Lecture 8

Band structure of p-orbitals

Let us consider situation when atomic orbitals are degenerate. The simplest case is the p-orbitals with angular momentum $l = 1$. This is 3-fold degenerate state with the wave function of the form

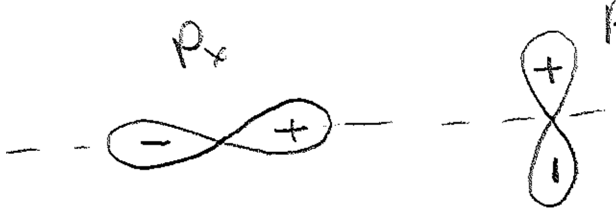
$$\psi_x(r) = x f(r), \quad \psi_y(r) = y f(r), \quad \psi_z(r) = z f(r),$$

with $f(r)$ - rotation symmetric function.

We consider a simple cubic lattice, then these orbitals remain degenerate,

$$E_x = E_y = E_z = E_p$$

For nearest neighbor coupling orbitals with different symmetry do not mix

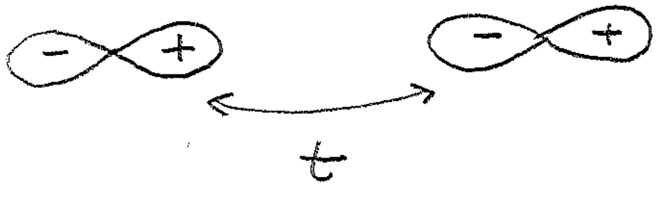


$t_{xy} = 0$

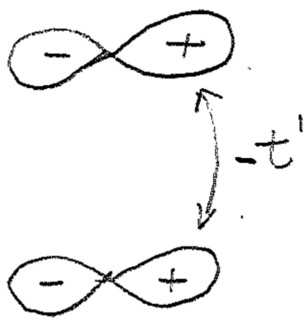
Rotation by 180° will change sign of p_y orbital and should change sign of the coupling $\Rightarrow t_{xy} = 0$

Coupling between the same kind of orbitals can be of two types

σ - bonding



π - bonding



π - bonding coupling is usually weaker than the σ - bonding and of the opposite sign. The sign difference is due to the fact that "overlapping" parts of the wave functions have different signs for the σ-bonding and the same sign for π - bonding.

For p_x orbitals tight binding Hamiltonian has the form

$$H = E_p - \sum_{ij} t_{ij} c_i^+ c_j + h.c.$$

with $t_{ij} = t$ for nearest neighbor along the x axis and $t_{ij} = -t'$ for neighbours along y axis

Going to the Fourier space

$$c_j = \frac{1}{\sqrt{N}} \sum_k a_k e^{ik \cdot R_j}$$

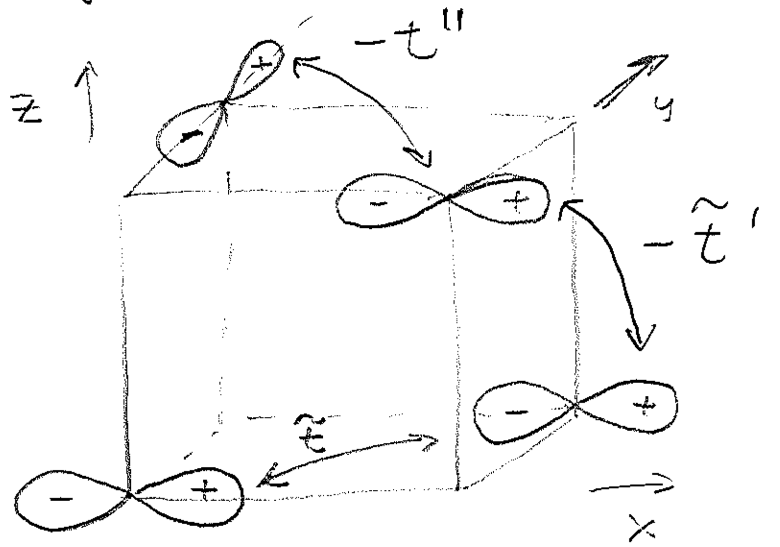
we can diagonalize it and

$$\varepsilon_x(k) = E_p + 2t\cos(k_x a) - 2t'(\cos(k_y a) + \cos(k_z a))$$

Analagous expression will be for p_y and p_z orbitals with replacing $k_x \to k_y, k_z$

