PY4T01 Condensed Matter Theory: Lecture 7

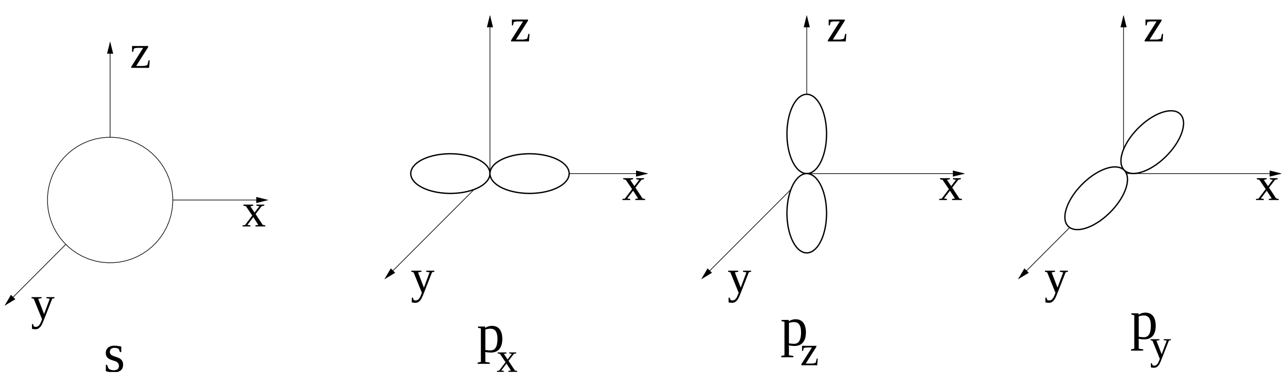
Including more molecular orbitals: Tight-binding method

Consider an infinite chain of C atoms.

Atomic C: $2s^2 2p^2$

In most solids C: $2s^1 2p^3$

It means that both the s and p states are relevant!!!



We can then expand our molecular state $|\psi\rangle$ as follows

$$|\psi\rangle = \sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha} |j\alpha\rangle$$

where $|j\alpha\rangle$ is the molecular orbital α of the atom j

So the Schrödinger equation takes the form

$$\sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha} H|j\alpha\rangle = E \sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha}|j\alpha\rangle$$

Again multiplying by $\langle l\beta|$

$$\sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha} \langle l\beta|H|j\alpha\rangle = E \sum_j^N \sum_\alpha^{N_\alpha} \psi_{j\alpha}\langle l\beta|j\alpha\rangle$$

Since translational symmetry, we can apply Bloch's Theorem:

$$\psi_{j\alpha} = A_\alpha \mathrm{e}^{iKj}$$

So we obtain the secular equation:

$$\sum_j^N \sum_\alpha^{N_\alpha} A_\alpha \mathrm{e}^{iKj} \langle l\beta|H|j\alpha\rangle = E \sum_j^N \sum_\alpha^{N_\alpha} A_\alpha \mathrm{e}^{iKj}\langle l\beta|j\alpha\rangle$$

Atomic orbital with $l > 0$

The hydrogen atom wave-function are:

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi)$$

Note that:

- $R_{nl}(r)$ are real functions
- $Y_{lm}(\theta,\phi)$ may be complex

For instance for $n = 2$, $l = 1$ we have

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \, \mathrm{e}^{\pm i\phi}$$

It is usually convenient to work with a linear combination of the spherical harmonics:

$$\Psi_{n1m}(r,\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n1}(r) \left\{ \begin{array}{l} x/r \\ y/r \\ z/r \end{array} \right.$$

Note that these orbitals have an odd parity (change sign under inversion)

Let us now calculate the matrix elements

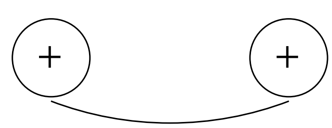
Orthogonal basis set:

$$\langle l\beta | j\alpha \rangle = \delta_{\alpha\beta}\delta_{lj}$$

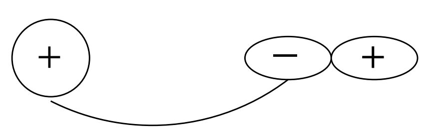
Nearest-neighbors interaction

$$\langle l\beta | H | j\alpha \rangle = \begin{cases} \text{If} \;\; j = l & \begin{cases} \epsilon_\alpha & \text{for} \quad \alpha = \beta \\ 0 & \text{for} \quad \alpha \neq \beta \end{cases} \\ \\ \text{If} \;\; j = l \pm 1 & \begin{cases} \gamma_\alpha & \text{for} \quad \alpha = \beta \\ \gamma_{\alpha\beta} & \text{for} \quad \alpha \neq \beta \end{cases} \end{cases}$$

