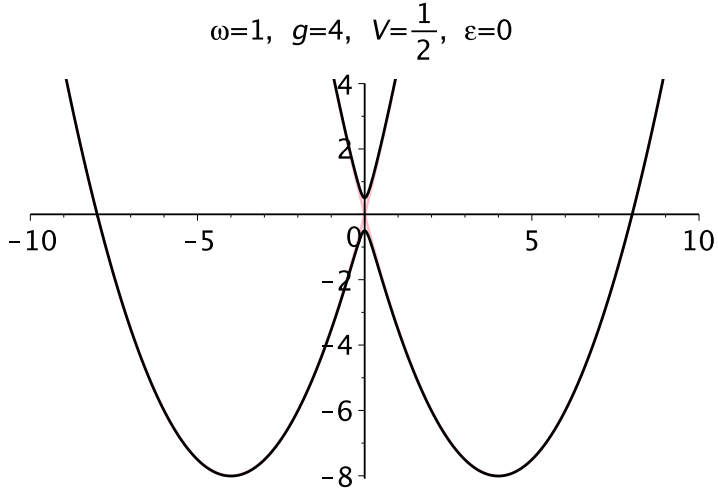
- Electron and energy transfer
- Some molecular motions

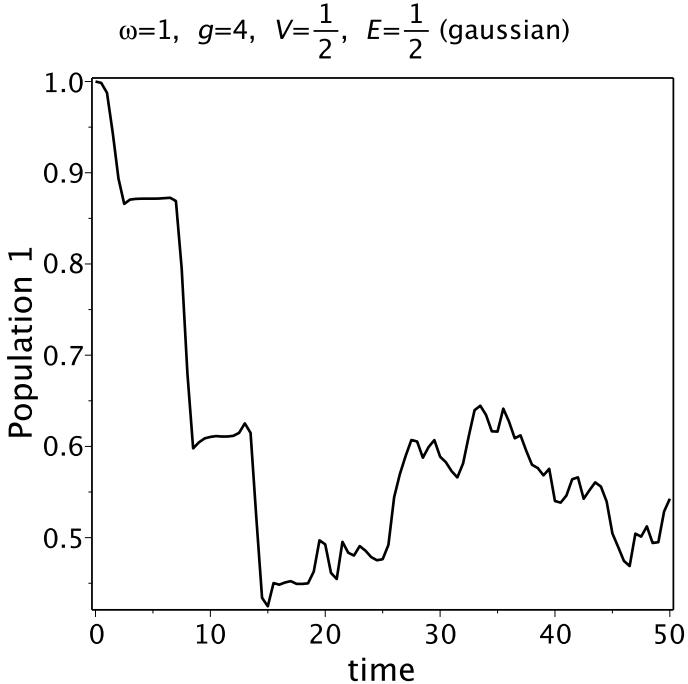


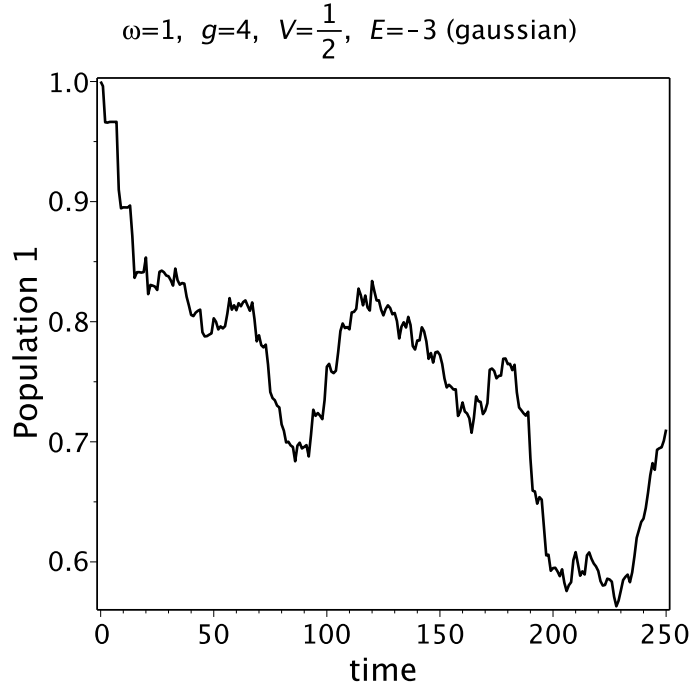
Example: simple model of electron transfer

Two-site Holstein model:

$$H = \begin{pmatrix} \tilde{g}x & V \\ V & -\tilde{g}x \end{pmatrix} + \frac{M\dot{x}^2}{2} + \frac{kx^2}{2}$$







Evolution: real space and coefficients

Minimal list of quantum models to be familiar with

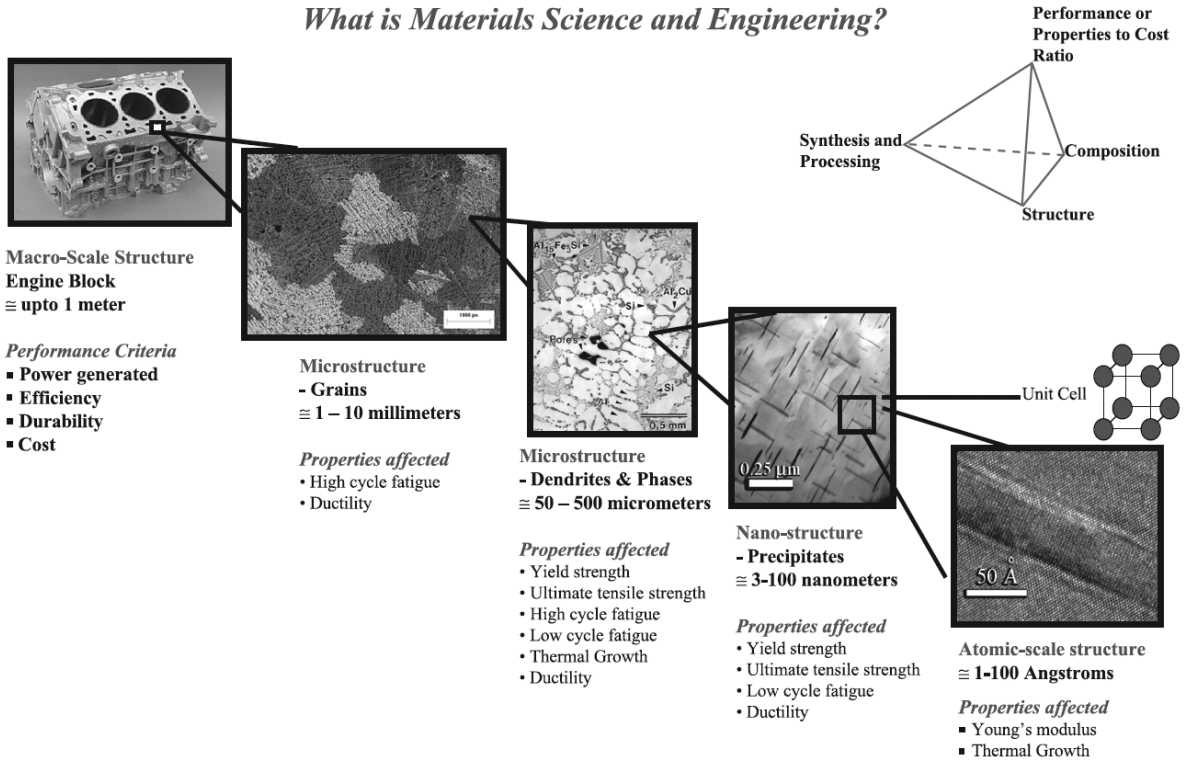
potential	ψ_n	E_n	quant.numbers
free particle	$\mathrm{e}^{\mathrm{i}\boldsymbol{kr}}$	$\frac{\hbar^2 k^2}{2m}$	$\boldsymbol{k} \in \mathbb{R}^3$
potential box	$\sin \frac{\pi n x}{a}$	$\frac{\pi^2 \hbar^2 n^2}{2ma^2}$	$n = \overline{1, \infty}$
oscillator	$H_n(\xi)\mathrm{e}^{-\xi^2/2}$	$\hbar\omega\left(n + \frac{1}{2}\right)$	$n = \overline{0, \infty}$
Coulomb	$r^l L^{2l+1}_{n-l-1}\left(\frac{2r}{n}\right)\mathrm{e}^{-\frac{r}{n}} Y_{lm}(\theta, \phi)$	$-\frac{\alpha}{2an^2}$	$\lvert m\rvert \leqslant l < n \in \mathbb{N}$

Let's discuss:

1. Degeneracy, nodal structure, discrete/continuum, selection rules
2. How these models are used in materials science
3. Spin: $(S/\hbar)^2 = s(s+1)$, $S_z/\hbar = \overline{-s, s}$; fermion/boson

Electronic structure of materials

Remember the scale problem



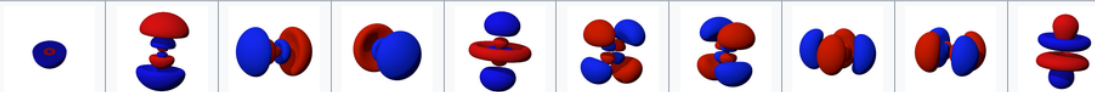
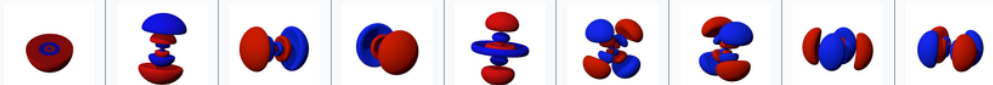
A real-world example of important microstructural features at different length-scales, resulting from the sophisticated synthesis and processing used, and the properties they influence. The atomic, nano, micro, and macro-scale structures of cast aluminum alloys (for engine blocks) in relation to the properties affected and performance are shown. The materials science and engineering (MSE) tetrahedron that represents this approach is shown in the upper right corner.