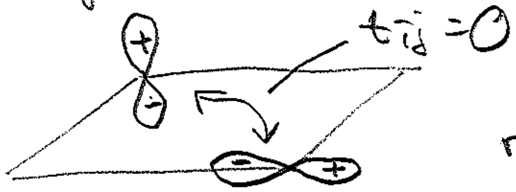
These bands do not mix in this approximation

Consider now next-nearest neighbour coupling (along the diagonal)



In this order we have two kinds of intra-band couplings $\tilde{t}$ and $-\tilde{t}'$ and inter band coupling $-t''$

No coupling is present for two orbitals where one orbital lies in the common plane and another is orthogonal to it



This is because mirror reflection in this plane changes sign of one orbital without changing sign of another.

Considering only intraband coupling we have again similar model to that studied in Lecture 5 with only difference in anisotropy of the hoppings.

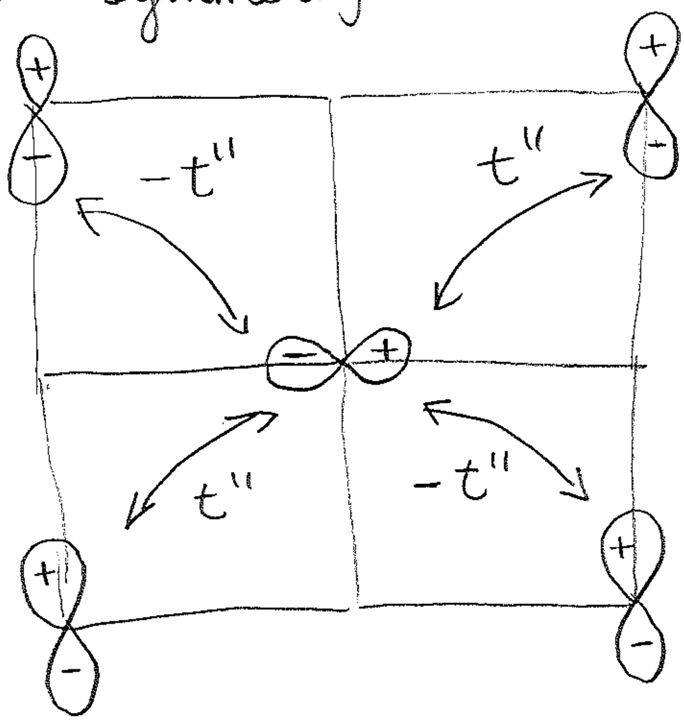
Then the bands are

$$\varepsilon_x = E_p + 2t\cos(k_x a) - 2t'\left[\cos k_y a + \cos k_z a\right]$$
$$+ 4\tilde{t}\cos(k_x a)\left[\cos(k_y a) + \cos(k_z a)\right] - 4\tilde{t}'\cos(k_y a)\cos(k_z a)$$

$\varepsilon_y = \ldots$

The products of cos are obtained from 4 diagonal couplings $\cos[(k_x + k_y)a] + \cos[(k_x - k_y)a]$

Inter band coupling mixes orbitals with different symmetry



Now the couplings between different neighbours have different sign

Then we have

$$2t''\left[\cos((k_x+k_y)a) - \cos((k_x-k_y)a)\right] a^+_{xk} a_{yk}$$

$$= -4t'' \sin k_x a \sin k_y a \; a^+_{xk} a_{yk}$$

Here a_{xk}, a_{yk} are annihilation operators for p_x and p_y orbitals

The resulting Hamiltonian can be presented in the matrix form

$$H = \sum_k \begin{pmatrix} a^+_{xk} \\ a^+_{yk} \\ a^+_{zk} \end{pmatrix}' \hat{\mathcal{H}} \begin{pmatrix} a_{xk} \\ a_{yk} \\ a_{zk} \end{pmatrix}$$

with

$$\hat{\mathcal{H}} = \begin{pmatrix} \varepsilon_x(k) & -4t'' \sin(k_x a) \sin(k_y a) & -4t'' \sin(k_x a) \sin(k_z a) \\ -4t'' \sin k_x a \sin k_y a & \varepsilon_y(k) & -4t'' \sin(k_y a) \sin(k_z a) \\ -4t'' \sin(k_x a) \sin(k_z a) & -4t'' \sin(k_y a) \sin(k_z a) & \varepsilon_z(k) \end{pmatrix}$$