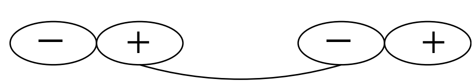
How many orbitals shall we use?



$ss\sigma$



$sp\sigma$



$pp\sigma$

Then $N_\alpha = 2$

$$\sum_j^N \sum_\alpha^{N_\alpha} A_\alpha \mathrm{e}^{iK(j-l)} \langle l\beta|H|j\alpha\rangle = EA_\beta$$

Since our hypothesis on the matrix elements

$$EA_\beta = \sum_\alpha^{N_\alpha} A_\alpha \left[\langle l\beta|H|l\alpha\rangle + \right.$$

$$\left. + \,\mathrm{e}^{iK} \langle l\beta|H|(l+1)\alpha\rangle + \mathrm{e}^{-iK} \langle l\beta|H|(l-1)\alpha\rangle + \right]$$

This can be written in a simpler matrix form

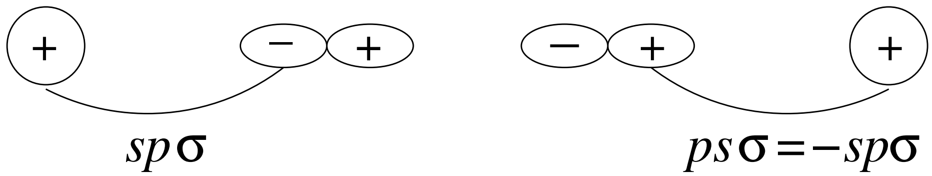
$$E \begin{pmatrix} A_s \\ A_p \end{pmatrix} = \left[\begin{pmatrix} \epsilon_s & 0 \\ 0 & \epsilon_p \end{pmatrix} + \right.$$

$$\left. + \begin{pmatrix} \gamma_{ss\sigma} & \gamma_{sp\sigma} \\ -\gamma_{sp\sigma} & \gamma_{pp\sigma} \end{pmatrix} \mathrm{e}^{iK} + \begin{pmatrix} \gamma_{ss\sigma} & -\gamma_{sp\sigma} \\ \gamma_{sp\sigma} & \gamma_{pp\sigma} \end{pmatrix} \mathrm{e}^{-iK} \right] \begin{pmatrix} A_s \\ A_p \end{pmatrix}$$

which reduces to

$$\begin{pmatrix} \epsilon_s + 2\gamma_{ss\sigma}\cos K & 2i\gamma_{sp\sigma}\sin K \\ -2i\gamma_{sp\sigma}\sin K & \epsilon_p + 2\gamma_{pp\sigma}\cos K \end{pmatrix} \begin{pmatrix} A_s \\ A_p \end{pmatrix} = E \begin{pmatrix} A_s \\ A_p \end{pmatrix}$$

Note that:

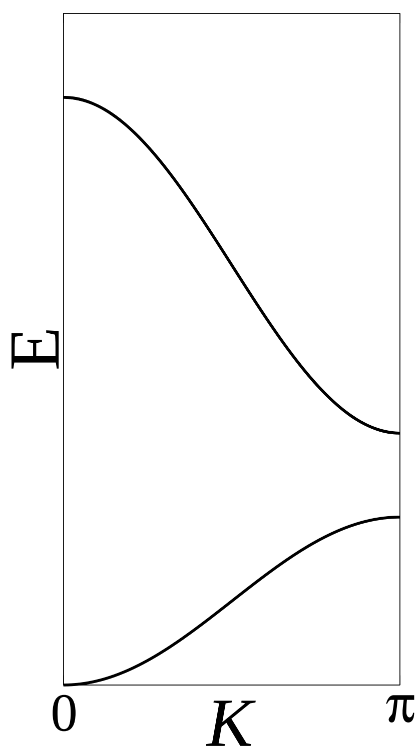


Simple solution: $\gamma_{sp\sigma} = 0$

Then

$$E = \begin{cases} \epsilon_s + 2\gamma_{ss\sigma}\cos K = \epsilon_s(K) \\ \\ \epsilon_p + 2\gamma_{pp\sigma}\cos K = \epsilon_p(K) \end{cases}$$

