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3.23 Electrical, Optical, and Magnetic Properties of Materials

Fall 2007

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3.23 Fall 2007 – Lecture 10

TIGHT-BINDING

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Last time

1. Explicit solution for the Bloch orbitals
2. Free electrons
3. Band structure of free electron vs. silicon
4. Band edges
5. $\Psi_{nk}(r)$ is not a momentum eigenstate
6. Group velocity, effective mass
7. Fermi energy, Fermi surface

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Study

- Chap. 4 Singleton

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Plane wave expansion

$$\psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}) \exp(i\vec{k} \cdot \vec{r})$$

periodic u is expanded in planewaves, labeled according to the reciprocal lattice vectors

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\vec{G} \cdot \vec{r})$$

Explicit solution for the Bloch orbitals

$$\left(\frac{\hbar^2 (q-G')^2}{2m} - E \right) C_{q-G'} + \sum_{\vec{G}'} V_{G'-G'} C_{q-G'} = 0$$

$$\begin{pmatrix} \frac{\hbar^2}{2m}(q-2G)^2 & V_{-G} & V_{-2G} & V_{-3G} & V_{-4G} \\ V_G & \frac{\hbar^2}{2m}(q-G)^2 & V_{-G} & V_{-2G} & V_{-3G} \\ V_{2G} & V_G & \frac{\hbar^2}{2m}(q)^2 & V_{-G} & V_{-2G} \\ V_{3G} & V_{2G} & V_G & \frac{\hbar^2}{2m}(q+G)^2 & V_{-G} \\ V_{4G} & V_{3G} & V_{2G} & V_G & \frac{\hbar^2}{2m}(q+2G)^2 \end{pmatrix} \begin{pmatrix} C_{q-2G} \\ C_{q-G} \\ C_q \\ C_{q+G} \\ C_{q+2G} \end{pmatrix} = E \begin{pmatrix} C_{q-2G} \\ C_{q-G} \\ C_q \\ C_{q+G} \\ C_{q+2G} \end{pmatrix}$$

What choice for a basis ?

- For molecules: often atomic orbitals, or localized functions as Gaussians
- For solids, periodic functions such as sines and cosines (plane waves)

The plane waves basis set

- Systematic improvement of completeness/resolution
- Huge number of basis elements – only possible because of pseudopotentials
- Allows for easy evaluation of gradients and Laplacian
- Kinetic energy in reciprocal space, potential in real space
- Basis set does not depend on atomic positions: there are no Pulay terms in the forces

Hamiltonian in the Bloch representation

$$\psi_k = e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})$$

$$-\frac{\hbar^2}{2m} \nabla^2 (e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})) + V e^{i\vec{k}\cdot\vec{r}} u_k = E e^{i\vec{k}\cdot\vec{r}} u_k$$

$$\nabla^2 (e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})) = \vec{\nabla} \cdot (e^{i\vec{k}\cdot\vec{r}} \nabla u_k + ik e^{i\vec{k}\cdot\vec{r}} u_k)$$

$$= (e^{i\vec{k}\cdot\vec{r}} \nabla^2 u_k + \nabla u_k \cdot (ik) e^{i\vec{k}\cdot\vec{r}} + (ik)(ik) e^{i\vec{k}\cdot\vec{r}} u_k)$$

$$\frac{\hbar^2}{2m} (\nabla^2 u_k + 2ik \nabla u_k - k^2 u_k) + V u_k = E u_k$$

$$-\frac{\hbar^2}{2m} (\sigma + ik)^2 u_k + V u_k = E u_k$$

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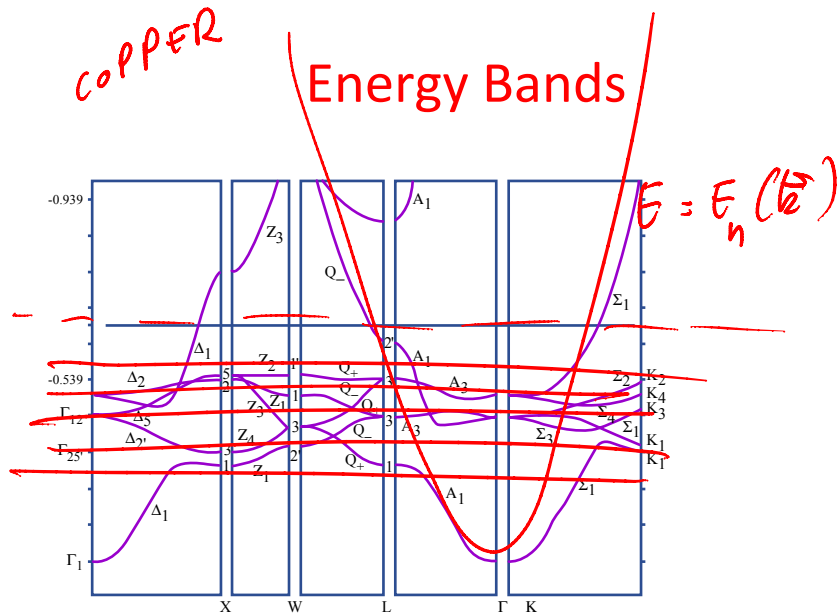