with $\varepsilon_x, \varepsilon_y, \varepsilon_z$ from the page 4

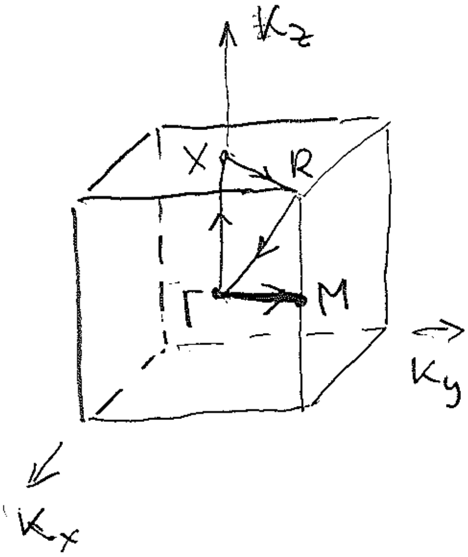
To diaganlize it

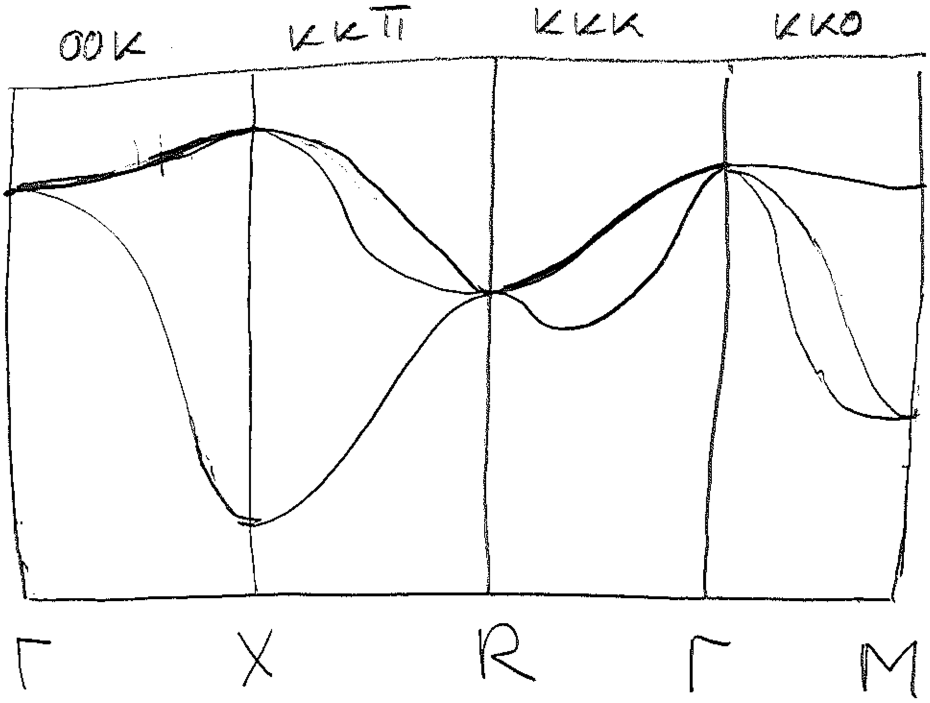
$$\tilde{\mathcal{H}} \begin{pmatrix} a_{xk} \\ a_{yk} \\ a_{zk} \end{pmatrix} = E \begin{pmatrix} a_{xk} \\ a_{yk} \\ a_{zk} \end{pmatrix}$$

we should find determinant $|\mathcal{H} - E| = 0$

$$\begin{vmatrix} \varepsilon_x(k) - E & -4t'' \sin(k_x a) \sin(k_y a) & -4 \sin(k_x a) \sin(k_z a) \\ -4t'' \sin(k_x a) \sin(k_y a) & \varepsilon_y(k) - E & -4t'' \sin(k_y a) \sin(k_z a) \\ -4t'' \sin(k_x a) \sin(k_z a) & -4t'' \sin(k_y a) \sin(k_z a) & \varepsilon_z(k) - E \end{vmatrix}$$

Numerical solution gives the following plot.





