

Survey of Materials. Lecture 3

Electronic structure of materials

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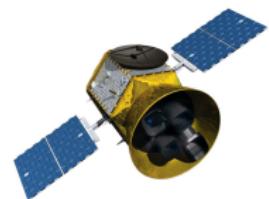
Outline

- Quantum mechanics and Schrodinger equation
- Electronic structure of atoms and molecules
- Electronic structure of crystals
- Atomic motions
- Total energy
- Electronic properties
- Defects

Why do we need to know Quantum Mechanics



- mechanical
- thermal
- at macroscale



- electronic
- chemical
- anything at nanoscale

Pragmatic approach to Quantum Mechanics

Let's start with a single particle

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

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

Any observable can be calculated as follows:

$$A = \langle \psi | A | \psi \rangle \equiv \int \overline{\psi(\mathbf{r}, t)} (A\psi)(\mathbf{r}, t) dV$$

For example, average position:

$$\bar{\mathbf{r}}(t) = \int \mathbf{r} |\psi(\mathbf{r}, t)|^2 dV$$

Example: particle in uniform field

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

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

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

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

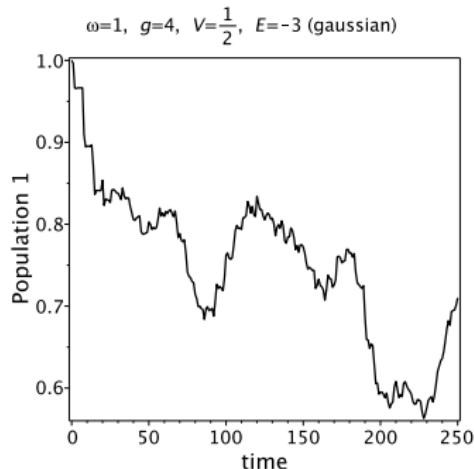
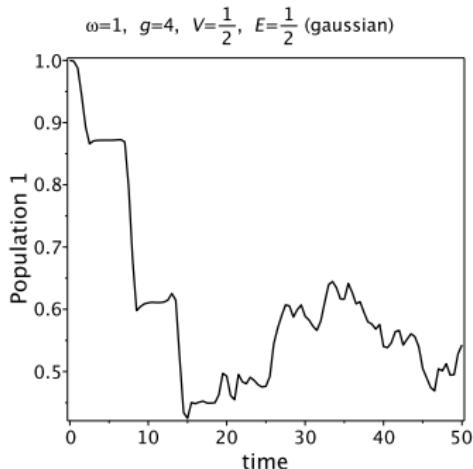
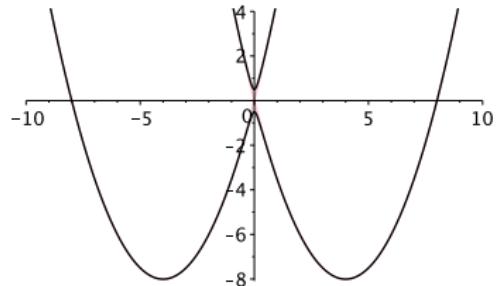
\implies classical dynamics + gaussian broadening

Example: simple model of electron transfer

$$\omega=1, g=4, V=\frac{1}{2}, \varepsilon=0$$

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

Stationary Schrodinger equation

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

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

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

$$H\psi = E\psi$$

Examples

potential	ψ_n	E_n	
free particle	e^{ikr}	$\frac{\hbar^2 k^2}{2m}$	$k \in \mathbb{R}^3$
potential box	$\sin \frac{\pi n x}{a}$	$\frac{\pi^2 \hbar^2 n^2}{2ma^2}$	$n = \overline{1, \infty}$
oscillator	$H_n(\xi) e^{-\xi^2/2}$	$\hbar\omega \left(n + \frac{1}{2}\right)$	$n = \overline{0, \infty}$
Coulomb	$r^l L_{n-l-1}^{2l+1} \left(\frac{2r}{n}\right) e^{-\frac{r}{n}} Y_{lm}(\theta, \phi)$	$-\frac{\alpha}{2an^2}$	$n \in \mathbb{N},$ $l < n, m \leq l$