(Illustrations Courtesy of John Allison and William Donlon, Ford Motor Company)

There is a lot of approximations and special approaches to describe quantum world of 10^{23} particles

Practical considerations: basis set

Plane waves or atomic orbitals (AO)

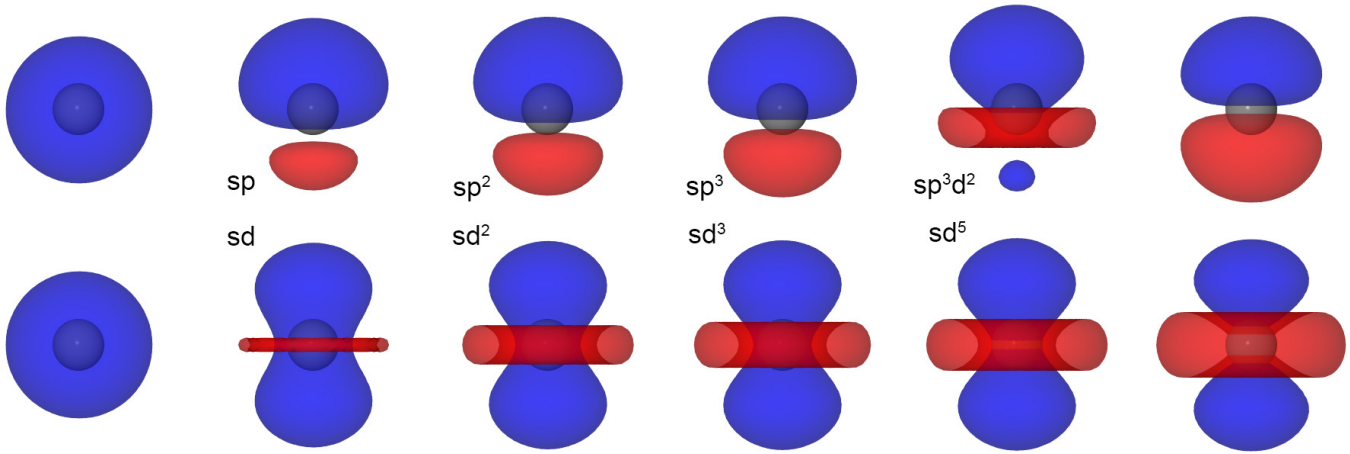
	s ($\ell = 0$)	p ($\ell = 1$)			d ($\ell = 2$)					f ($\ell = 3$)						
	$m = 0$	$m = 0$	$m = \pm 1$		$m = 0$	$m = \pm 1$		$m = \pm 2$		$m = 0$	$m = \pm 1$		$m = \pm 2$		$m = \pm 3$	
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	f_{z^3}	f_{xz^2}	f_{yz^2}	f_{xyz}	$f_{z(x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{y(3x^2-y^2)}$
$n = 1$																
$n = 2$																
$n = 3$																
$n = 4$																
$n = 5$										…	…	…	…	…	…	…
$n = 6$					…	…	…	…	…	…	…	…	…	…	…	…
$n = 7$		…	…	…	…	…	…	…	…	…	…	…	…	…	…	…

Wikipedia

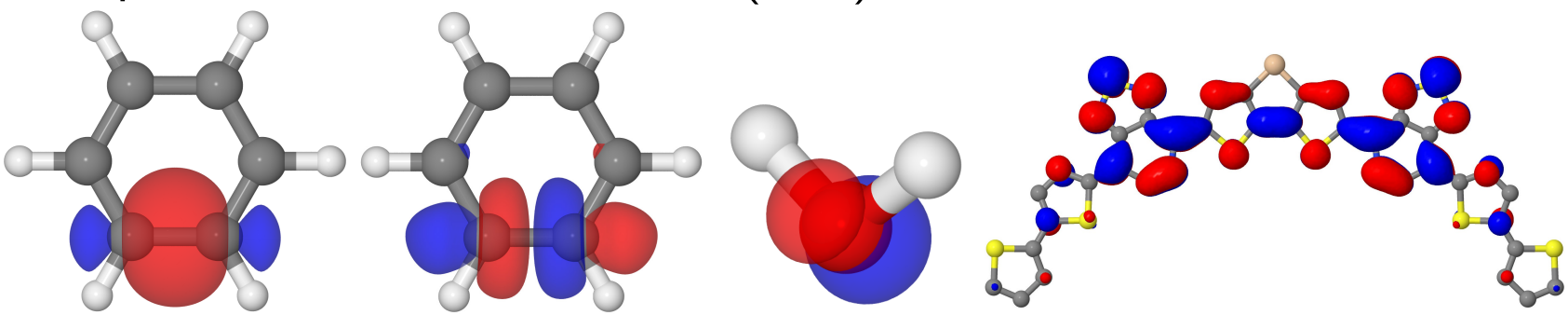
We never solve PDE – we always solve matrix eigenvalue problem

Combination of atomic orbitals

Intra-atomic combinations – hybrid AO:



Interatomic combinations: from bonding/antibonding orbitals and lone pairs to molecular orbitals (MO):



Many particle systems: fermions

Slater determinant – basis for many-body systems:

$$\Psi(\xi_1, \ldots, \xi_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\xi_1) & \psi_1(\xi_2) & \ldots & \psi_1(\xi_N) \\ \psi_2(\xi_1) & \psi_2(\xi_2) & \ldots & \psi_2(\xi_N) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_N(\xi_1) & \psi_N(\xi_2) & \ldots & \psi_N(\xi_N) \end{vmatrix}$$

where ψ_i is i-th orbital and ξ_j is coordinate+spin of j-th electron.

Methods:

- Hartree–Fock (HF) – take single Slater determinate
- DFT – the same but modify energy functional
- post-HF – expand in basis of finite excitations

One-electron orbitals — return to single-particle world

The main idea is to reduce many-body problem to a single-electron problem with some effective one-electron Hamiltonian:

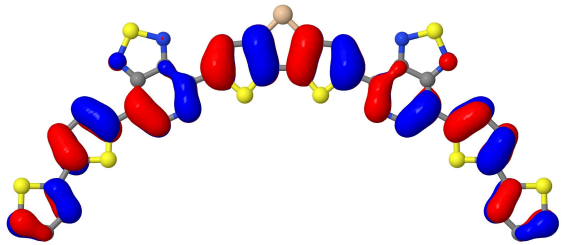
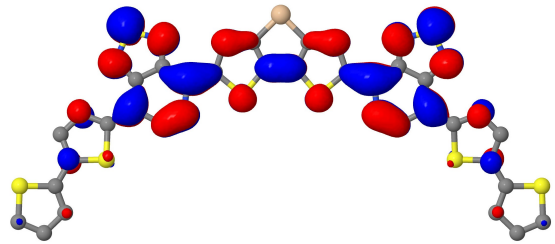
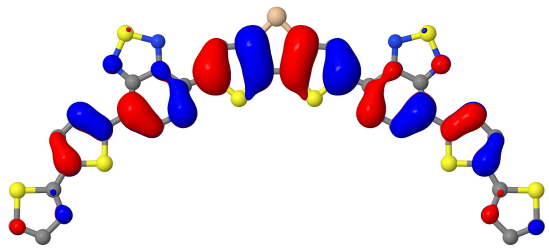
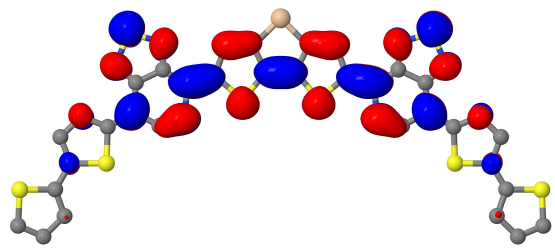
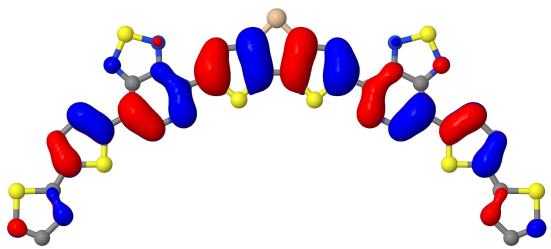
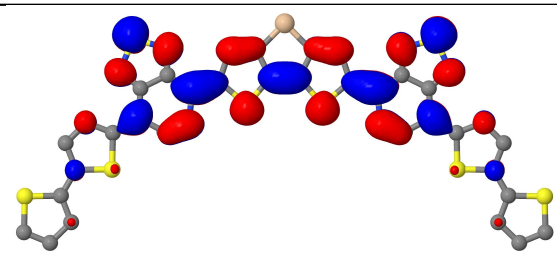
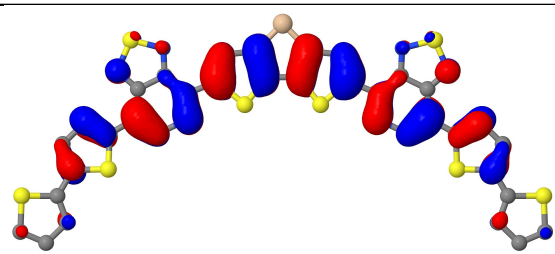
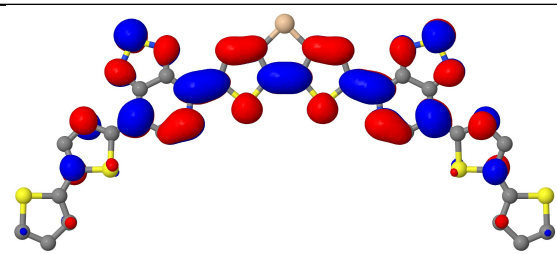
- molecular orbitals (MO) – eigenfunctions of one-electron Hamiltonian (HF/DFT)

Other one-electron orbitals:

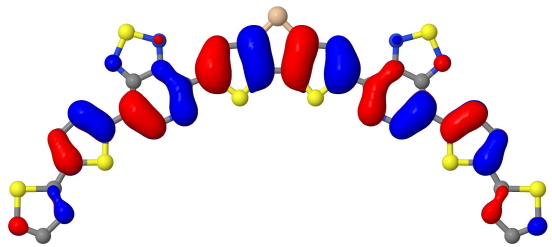
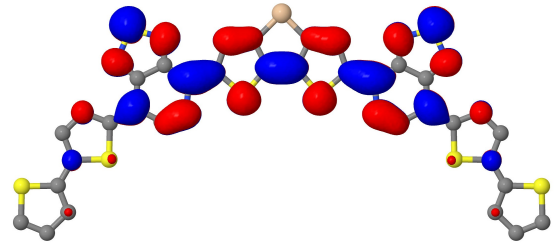
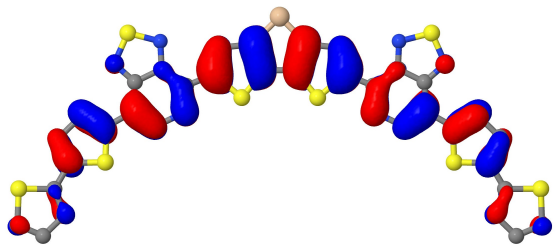
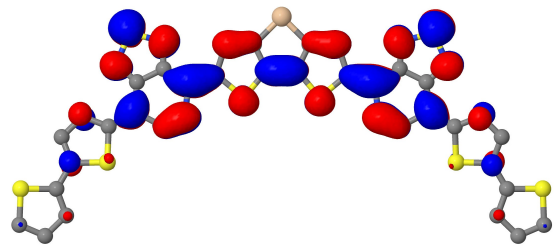
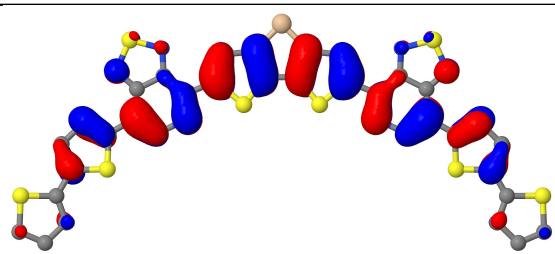
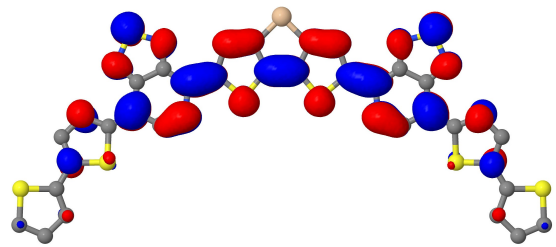
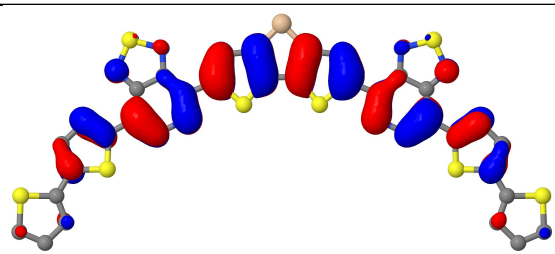
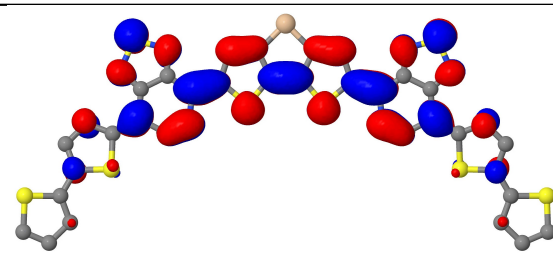
- localized molecular orbitals (LMO) – a rotation of MOs localizing each orbital in space while keeping orthogonality
- natural orbitals (NO) – eigenfunctions of one-electron density matrix $\rho^{1e}_{\Psi}(\xi;\eta) = N \int \Psi(\xi, \zeta_2, \ldots, \zeta_N)\overline{\Psi}(\eta, \zeta_2, \ldots, \zeta_N)\,\mathrm{d}\zeta$
- natural transition orbitals (NTO) – the same for transition density matrix $\rho^{1e}_{\Psi\Phi}(\xi;\eta) = N \int \Psi(\xi, \zeta_2, \ldots, \zeta_N)\overline{\Phi}(\eta, \zeta_2, \ldots, \zeta_N)\,\mathrm{d}\zeta$

Explore examples here

Examples: MO vs NO

	HOMO	LUMO
ground state $n_h = 2$ $n_e = 0$		
	hole NO	electron NO
cation/anion $n_{h/e} = 1$ $\Delta n_2 = .07/.06$		
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		

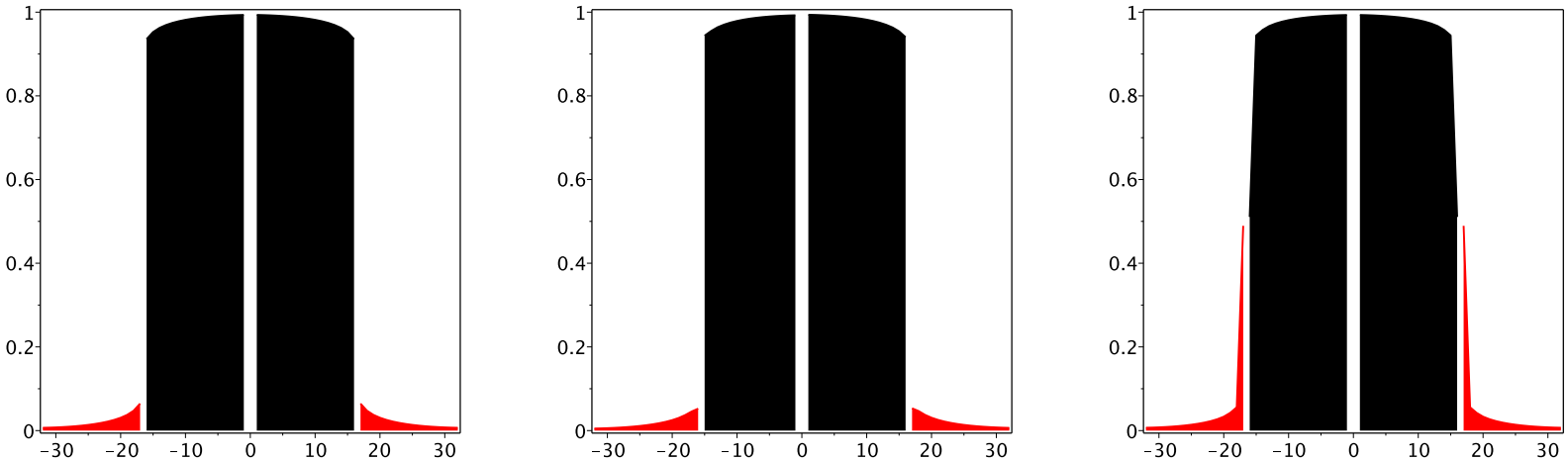
Examples: NO vs NTO

	hole NTO/NO	electron NTO/NO
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
singlet transition $n_{h/e} = 1 \pm .17$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		
triplet transition $n_{h/e} = 1 \pm .25$		