Here we go along the line $\Gamma - X - R - \Gamma - M$ in the Brillouin zone with parameters $t' = 0.2t$, $\tilde{t} = 0.1t$, $\tilde{t}' = 0.05t$, $t'' = 0.15t$

Although we cannot find spectrum everywhere analytically for special directions of $\vec{k}$ something can be understood. For example along the $\Gamma - X$ line $\vec{k} = (k_z, 0, 0)$. Then nondiagonal terms $\sin(k_i a)\sin(k_j a)$ are absent, bands do not mix and we have

$$E_x = E_y = \mathcal{E}_x = \mathcal{E}_y = E_p + 2t - 2t'\left[1 + \cos(k_z a)\right] +$$
$$+ 4\tilde{t}\left[1 + \cos(k_z a)\right] - 4\tilde{t}' \cos(k_z a).$$

$$E_z = \mathcal{E}_z = E_p + 2t\cos(k_z a) - 2t' +$$
$$+ 8\tilde{t}\cos(k_z a) - 4\tilde{t}'$$

Thus we have two-fold degeneracy for p_x, p_y orbitals with separated p_z orbital

In the center of the Brillouin zone $K=0$

Then again there is no interband mixing

$\sin k_i a = 0$ and all $\cos k_i a = 1 \Rightarrow$

$E_x = E_y = E_z$ and we have 3-fold degeneracy

The same happens at R point where

$K_x = K_y = K_z = \frac{\pi}{a}$. Here $\sin k_i a = 0$, $\cos k_i a = -1$

Along the R−Γ diagonal line $K_x = K_y = K_z = K$

$\mathcal{E}_x = \mathcal{E}_y = \mathcal{E}_z = \mathcal{E}(k)$ and determinant

$$\begin{vmatrix} \delta\mathcal{E} & g & g \\ g & \delta\mathcal{E} & g \\ g & g & \delta\mathcal{E} \end{vmatrix} = 0$$

with $g = -4t^4 \sin^2(ka)$

$\delta\mathcal{E} = \mathcal{E}(k) - E$

$$\delta\mathcal{E}^3 - 3\delta\mathcal{E}^2 g + 2g^3 = 0$$

$$(\delta\mathcal{E} - g)^2 (\delta\mathcal{E} + 2g)$$

Thus we have doubly degenerate level

$\delta\mathcal{E} = g$ and nondegerate $\delta\mathcal{E} = -2g$

The degeneracy of the levels can be understood from the general group representation theory

Cubic group has the following elements

$6\ C_4$ – rotation by 90° about x, y, z axes

$3\ C_2 = 3\ C_4^2$ – rotations by 180° about x, y, z axes

$6\ C_2'$ – rotations by 180° about diagonals of the square

$8\ C_3$ – 120° rotations about cube diagonal

1 unity

Total 5 classes. Thus – 5 irreducable representations. The character table

O	I	$6C_4$	$3C_2 = 3C_4^2$	$6C_2'$	$8C_3$
A_1	1	1	1	1	1
A_2	1	−1	1	−1	1
E	2	0	2	0	−1
F_1	3	1	−1	−1	0
F_2	3	−1	−1	1	0

One dimensional representations can be easily obtained from symmetrizing A_1 and B_1 for the group of square D_4 considered in the Lecture 7. Their basis functions behave as

$x^4 + y^4 + z^4$ for A_1 and

$(x^2-y^2)(y^2-z^2)(x^2-z^2)$ for A_2

3-dimensional representations behave as (x, y, z) and the same multiplied by A_2. The 2-d representation can be found from orthogonality relations.

Now consider different points of the Brillouin zone. Having additional vector $\vec{k}$ in the problem the point group is reduced to those operations that preserve the wave vector $\vec{k}$. It is called <u>small point group</u>.

At Γ point $\vec{k} = 0$ and we have full cubic symmetry thus 3-fold degeneracy. Along the $\Gamma - X$ line the small point group is tetragonal D_4 that has 2 dimensional representation $\Rightarrow$ 3-fold degeneracy is split to 2-fold (x, y) and (z).

Along the $\Gamma - R$ line the point group is D_3 considered in the last lecture. It also has 2-dimensional representation thus 2 fold degeneracy. At R point symmetry is again cubic since all diagonals are differerent by $\left(\frac{2\pi}{a}, \frac{2\pi}{a}, 0\right)$ thus equivalent $\Rightarrow$ 3 fold degeneracy. For other directions of $\vec{k}$ the symmetry is lowered to the groups that have only one dimensional representations $\Rightarrow$ nondegenerate levels.