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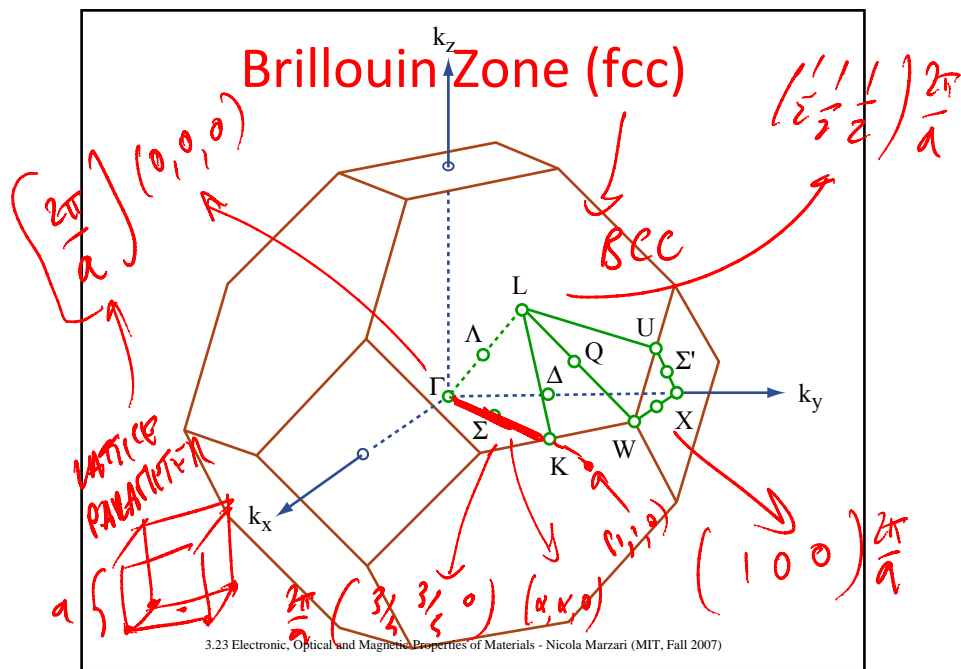


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The Fermi surface

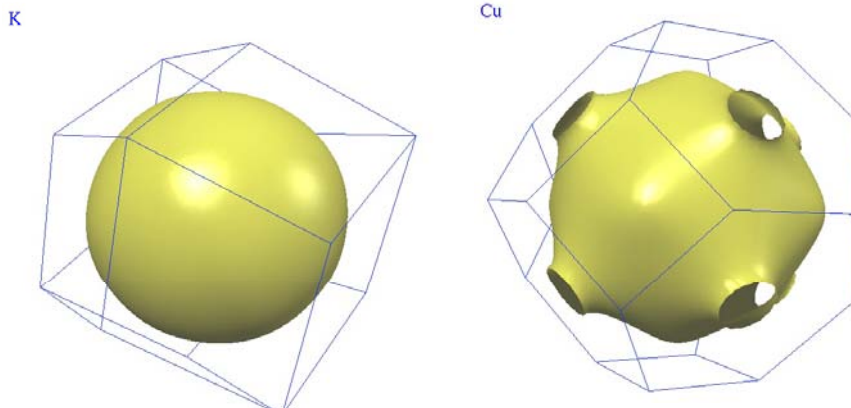
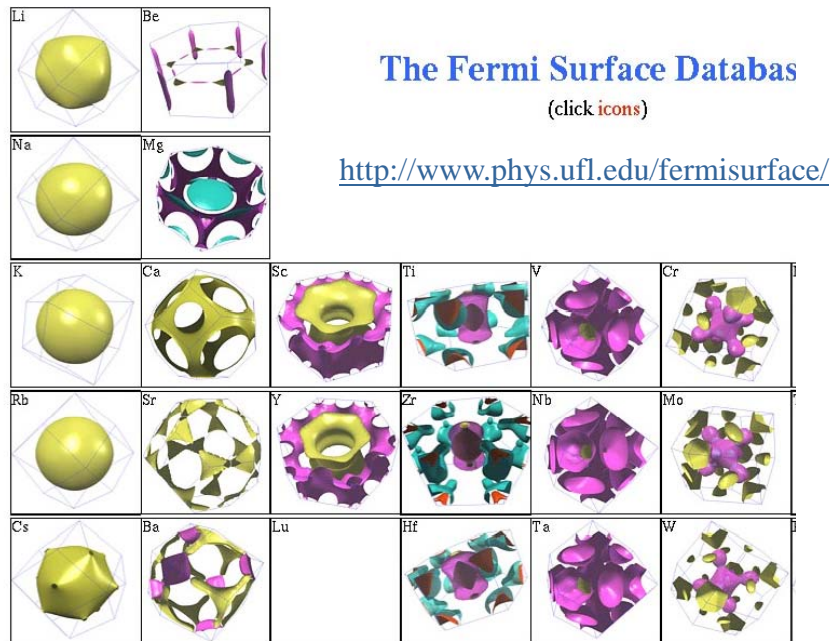


