

## Survey of Materials. Lecture 3

# Electronic structure of materials

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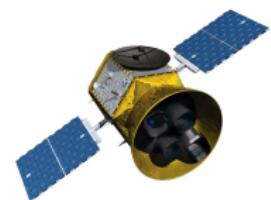
### *Outline*

- 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  $\psi$  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

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

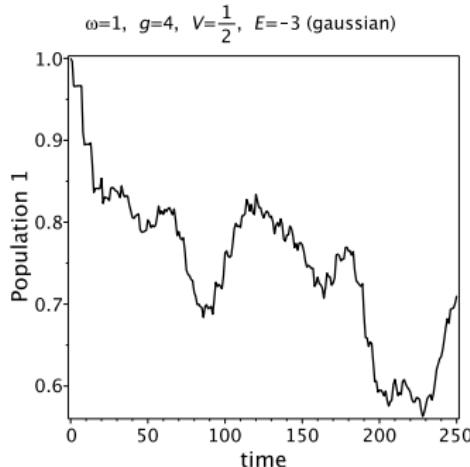
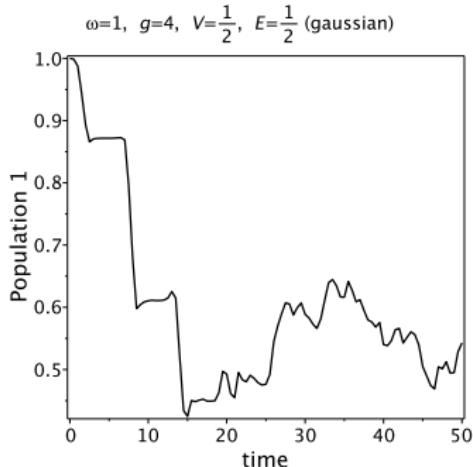
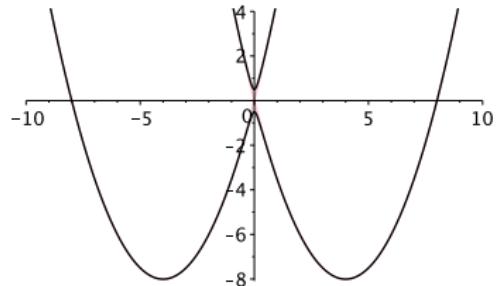
$\implies$  classical dynamics + gaussian broadening

# 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  $(E_n, \psi_n)$  are eigenvalues and eigenfunctions of the stationary Schrodinger equation:

$$H\psi = E\psi$$

## Examples

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potential	$\psi_n$	$E_n$	
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	$r^l L_{n-l-1}^{2l+1} \left(\frac{2r}{n}\right) e^{-\frac{r}{n}} Y_{lm}(\theta, \phi)$	$-\frac{\alpha}{2an^2}$	$n \in \mathbb{N},$ $l < n,  m  \leq l$

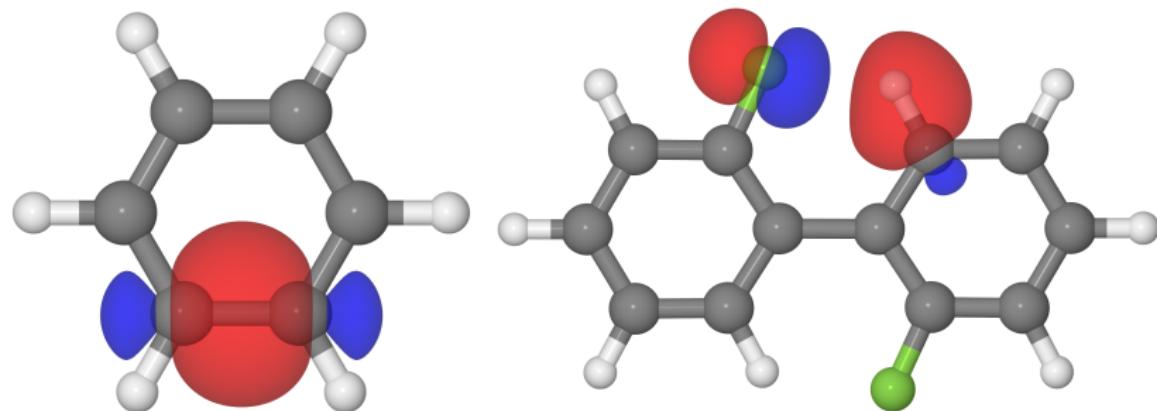
# Practical considerations: basis set

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  $\psi_i$  is  $i$ -th orbital and  $\xi_j$  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
- natural orbitals (NO) – eigenfunctions of one-electron density matrix  $\rho_{\Psi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \overline{\Psi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$
- natural transition orbitals (NTO) – the same for transition density matrix  $\rho_{\Psi\Phi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \overline{\Phi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$