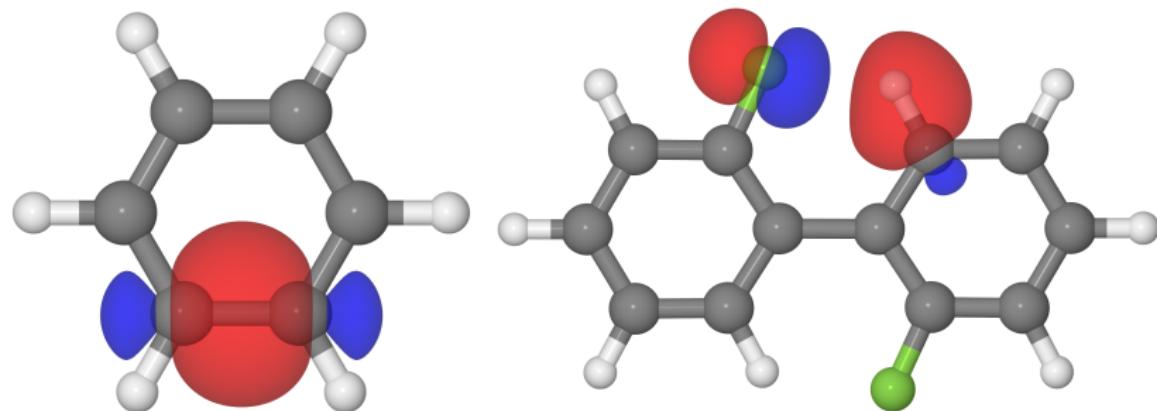
Practical considerations: basis set

Plane waves or atomic orbitals

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_{xy^2}	$f_{d(x^2-y^2)}$	$f_{d(x^2-3y^2)}$	$f_{d(3x^2-y^2)}$	
$n = 1$		•																
$n = 2$		•																
$n = 3$		•																
$n = 4$		•																
$n = 5$		•				
$n = 6$		•			
$n = 7$		•			

Wikipedia

Combination of atomic orbitals: examples



Many particle systems: fermions

Slater determinant – basis for many-body systems:

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

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

- molecular orbitals (MO) – eigenfunctions of one-electron Hamiltonian (HF/DFT)
- 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 $\rho_{\Psi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \bar{\Psi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$
- natural transition orbitals (NTO) – the same for transition density matrix $\rho_{\Psi\Phi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \bar{\Phi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$

Explore examples [here](#)

More examples: MO vs NO

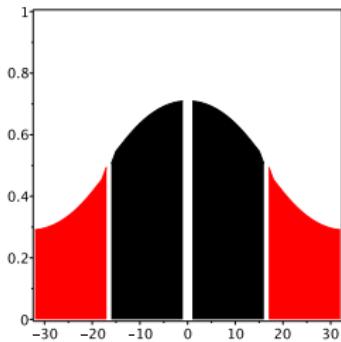
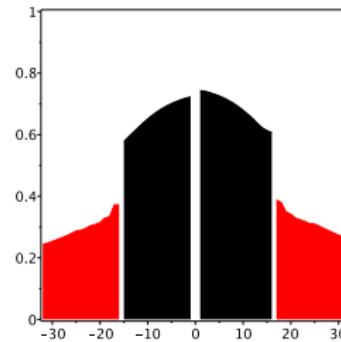
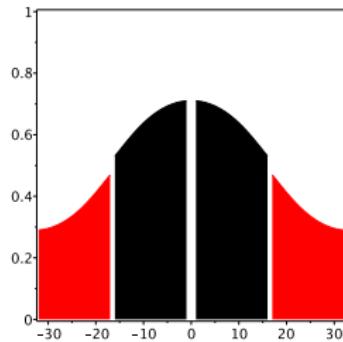
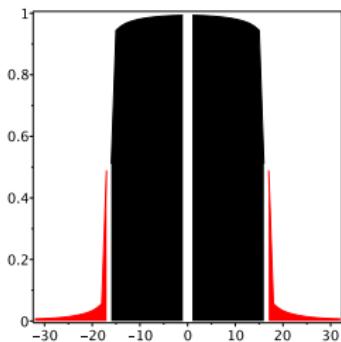
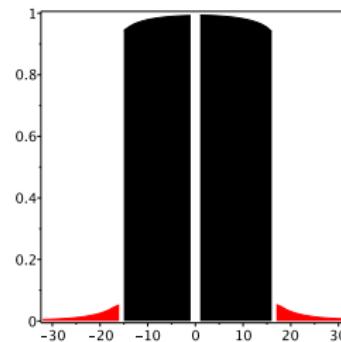
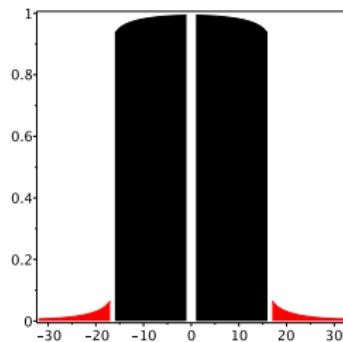
	HOMO	LUMO
ground state $n_h = 2$ $n_e = 0$		
cation/anion $n_{h/e} = 1$ $\Delta n_2 = .07/.06$		
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		