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<http://www.phys.ufl.edu/fermisurface/jpg/Cu.jpg>.



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Energy of a collection of atoms

$$\hat{H} = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{e-N} + V_{N-N}$$

$$\hat{T}_e = -\frac{1}{2} \sum_i \nabla_i^2 \quad \hat{V}_{e-N} = \sum_i \left[\sum_I V(\vec{R}_I - \vec{r}_i) \right] \quad \hat{V}_{e-e} = \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

- T_e : quantum kinetic energy of the electrons
- V_{e-e} : electron-electron interactions
- V_{e-N} : electrostatic electron-nucleus attraction (electrons in the field of all the nuclei)
- V_{N-N} : electrostatic nucleus-nucleus repulsion

Molecules and Solids: Electrons and Nuclei

$$\hat{H}\psi(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_1, \dots, \vec{R}_N) = E_{tot}\psi(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_1, \dots, \vec{R}_N)$$

- We treat only the electrons as quantum particles, in the field of the fixed (or slowly varying) nuclei
- This is generically called the **adiabatic** or **Born-Oppenheimer** approximation
- “Adiabatic” means that there is no coupling between different electronic surfaces; “B-O” implies there is no influence of the ionic motion on one electronic surface

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Complexity of the many-body Ψ

“...Some form of approximation is essential, and this would mean the construction of tables. The tabulation function of one variable requires a page, of two variables a volume and of three variables a library; but the full specification of a single wave function of neutral iron is a function of 78 variables. It would be rather crude to restrict to 10 the number of values of each variable at which to tabulate this function, but even so, full tabulation would require 10^{78} entries.”

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Mean-field approach

- Independent particle model (Hartree): each electron moves in an effective potential, representing the attraction of the nuclei and the average effect of the repulsive interactions of the other electrons
- This average repulsion is the electrostatic repulsion of the average charge density of all other electrons

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Hartree Equations

The Hartree equations can be obtained directly from the variational principle, once the search is restricted to the many-body wavefunctions that are written – as above – as the product of single orbitals (i.e. we are working with independent electrons)

$$\psi(\vec{r}_1, \dots, \vec{r}_n) = \varphi_1(\vec{r}_1) \varphi_2(\vec{r}_2) \cdots \varphi_n(\vec{r}_n)$$

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$$\left[-\frac{1}{2} \nabla_i^2 + \sum_l V(\vec{R}_l - \vec{r}_i) + \sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \epsilon \varphi_i(\vec{r}_i)$$

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The self-consistent field

- The single-particle Hartree operator is self-consistent ! It depends on the orbitals that are the solution of all other Hartree equations
- We have n simultaneous integro-differential equations for the n orbitals
- Solution is achieved iteratively

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_l V(\vec{R}_l - \vec{r}_i) + \sum_{j \neq i} \int |\varphi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_j - \vec{r}_i|} d\vec{r}_j \right] \varphi_i(\vec{r}_i) = \varepsilon \varphi_i(\vec{r}_i)$$

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Iterations to self-consistency

- Initial guess at the orbitals
- Construction of all the operators
- Solution of the single-particle pseudo-Schrodinger equations
- With this new set of orbitals, construct the Hartree operators again
- Iterate the procedure until it (hopefully) converges

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What's missing

- It does not include correlation
- The wavefunction is not antisymmetric
- It does remove $n!$ accidental degeneracy of the hydrogenoid atoms