Explore examples [here](#)

## More examples: MO vs NO

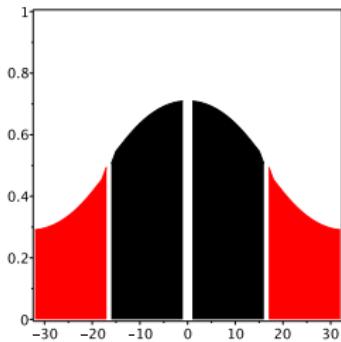
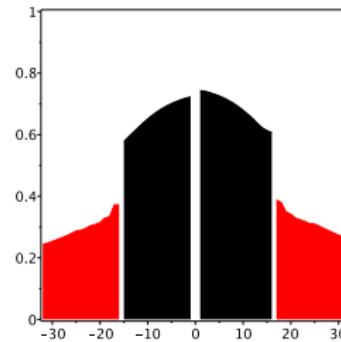
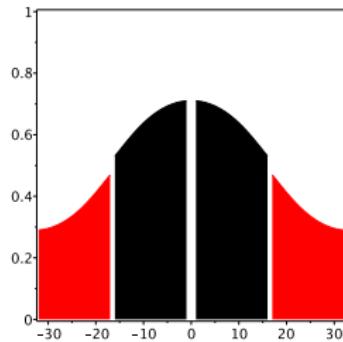
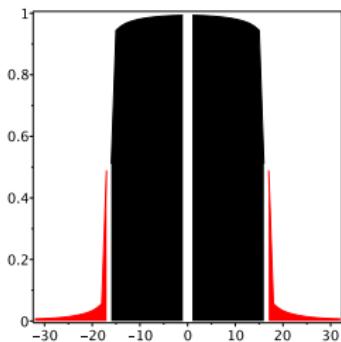
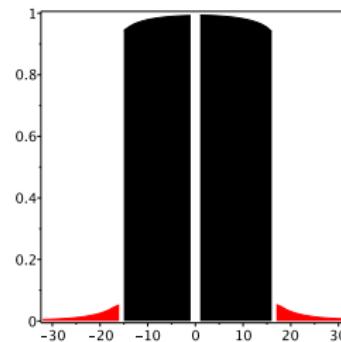
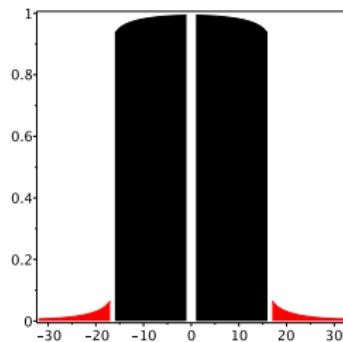
	HOMO	LUMO
ground state $n_h = 2$ $n_e = 0$		
cation/anion $n_{h/e} = 1$ $\Delta n_2 = .07/.06$		
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		

## 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

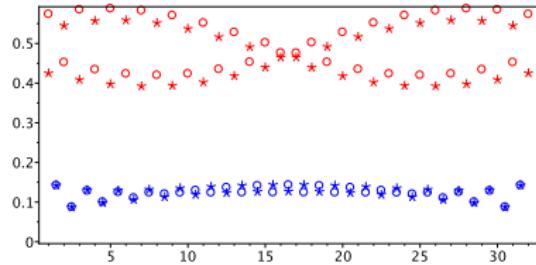
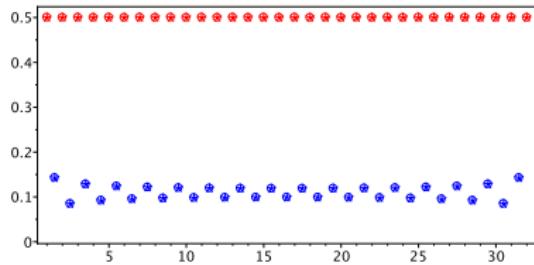
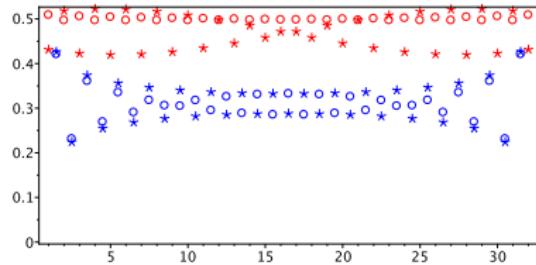
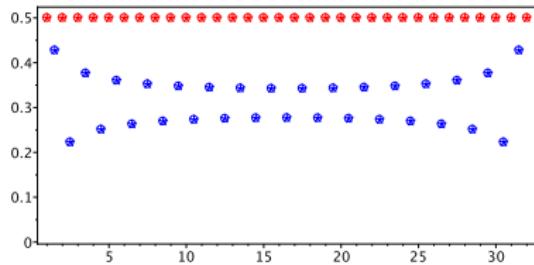
Population analysis: ground state, hole, exciton;  $U/V = 2/1$  vs  $16/4$