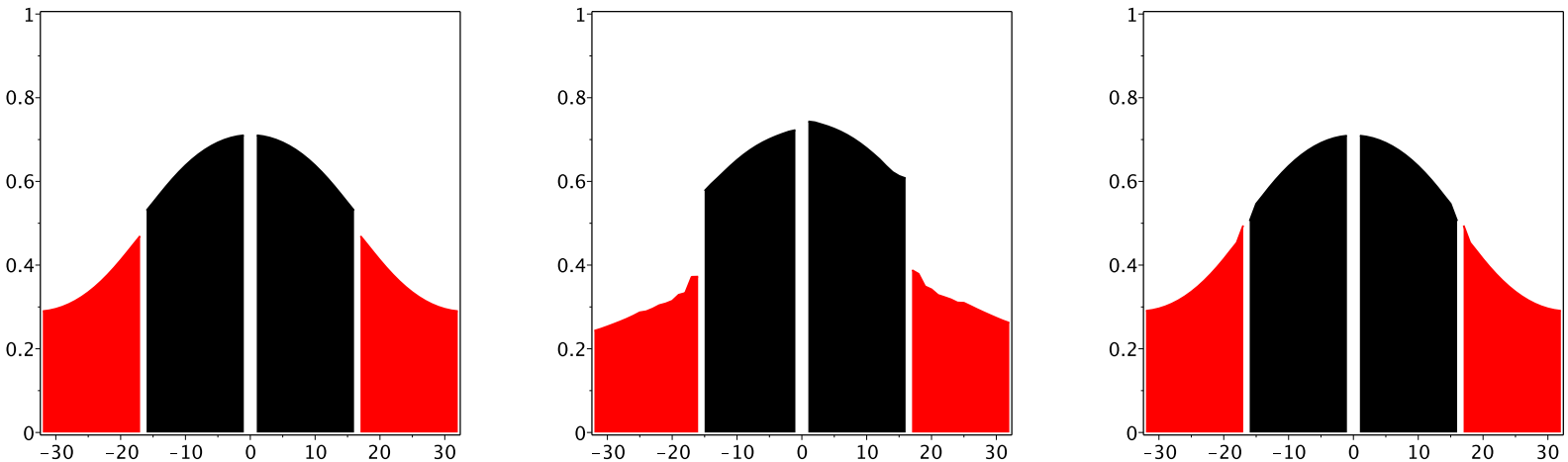
Be careful with strongly-correlated systems

Extended Hubbard model, 1e-orbital occupations: ground state, hole, exciton

$U/V = 2/1$ – single-particle description works well:



$U/V = 16/4$ – electron-electron correlations are strong:



Methods: Uniform electron gas approximation for simple metals (LDA)

Quantum mechanics of crystals

Bloch's theorem for one-electron wave-function:

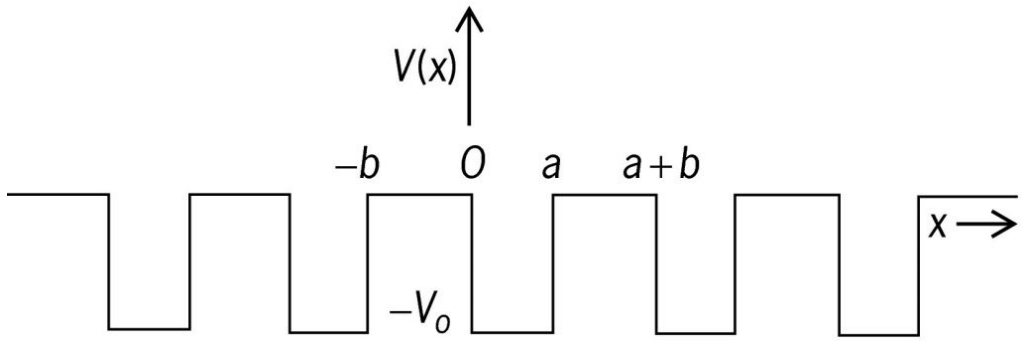
$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = u_n(\boldsymbol{r})\mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{r}}$$

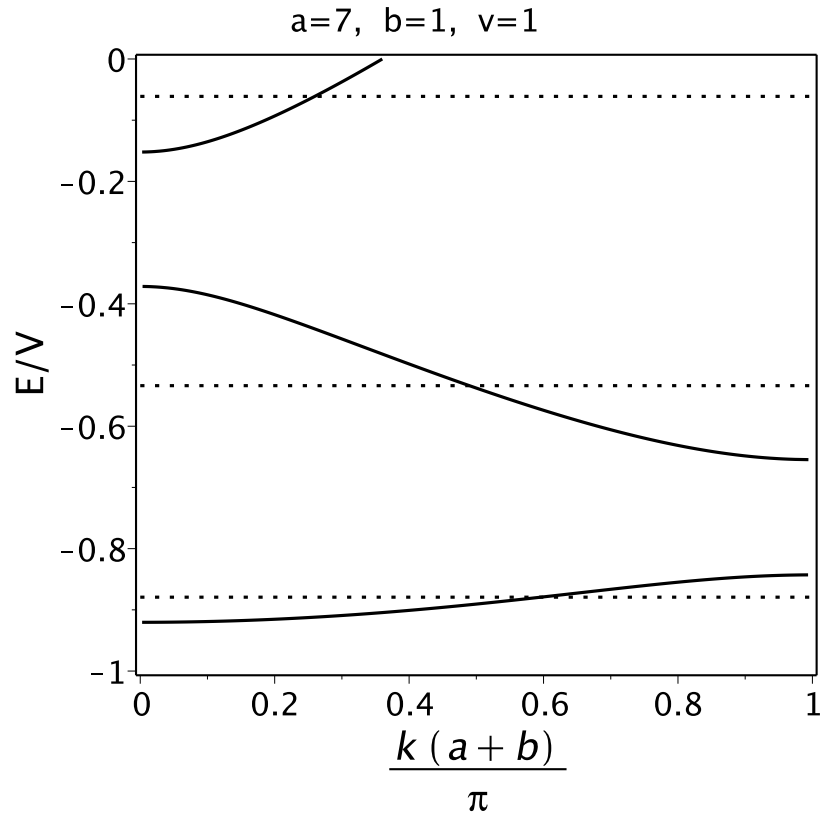
where u_n is periodic, n enumerates electronic bands, k is the wave-vector "periodic" in the reciprocal space define by vectors

$$\boldsymbol{b}_i = e_{ijk}\frac{2\pi}{\upsilon}\left(\boldsymbol{a}_j \times \boldsymbol{a}_k\right)$$

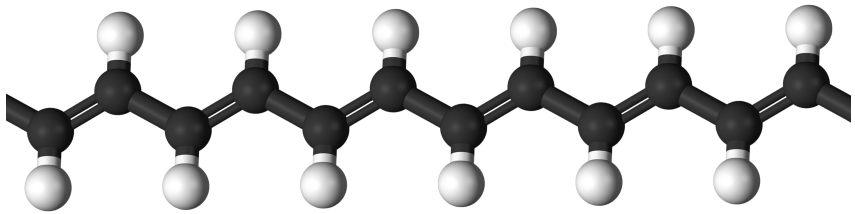
where $\upsilon = \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)$ is unit cell volume

Example: Kronig–Penney model

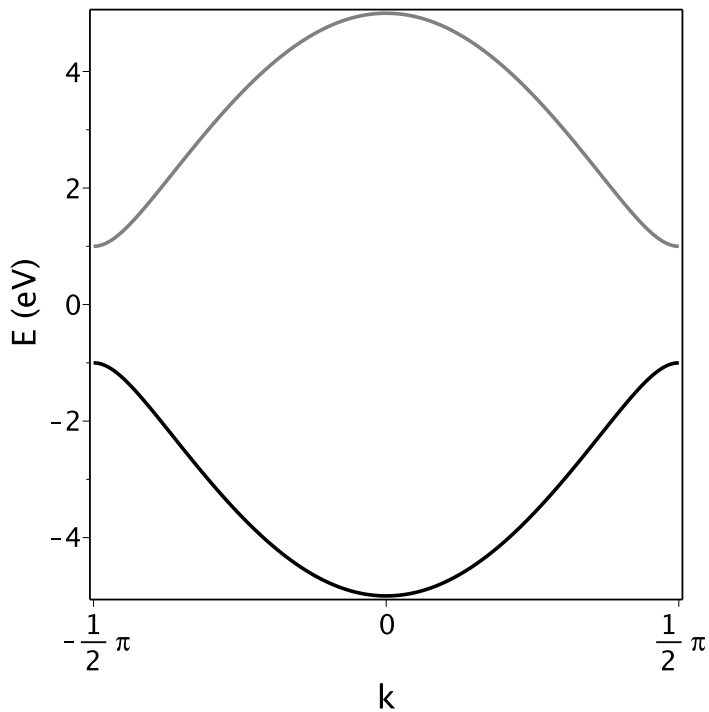




Example: Huckel model of trans-polyacetylene



$$\mathsf{H}_\pi^{1e} = \begin{pmatrix} \cdots & & & & \\ & 0 & -t_1 & 0 & \\ & -t_1 & 0 & -t_2 & \\ & 0 & -t_2 & 0 & \\ & & & & \cdots \end{pmatrix}$$