More 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 $n_{h/e} = 1 \pm .25$		

Strong correlations: Extended Hubbard model

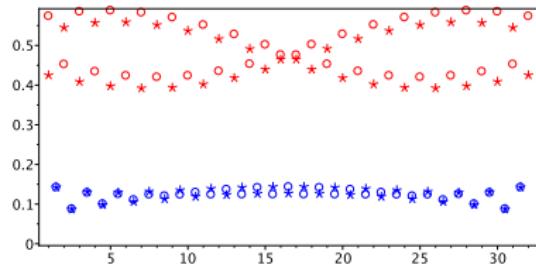
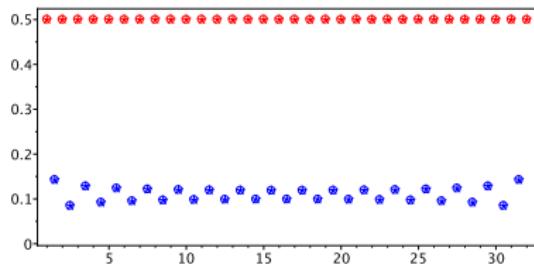
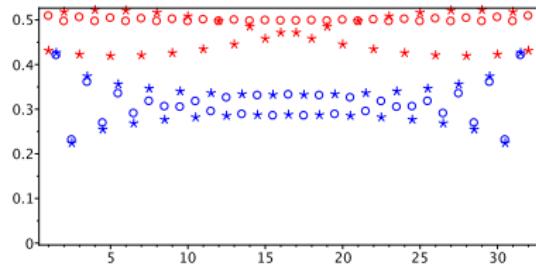
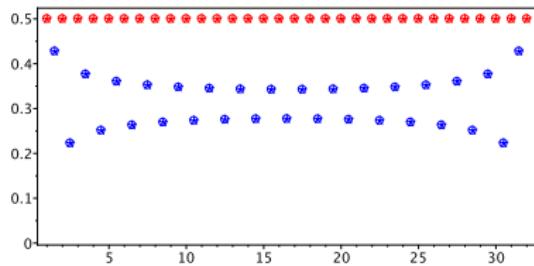
Population analysis: ground state, hole, exciton; $U/V = 2/1$ vs $16/4$



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

Extended Hubbard model: density waves

1e density matrix (diagonal & subdiagonal): ground state & hole; $U/V = 2/1$ vs $16/4$