This is equivalent to two independent chains one only with s electrons and one only with p



General Case:

One must solve the eigenvalues equation:

$$\left(\begin{array}{cc} \epsilon_s + 2\gamma_{ss\sigma}\cos K & 2i\gamma_{sp\sigma}\sin K \\ -2i\gamma_{sp\sigma}\sin K & \epsilon_p + 2\gamma_{pp\sigma}\cos K \end{array} \right) \left(\begin{array}{c} A_s \\ A_p \end{array} \right) = E \left(\begin{array}{c} A_s \\ A_p \end{array} \right)$$

which has solutions

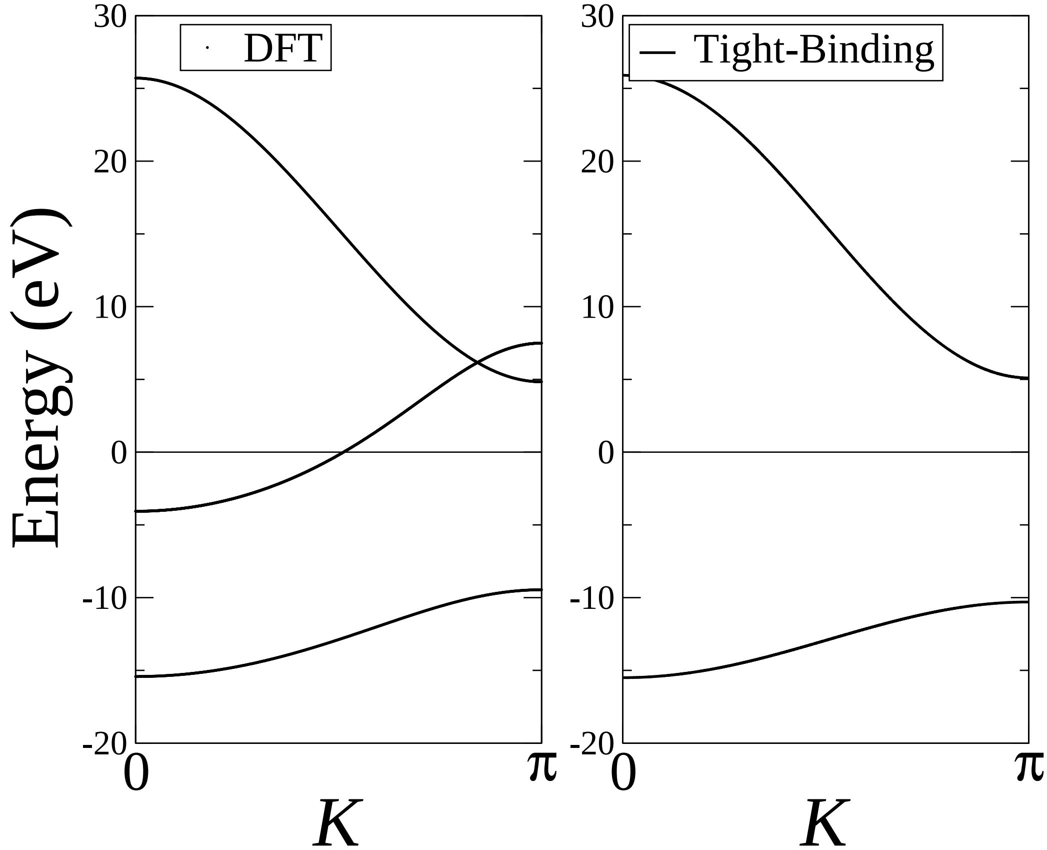
$$E = \frac{1}{2}\left[\epsilon_s(K) + \epsilon_p(K) \pm \sqrt{[\epsilon_s(K) - \epsilon_p(K)]^2 + 16\gamma_{sp\sigma}\sin^2 K}\right]$$

with

$$\epsilon_s(K) = \epsilon_s + 2\gamma_{ss\sigma}\cos K$$
$$\epsilon_p(K) = \epsilon_p + 2\gamma_{pp\sigma}\cos K$$

Note the correct limit for $\gamma_{sp\sigma} \to 0$

This work remarkably well !!!!