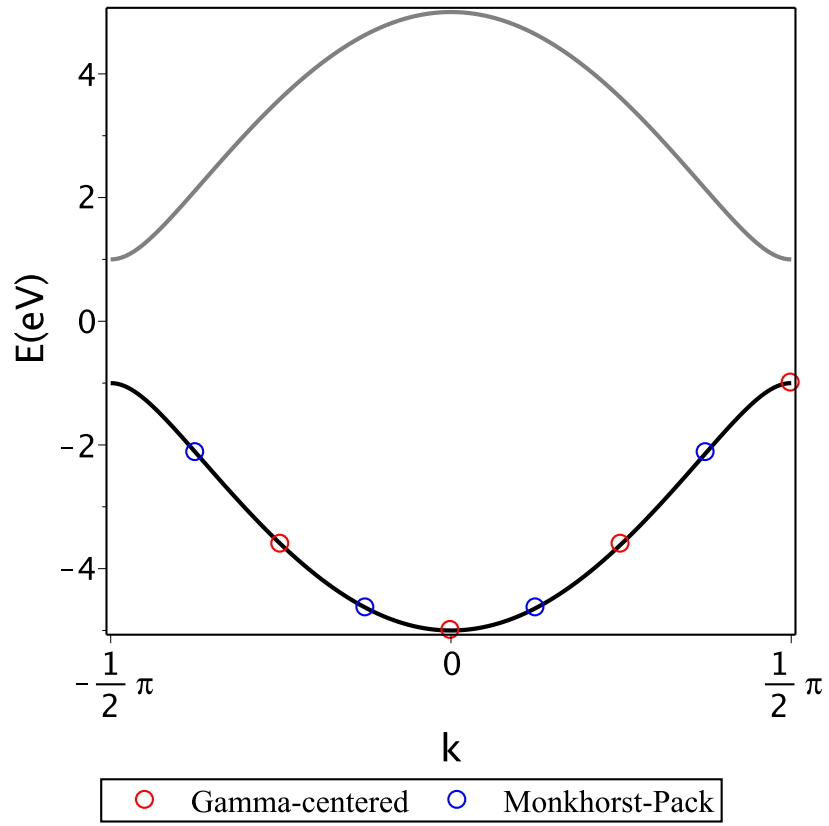
$$\psi_n = c_{1,2} e^{ikn}, \ n \in \mathbb{Z}, \ |k| \leqslant \pi/2$$

$$E(k) = \pm\sqrt{t_1^2 + t_2^2 + 2t_1 t_2 \cos 2k}$$

$$E_{\text{bandgap}} = 2|t_1 - t_2|, \ E_{\text{bandwidth}} = 2(t_1 + t_2)$$

Example: Total π-electron energy of trans-polyacetylene

The total electronic energy is the sum/integral of 1e-energies (MO/band energy) + ee-interaction energy



Band energy $\mathcal{E} = \frac{2}{\pi}\int_0^{\pi/2} E(k)\,\mathrm{d}k = -3.34$ eV

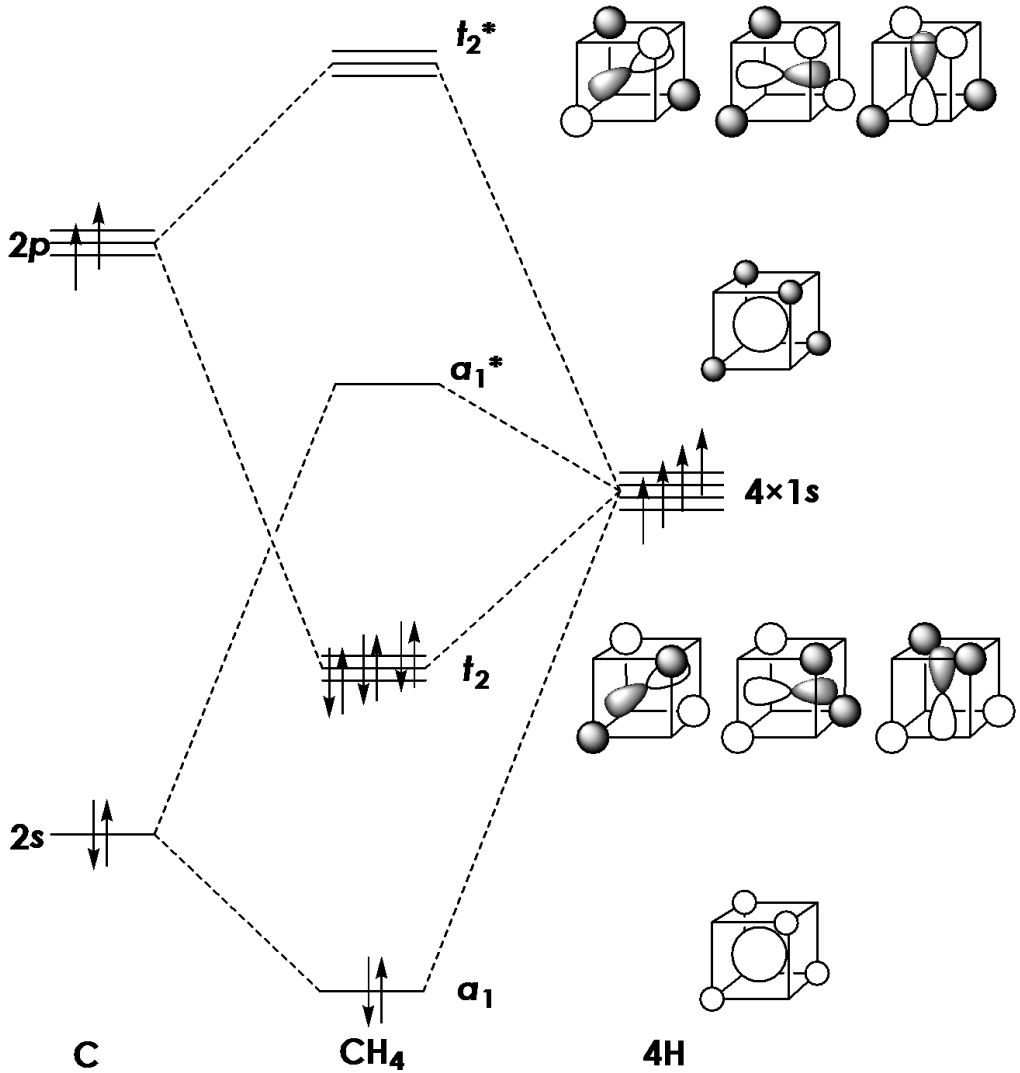
c.f. 4x supercell -3.30 — illustration of locality principle

Discussion

Let's discuss:

1. Go slide by slide
2. HOMO/LUMO, frontier orbitals, IP/EA, S0/S1/T1
3. VB/CB, bandgap/bandwidth
4. Quasiparticles: electron/hole, effective mass, exciton (Frenkel vs Wannier–Mott), electrons in metal and plasmon
5. Orbital symmetries

Examples: Methane molecule



Valence MO in basis of Csp^3 + Hs orbitals:

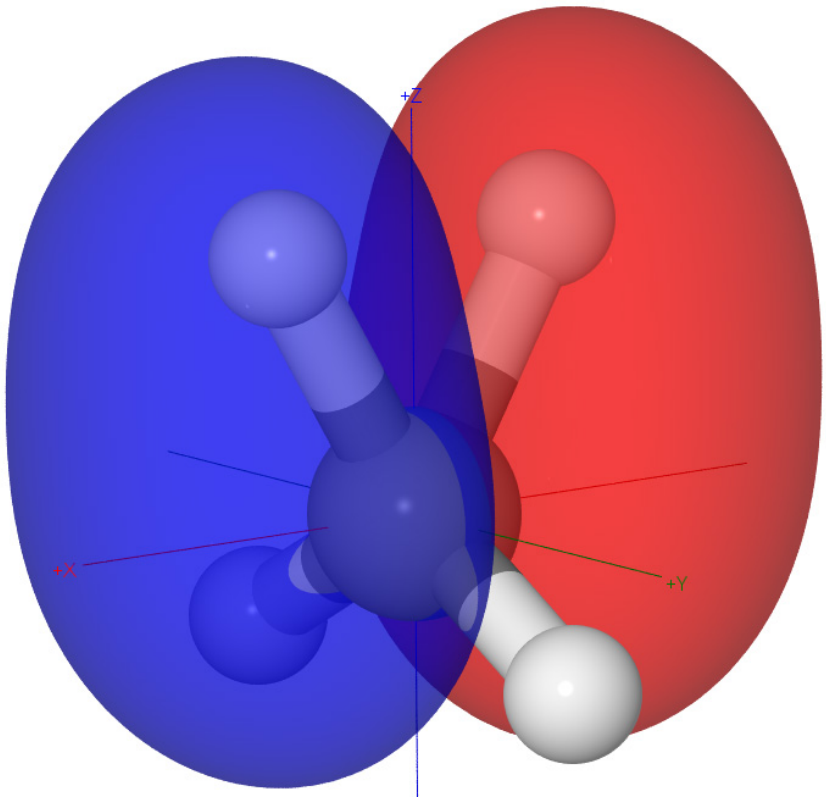
$$\begin{pmatrix} \varepsilon & -t & -t & -t \\ -t & \varepsilon & -t & -t \\ -t & -t & \varepsilon & -t \\ -t & -t & -t & \varepsilon \end{pmatrix}$$

$E_1 = \varepsilon - 3t$

$E_{2,3,4} = \varepsilon + t$

Examples: Methane molecule cation

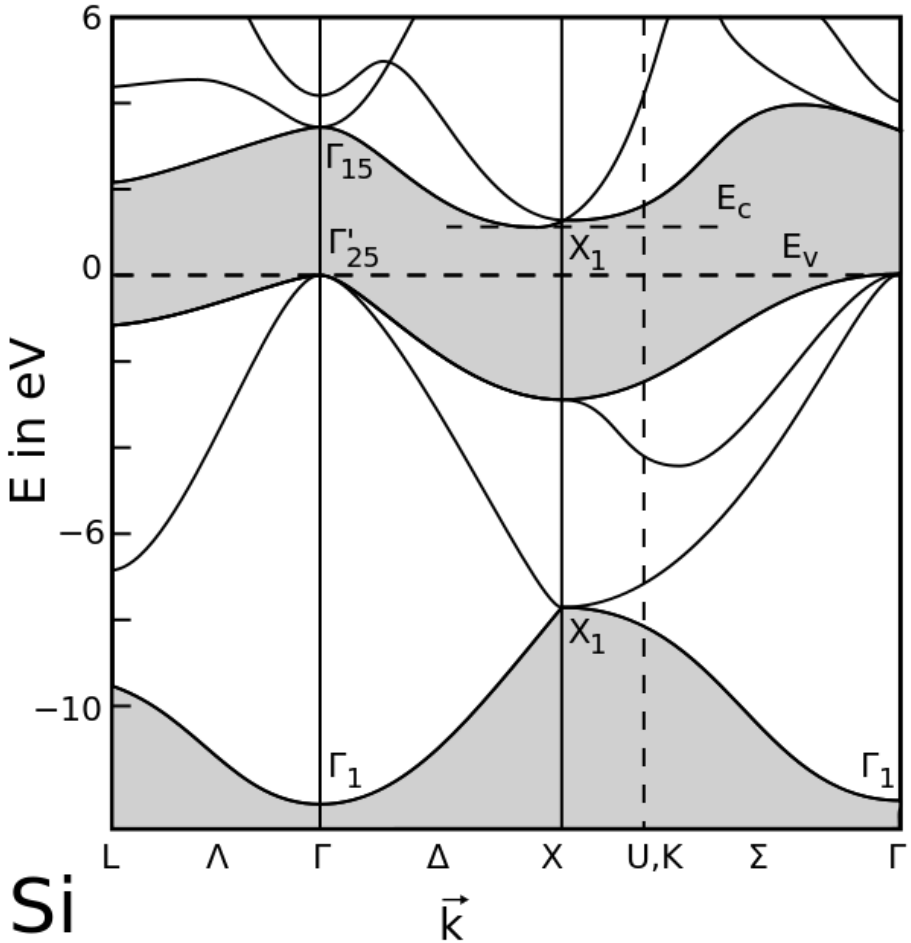
Jahn–Teller distortion



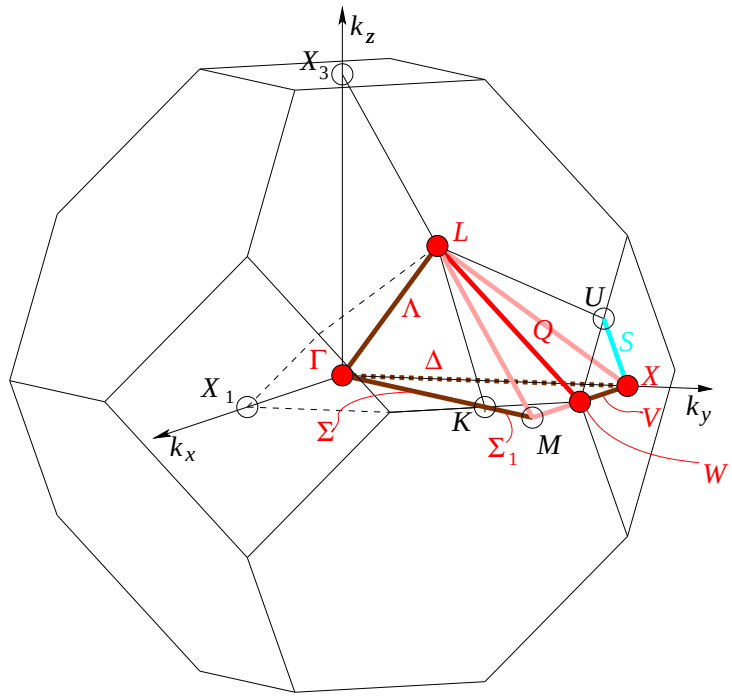
Three options:

- -42m (D_{2d})
- mm2 (C_{2v})
- 3m (C_{3v})