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Spin-Statistics

- All elementary particles are either **fermions** (half-integer spins) or **bosons** (integer)
- A set of identical (indistinguishable) fermions has a wavefunction that is antisymmetric by exchange

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_j, \dots, \vec{r}_k, \dots, \vec{r}_n) = -\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_k, \dots, \vec{r}_j, \dots, \vec{r}_n)$$

- For bosons it is symmetric

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Slater determinant

- An antisymmetric wavefunction is constructed via a Slater determinant of the individual orbitals (instead of just a product, as in the Hartree approach)

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1) \\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n) \end{vmatrix}$$

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Pauli principle

- If two states are identical, the determinant vanishes (i.e. we can't have two electrons in the same quantum state)

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Hartree-Fock Equations

The Hartree-Fock equations are, again, obtained from the variational principle: we look for the minimum of the many-electron Schroedinger equation in the class of all wavefunctions that are written as a single Slater determinant

$$\psi(\vec{r}_1, \dots, \vec{r}_n) = \|\text{Slater}\|$$

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_l V(\vec{R}_l - \vec{r}_i) \right] \varphi_\lambda(\vec{r}_i) +$$

$$\left[\sum_{\mu \neq \lambda} \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \right] \varphi_\lambda(\vec{r}_i) -$$

$$\sum_{\mu} \left[\int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] \varphi_\mu(\vec{r}_i) = \varepsilon \varphi_\lambda(\vec{r}_i)$$

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Koopmans' Theorems

- Total energy is invariant under unitary transformations
- It is not the sum of the canonical MO orbital energies
- Ionization energy, electron affinity are given by the eigenvalue of the respective MO, in the frozen orbitals approximation

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What is missing

- Correlations (by definition !)
 - **Dynamical correlations**: the electrons get too close to each other in H.-F.
 - **Static correlations**: a single determinant variational class is not good enough
- Spin contamination: even if the energy is correct (variational, quadratic) other properties might not (e.g. the UHF spin is an equal mixture of singlet and triplet)

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Linear Combination of Atomic Orbitals

- Most common approach to find out the ground-state solution – it allows a meaningful definition of “hybridization”, “bonding” and “anti-bonding” orbitals.
- Also known as LCAO, LCAO-MO (for molecular orbitals), or tight-binding (for solids)
- Trial wavefunction is a linear combination of atomic orbitals – **the variational parameters are the coefficients**:

$$\Psi_{trial} = \sum_{I,(nlm)} c^I_{(nlm)} \Psi^I_{(nlm)}(\vec{r} - \vec{R}_I)$$

$$E_{LCAO} = \min \frac{\langle \Psi_{trial} | \hat{H} | \Psi_{trial} \rangle}{\langle \Psi_{trial} | \Psi_{trial} \rangle}$$

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Hückel approach

- Hückel: Planar / quasi-planar systems with delocalized π bonding: two parameters
 - α : matrix element between same orbital
 - β : matrix element between neighboring orbitals
 - Hamiltonian between further neighbors is 0

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Example: Benzene (C_6H_6)

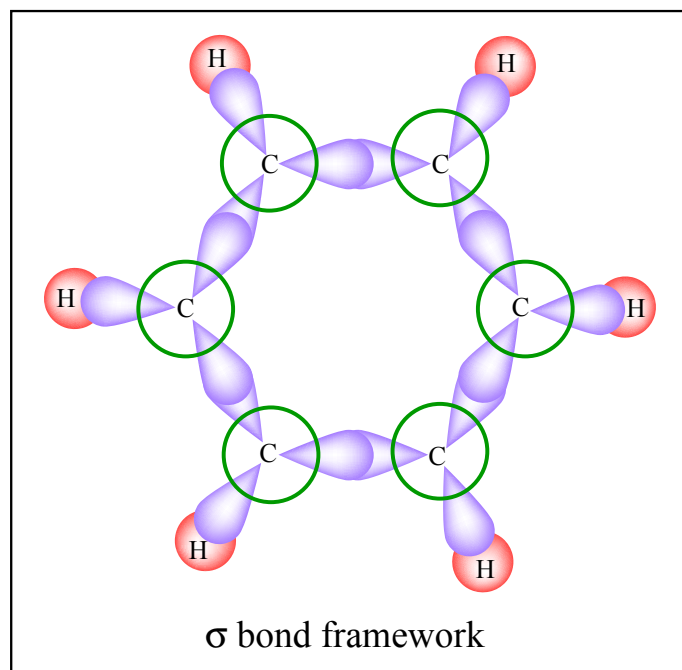
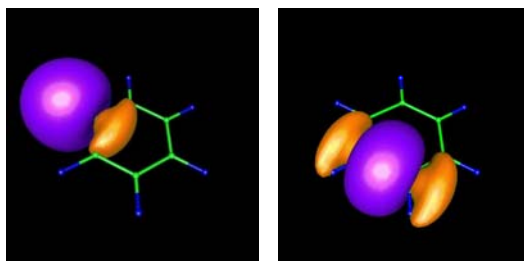
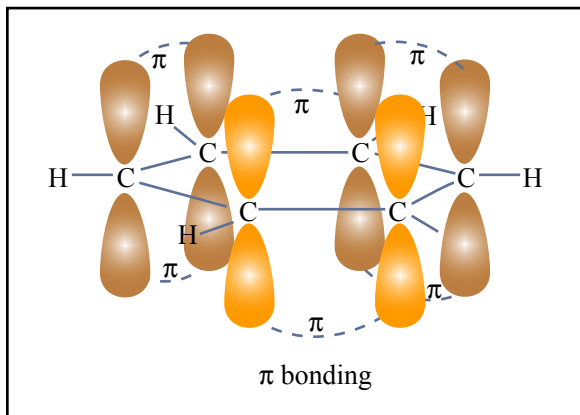