Quantum mechanics of crystals

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

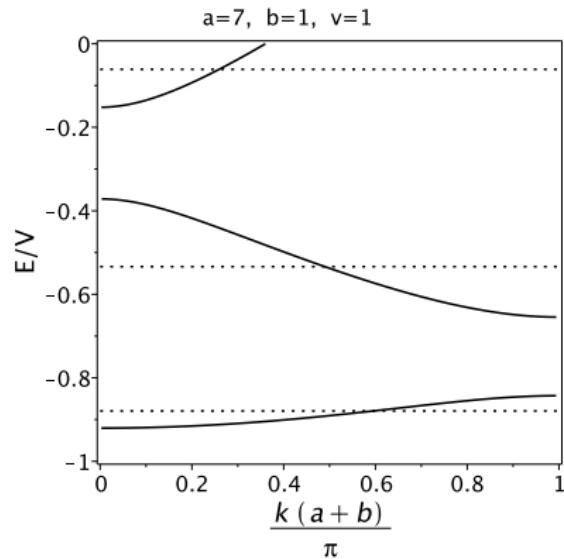
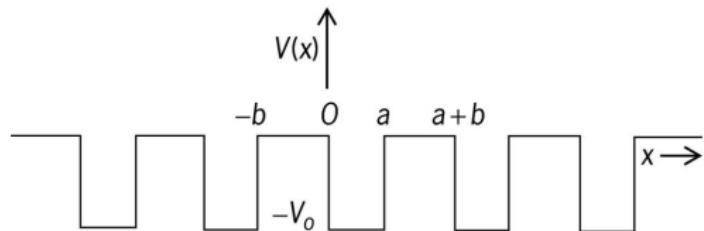
$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_n(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

where u_n is periodic, n enumerates electronic bands, \mathbf{k} is the wave-vector “periodic” in the reciprocal space define by vectors

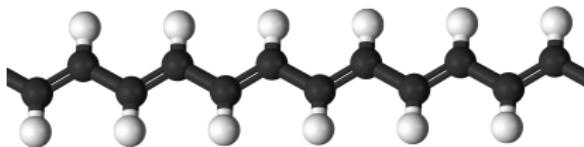
$$\mathbf{b}_i = e_{ijk} \frac{2\pi}{v} (\mathbf{a}_j \times \mathbf{a}_k)$$

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

Example 1: Kronig–Penney model



Example 2: Huckel model of trans-polyacetylene

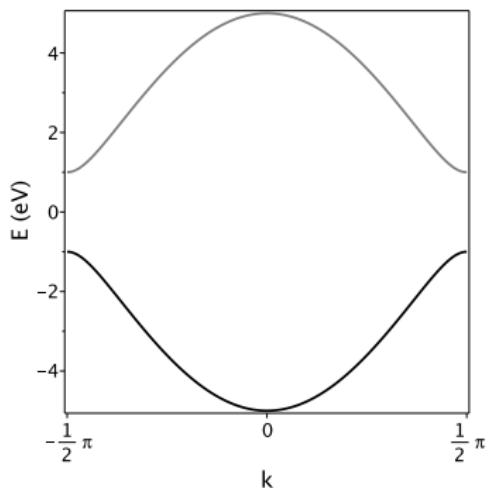


$$H = \begin{pmatrix} \dots & & & \\ & 0 & -t_1 & 0 \\ & -t_1 & 0 & -t_2 \\ & 0 & -t_2 & 0 \\ & & & \dots \end{pmatrix}$$

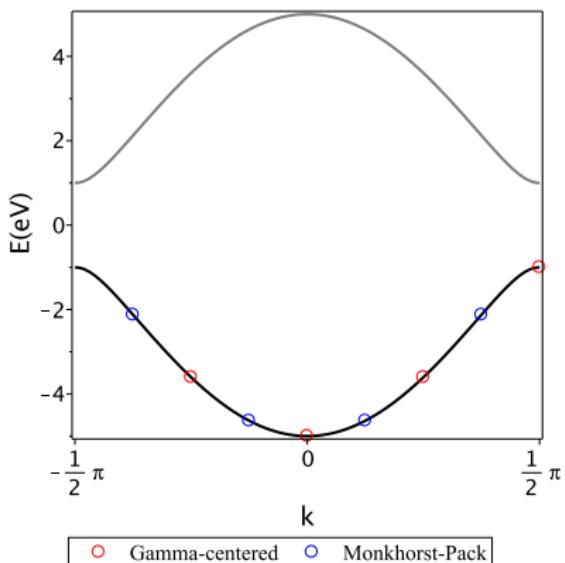
$$\psi_n = c_{1,2} e^{ikn}, \quad n \in \mathbb{Z}, \quad |k| \leq \pi/2$$