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:

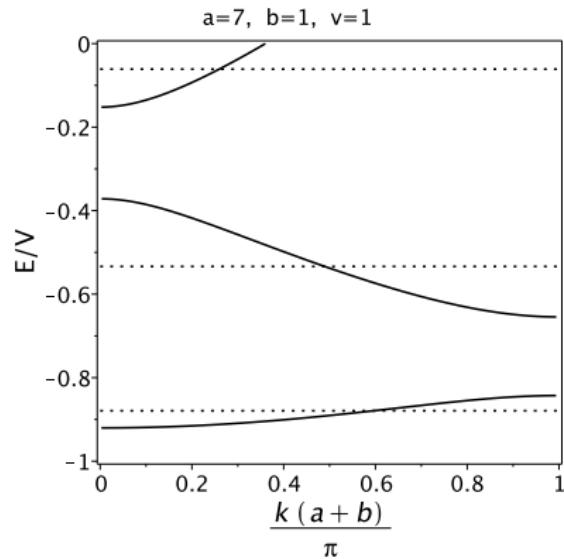
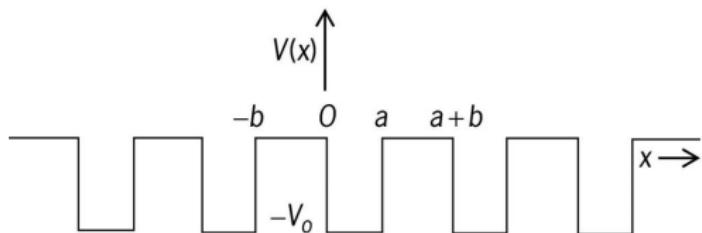
$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_n(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

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

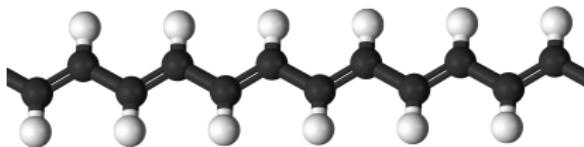
$$\mathbf{b}_i = e_{ijk} \frac{2\pi}{v} (\mathbf{a}_j \times \mathbf{a}_k)$$

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

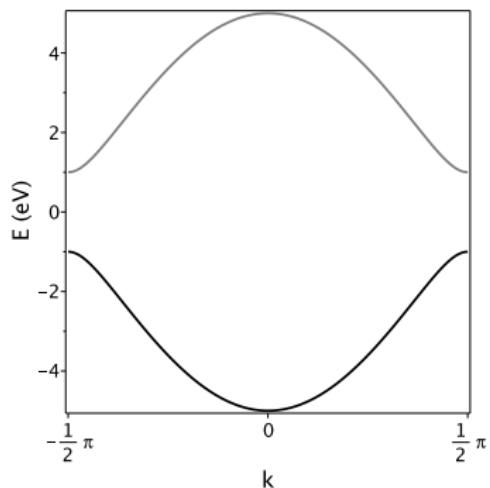


$$H = \begin{pmatrix} \dots & & & \\ & 0 & -t_1 & 0 \\ & -t_1 & 0 & -t_2 \\ & 0 & -t_2 & 0 \\ & & & \dots \end{pmatrix}$$