ϵ_s =-12.9 eV, ϵ_p =15.5 eV, $\gamma_{ss\sigma}$ =-1.3 eV, $\gamma_{pp\sigma}$ =5.2 eV, $\gamma_{sp\sigma}$ =0,5 eV

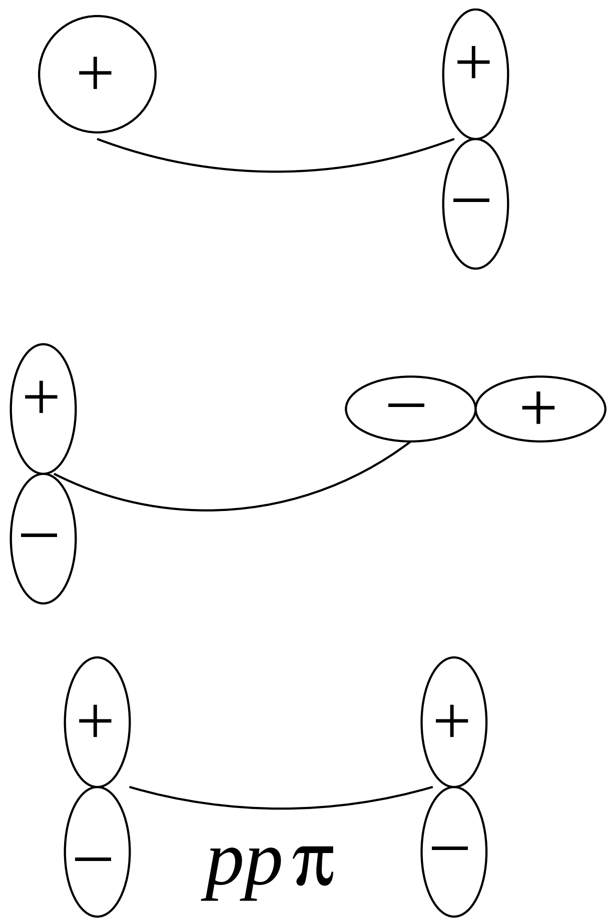
What about the remaining band?

We have to include the forgotten p_y and p_z

This gives us matrix elements such as:

$$\langle l^{p_y}|H|(l-1)^{s}\rangle\,,\quad \langle l^{p_y}|H|(l-1)^{p_x}\rangle\ \ ...$$

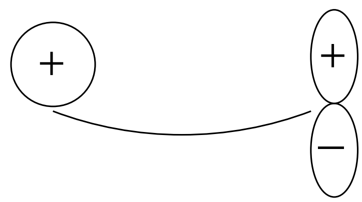
Let us see them in details. The new matrix elements are:



However only $pp\pi$ is not zero!!!

How to assign values to matrix elements?

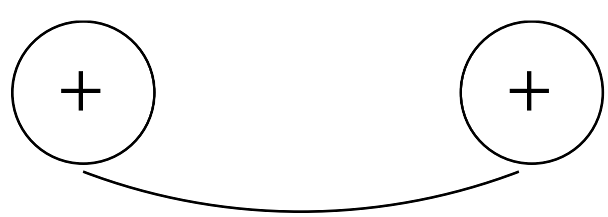
- The zeros are mostly given by symmetry



The rule is: *A matrix element* $\langle l^\beta|H|(l-1)^\alpha\rangle$ *is zero if the two atomic states at either end of the bond share the same angular momentum component about the bond axis*

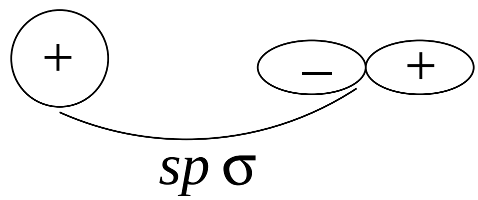
Consider a circuit of radius r around the bond axis. The length of the circuit is the $2\pi r = \lambda n$, where λ is the wave length, and n the number of time the circuit pass through two lobes with opposite sign. The linear momentum is $p = h/\lambda = nh/(2\pi r)$ The angular momentum is $pr = nh/2\pi \rightarrow m = n$