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

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

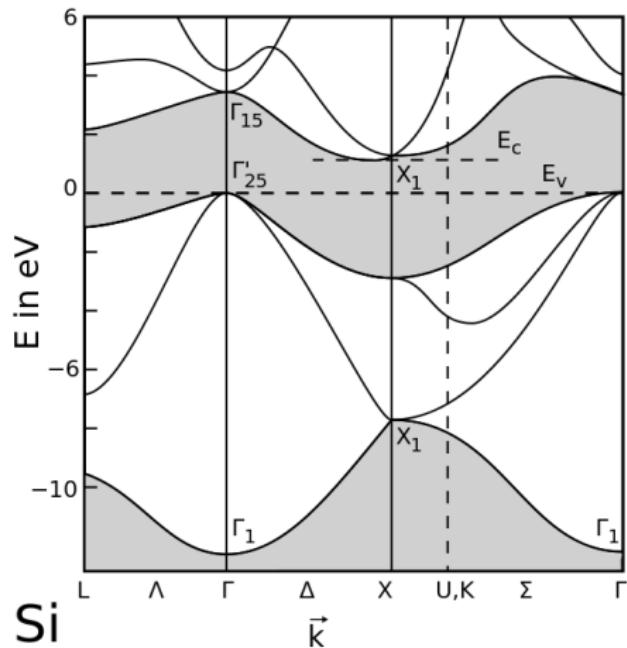


Example 2: Total π -electron energy of trans-polyacetylene

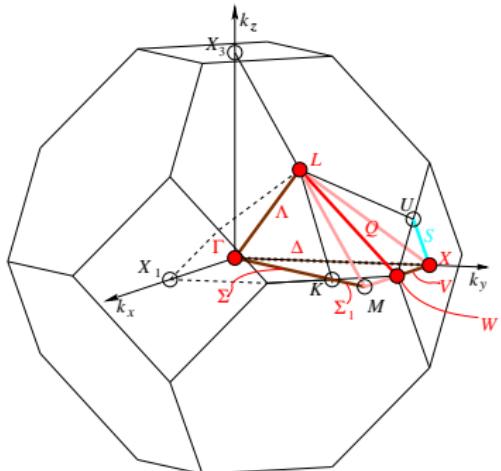


Total electronic energy $\mathcal{E} = \frac{2}{\pi} \int_0^{\pi/2} E(k) dk = -3.34$
4x supercell **-3.30**