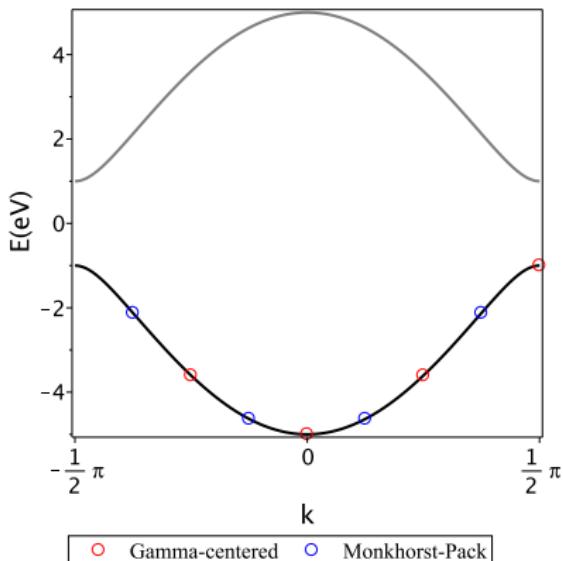
$$\psi_n = c_{1,2} e^{ikn}, \quad n \in \mathbb{Z}, \quad |k| \leq \pi/2$$

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

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

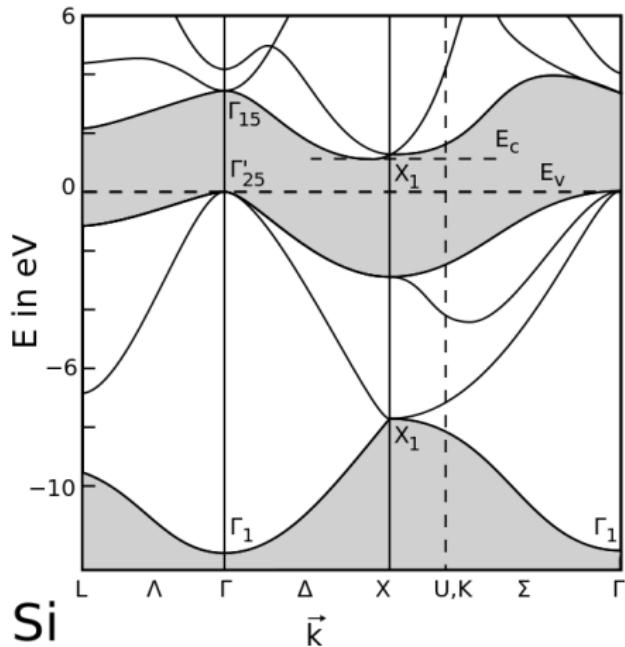


## Example 2: Total $\pi$ -electron energy of trans-polyacetylene

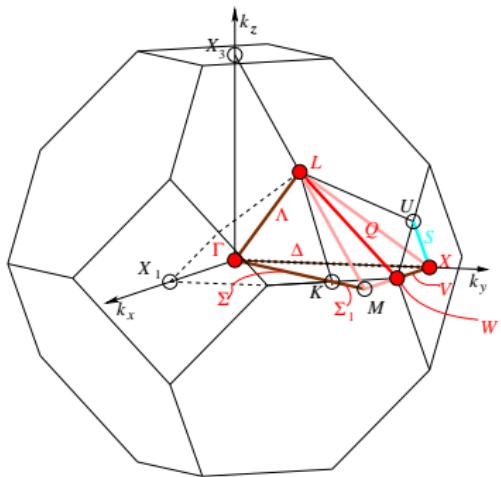


Total electronic energy  $\mathcal{E} = \frac{2}{\pi} \int_0^{\pi/2} E(k) dk = -3.34$   
4x supercell **-3.30**

## Example 3: Silicon crystal

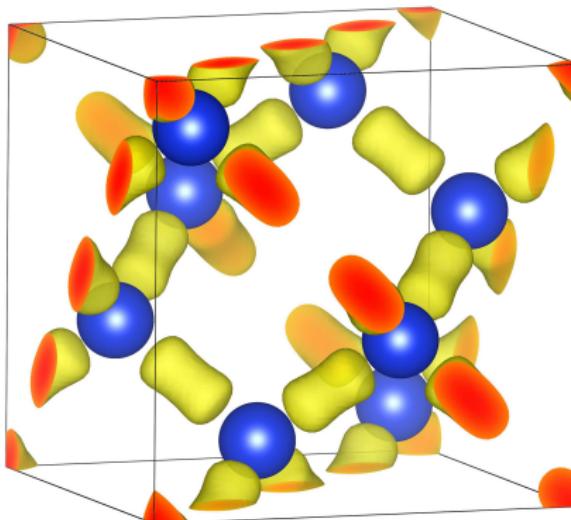


Band structure of Si



Brillouin zone for Fm-3m

## Silicon crystal: charge density



# 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