Example: Silicon crystal

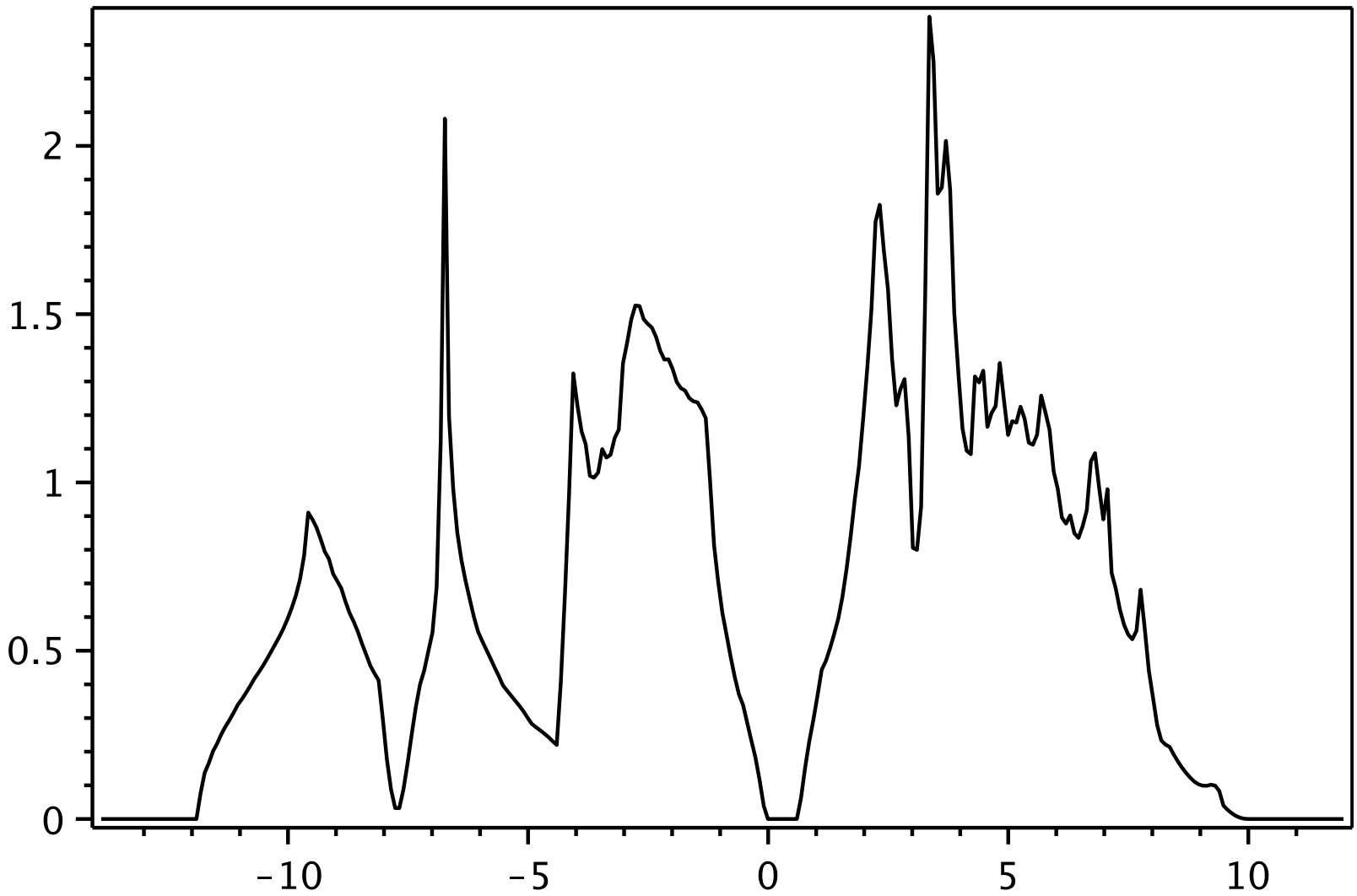


Band structure of Si

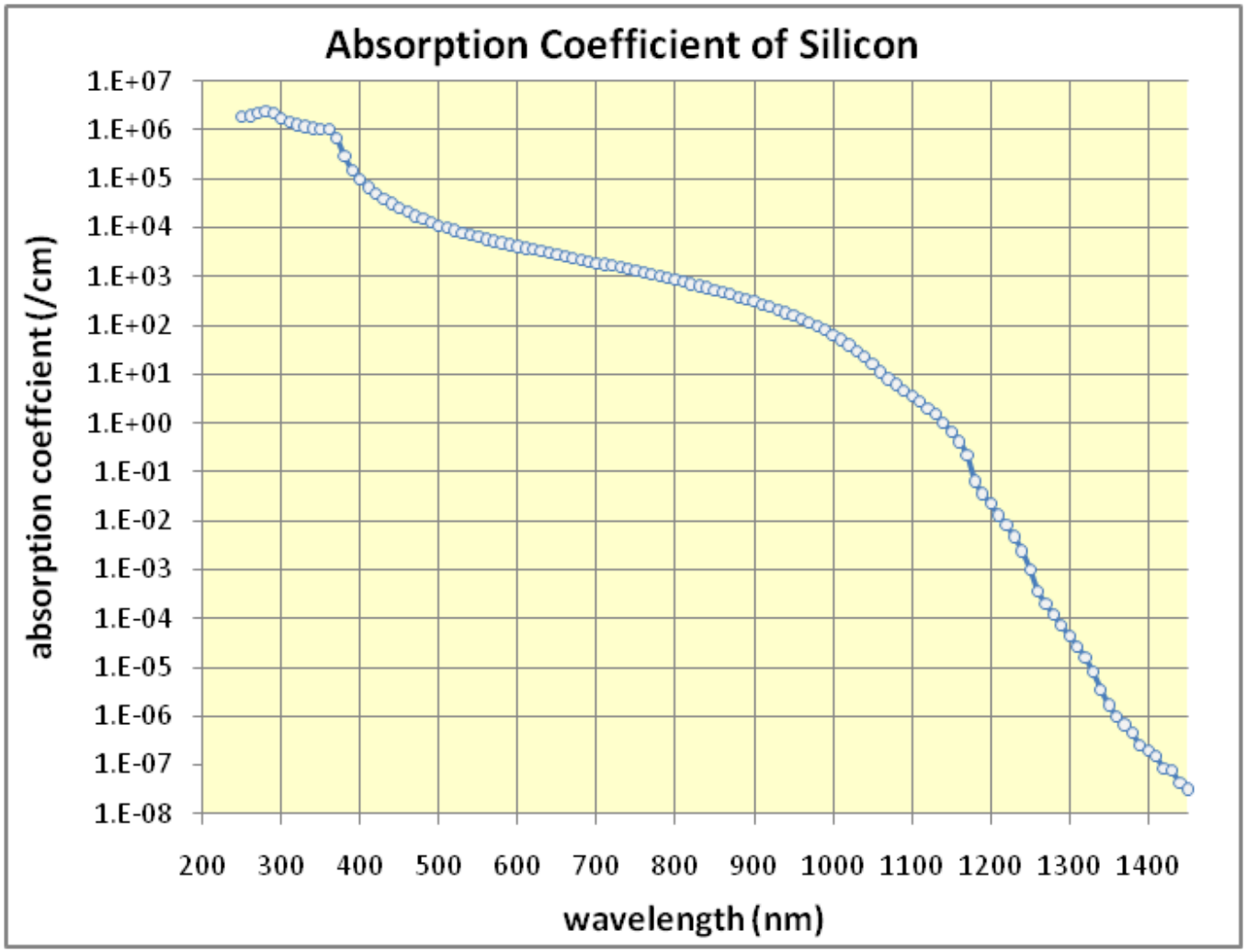


Brillouin zone for Fm-3m

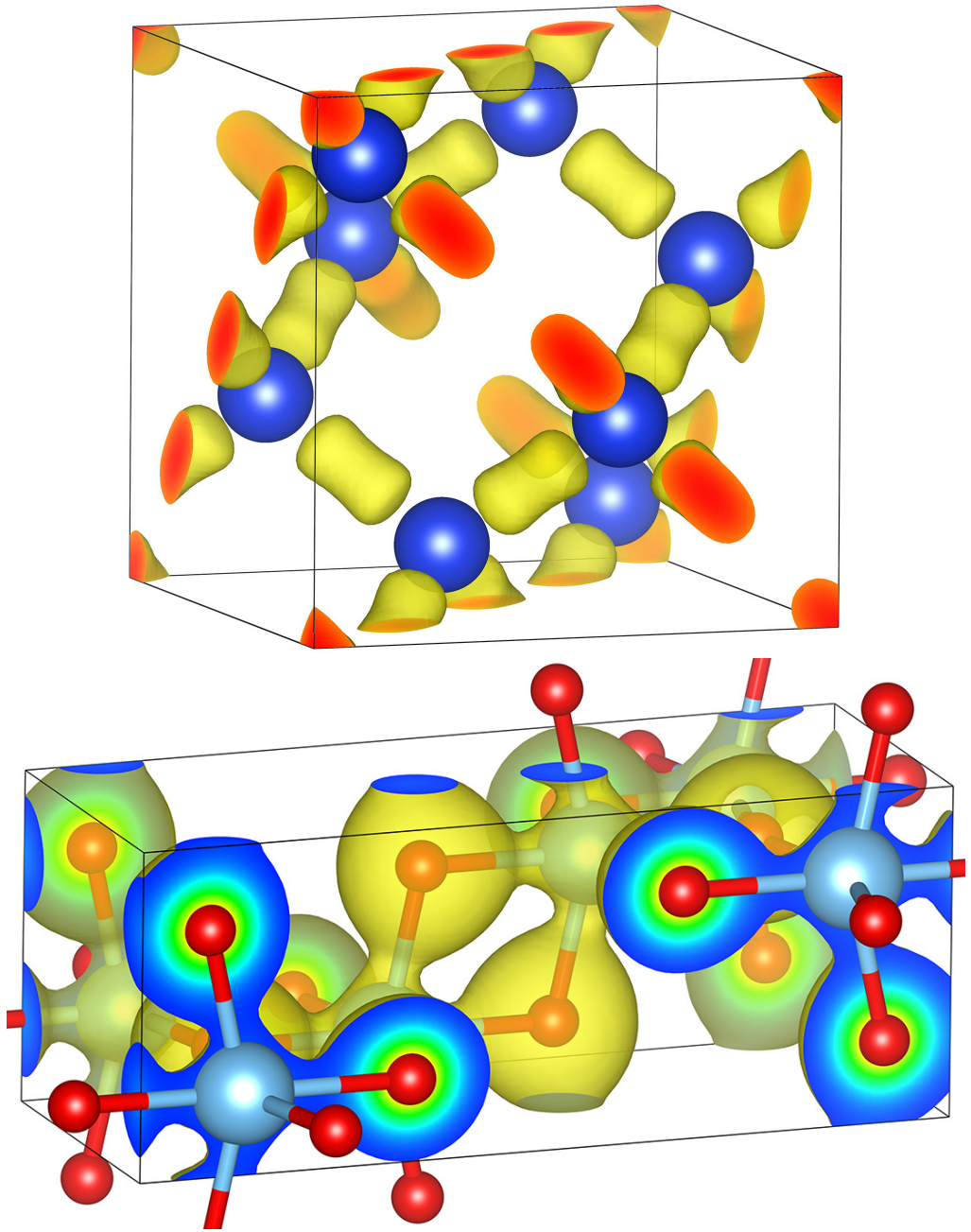
Silicon crystal: electronic density of states (DOS)