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Benzene – energy levels

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$$\det \begin{pmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{pmatrix} = 0$$

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Benzene – molecular orbitals

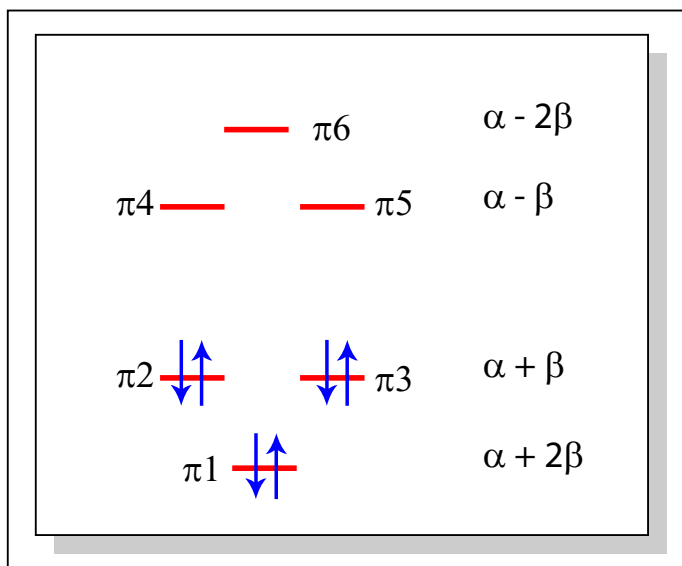


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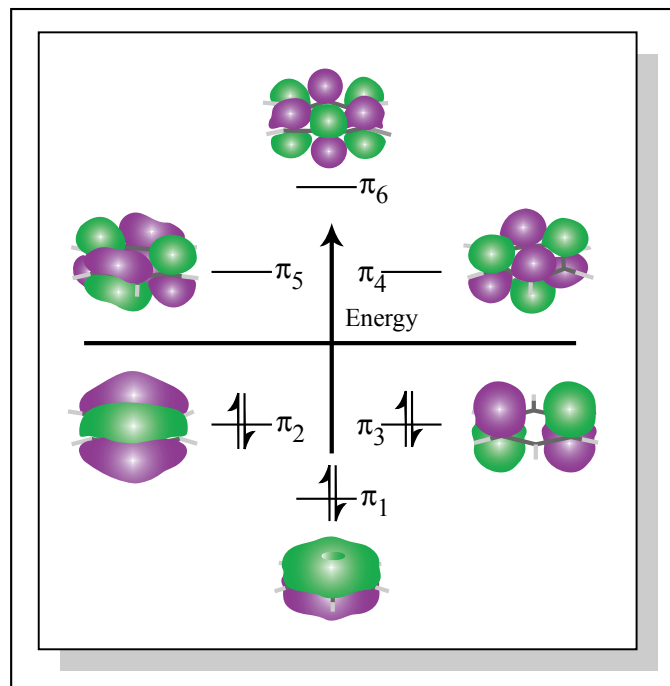


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Tight-binding (LCAO for solids)

- Hamiltonian $\hat{H} = \hat{H}_{at}^{(0)} + \Delta\hat{U}(\vec{r})$



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