Example 3: Silicon crystal

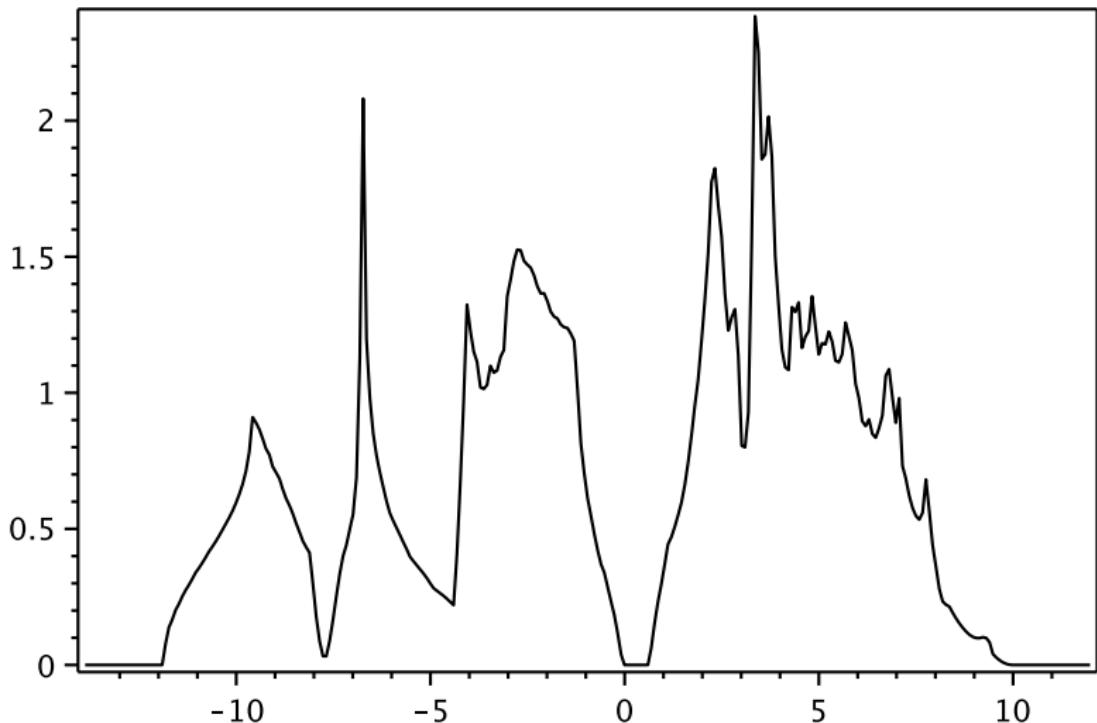


Band structure of Si

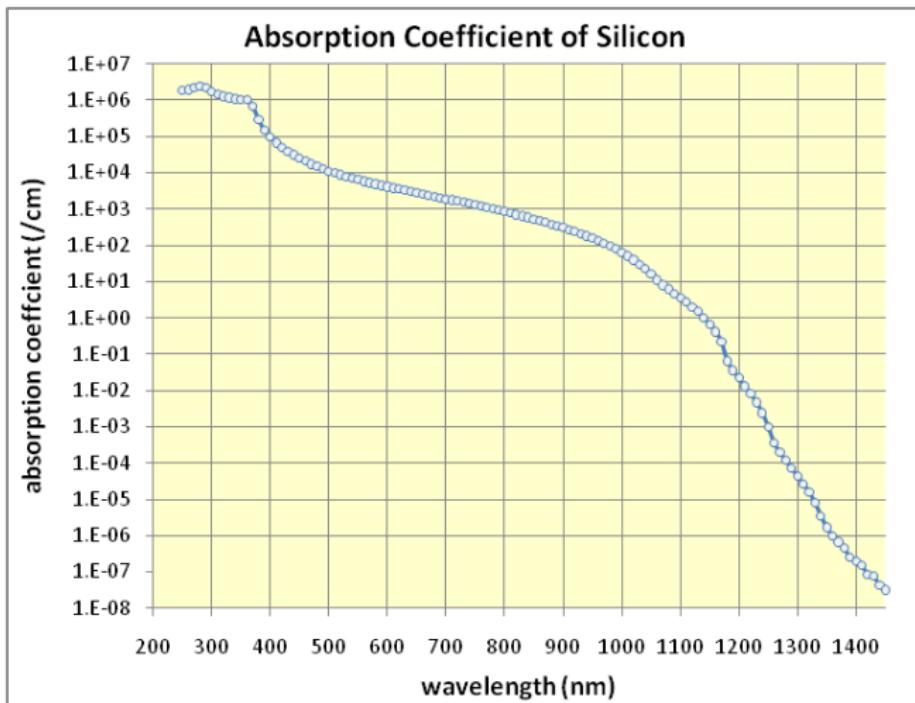


Brillouin zone for Fm-3m

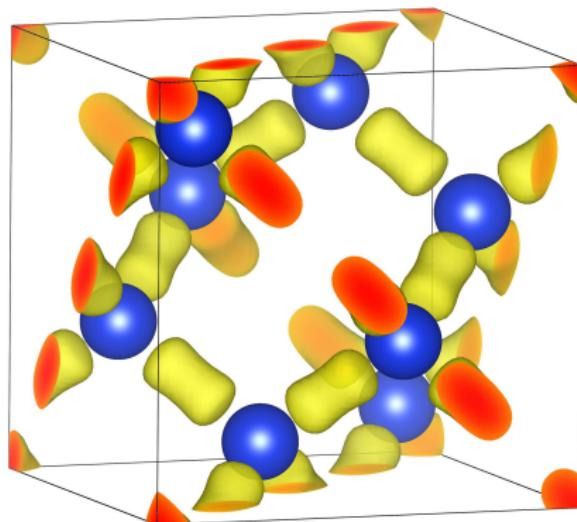
Silicon crystal: electronic density of states (DOS)