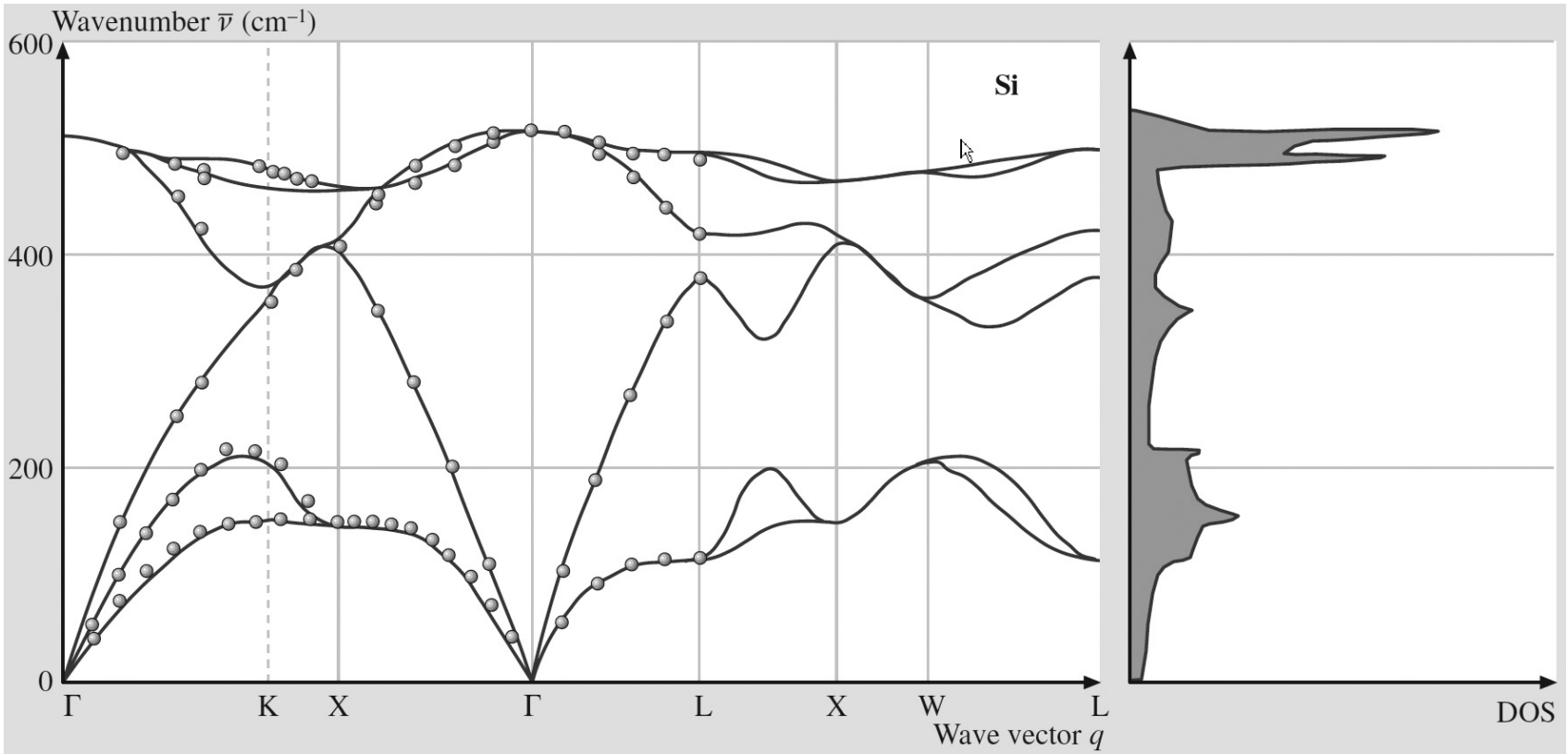
Silicon crystal: UV-Vis absorption spectrum



Silicon vs TiO2 crystal: charge density



Silicon crystal: phonons



Silicon crystal: dopants

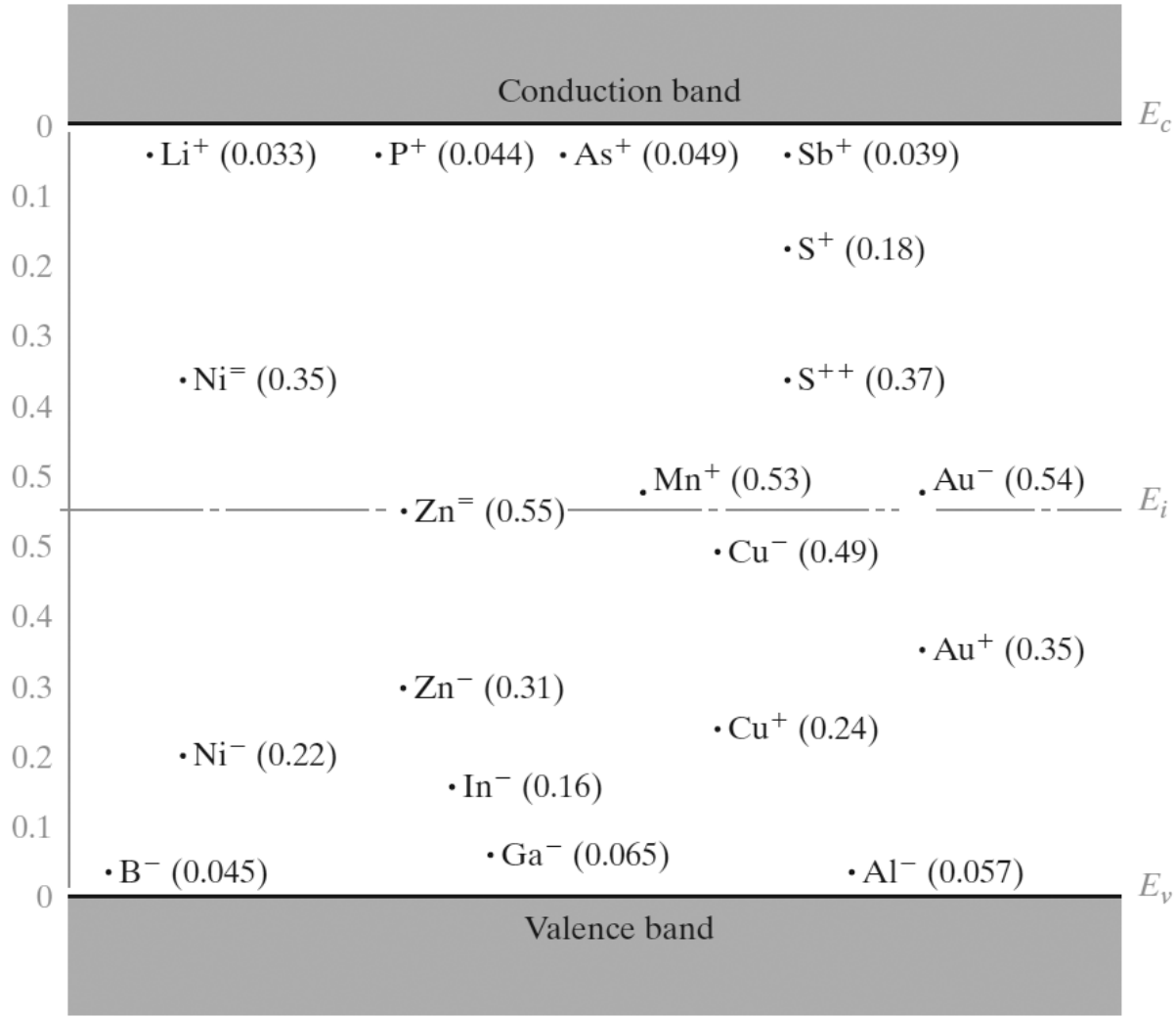


Figure 4–9
Energy levels of impurities in Si. The energies are measured from the nearest band edge (E_v or E_c); donor levels are designated by a plus sign and acceptors by a minus sign.

[4]References: S. M. Sze and J. C. Irvin, "Resistivity, Mobility, and Impurity Levels in GaAs, Ge and Si at 300 K," *Solid State Electronics*, vol. 11, pp. 599–602 (June 1968); E. Schibli and A. G. Milnes, "Deep Impurities in Silicon," *Materials Science and Engineering*, vol. 2, pp. 173–180 (1967).

Summary and Resources

See summary here

- Wikipedia
- Bilbao Crystallographic Server
- Quantum Mechanics course or Landau's textbook

A few textbooks out of many:

- C Kittel, Introduction to Solid State Physics (2005)
- N W Ashcroft, N D Mermin, Solid state physics (1976)

Visualization software:

- Jmol
- Vesta