- $ss\sigma$: $\langle s|H|s\rangle < 0$

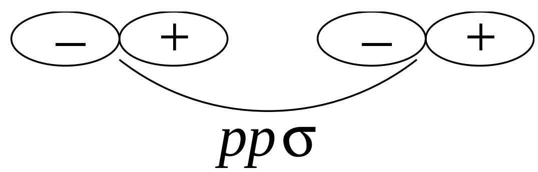


ss σ

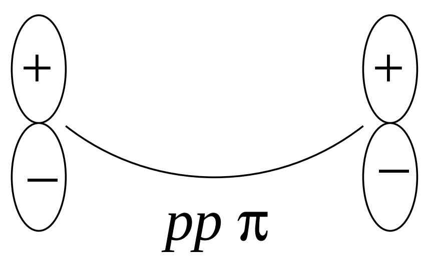
- $sp\sigma$: $\langle s|H|p_x\rangle > 0$



- $pp\sigma$: $\langle p_x|H|p_x\rangle > 0$



- $pp\pi$: $\langle p_y|H|p_y\rangle < 0$



- The amplitude of the matrix elements depends on the degree of overlap.

From this one can conclude:

1. The first band is mainly s and dominated by $ss\sigma$
2. The last band is mainly p and dominated by $pp\sigma$
3. The one in between must have something to do with p and $pp\pi$

Extension of the model

Include also p_y and p_z. Now N_α=4.

$$\sum_j^N \sum_\alpha^{N_\alpha} A_\alpha \mathrm{e}^{iK(j-l)} \langle l\beta|H|j\alpha\rangle = EA_\beta$$

Since our consideration on the overlap integrals we can write:

$$H_0 A + \mathrm{e}^{iK} H_1 A + \mathrm{e}^{-iK} H_1^\dagger A = AE$$

where now

$$A = \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \end{pmatrix} , \quad H_0 = \begin{pmatrix} \epsilon_s & 0 & 0 & 0 \\ 0 & \epsilon_{p_x} & 0 & 0 \\ 0 & 0 & \epsilon_{p_y} & 0 \\ 0 & 0 & 0 & \epsilon_{p_z} \end{pmatrix}$$

$$H_1 = \begin{pmatrix} \gamma_{ss\sigma} & \gamma_{sp\sigma} & 0 & 0 \\ -\gamma_{sp\sigma} & \gamma_{pp\sigma} & 0 & 0 \\ 0 & 0 & \gamma_{pp\pi} & 0 \\ 0 & 0 & 0 & \gamma_{pp\pi} \end{pmatrix}$$