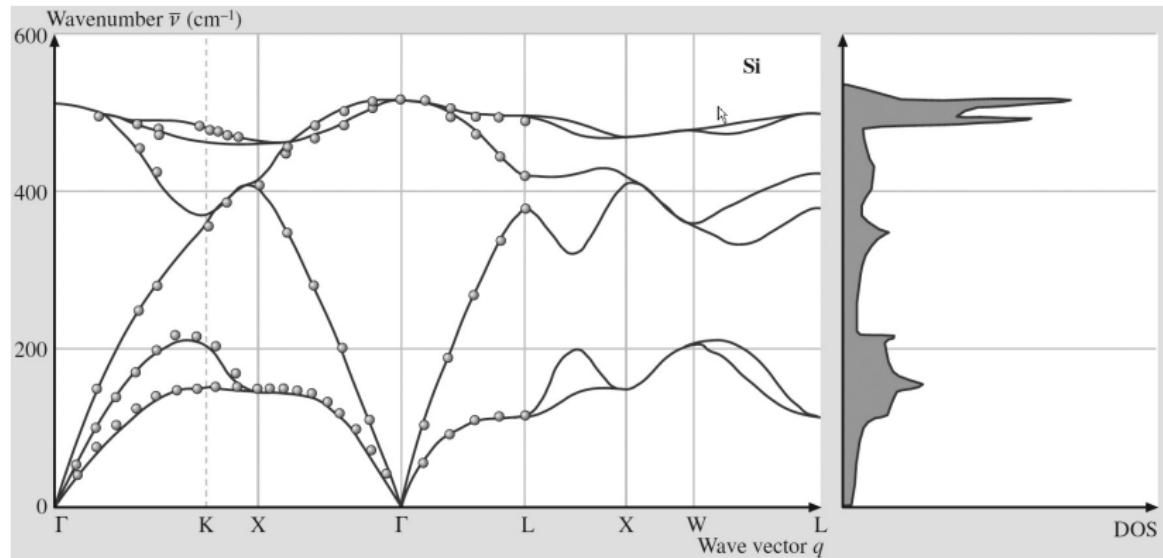
Silicon crystal: UV-Vis absorption spectrum



Silicon crystal: charge density



Silicon crystal: phonons



Silicon crystal: dopants

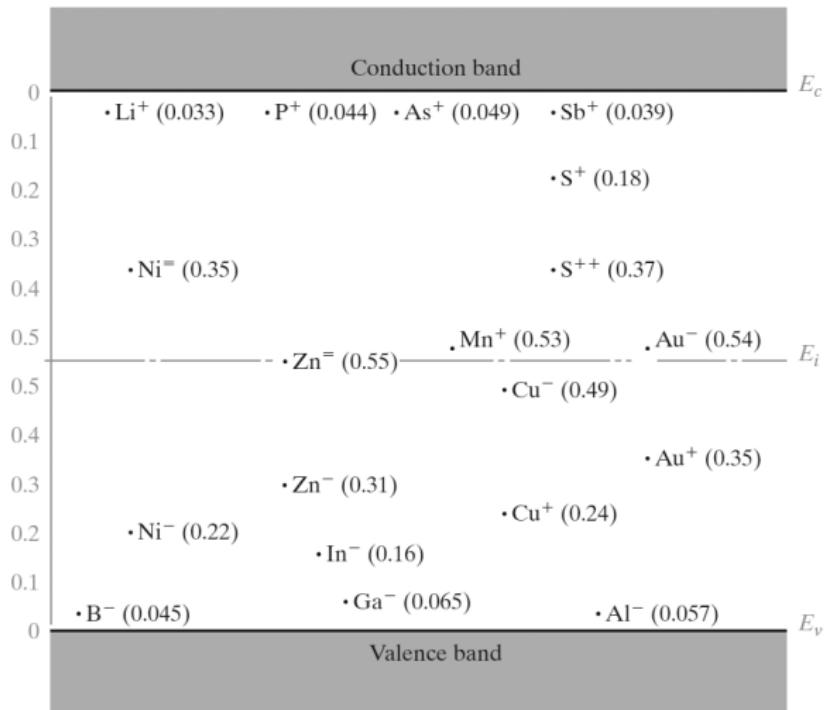


Figure 4-9
Energy levels of impurities in Si. The energies are measured from the nearest band edge (E_v or E_c); donor levels are designated by a plus sign and acceptors by a minus sign.

⁴References: 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

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](#)