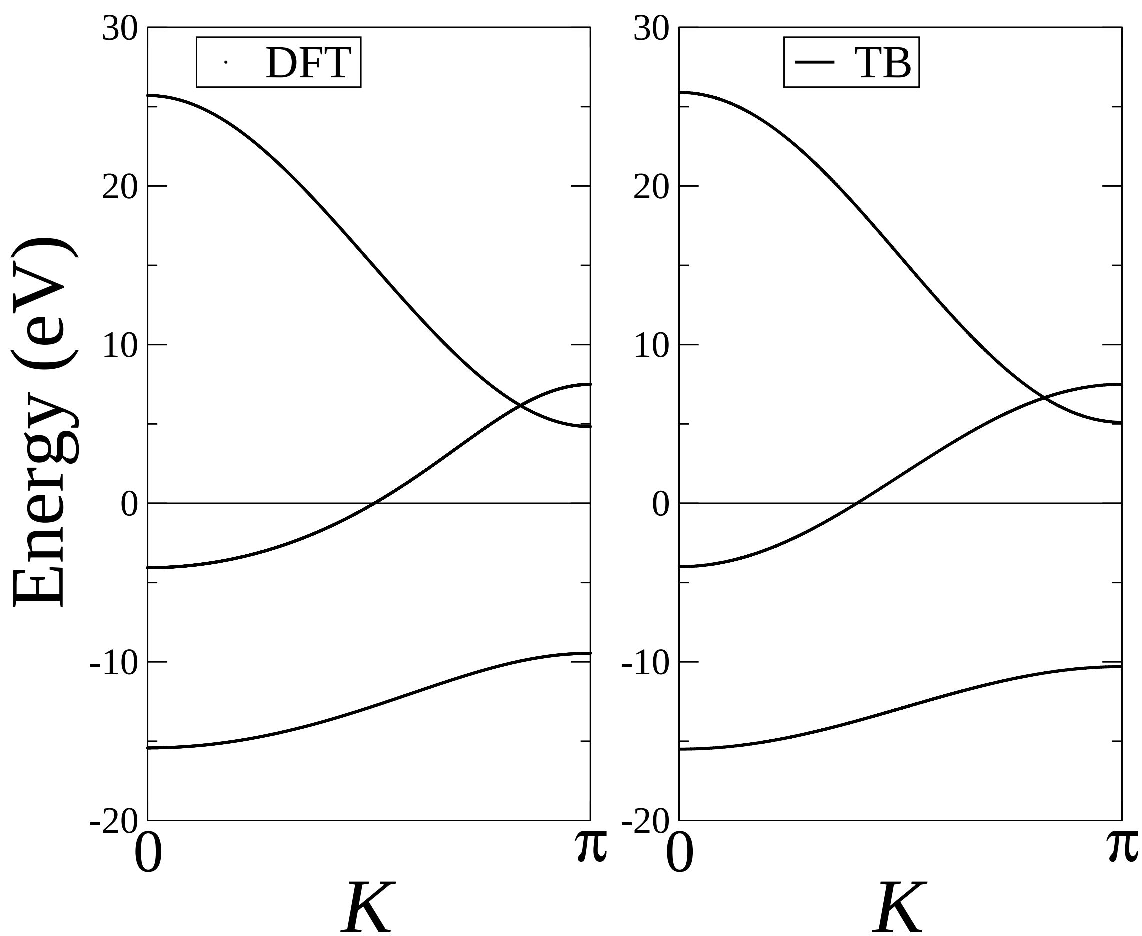
The solutions of the secular equation are:

$$E = \frac{1}{2}\left[\epsilon_s(K) + \epsilon_{p_x}(K) + \sqrt{[\epsilon_s(K) - \epsilon_{p_x}(K)]^2 + 16\gamma_{sp\sigma}\sin^2 K}\right]$$

$$E = \frac{1}{2}\left[\epsilon_s(K) + \epsilon_{p_x}(K) - \sqrt{[\epsilon_s(K) - \epsilon_{p_x}(K)]^2 + 16\gamma_{sp\sigma}\sin^2 K}\right]$$

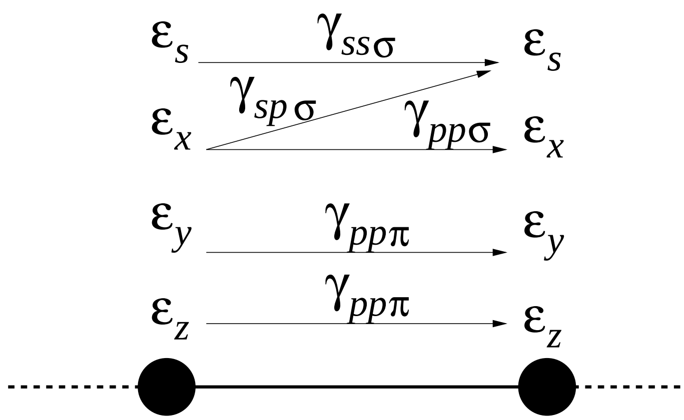
$$E = \epsilon_{p_y} + 2\gamma_{pp\pi}\cos(K)$$

$$E = \epsilon_{p_z} + 2\gamma_{pp\pi}\cos(K)$$



Constructing the secular equation

- Draw the system introducing the relevant degrees of freedom and their coupling



- The secular equation has the form:

$$[H_0 + H_1 \mathrm{e}^{ika} + H_1^\dagger \mathrm{e}^{-ika}]\Psi = E\Psi$$

where ($p_x = x$, $p_y = y$, $p_z = z$)

$$\Psi = \begin{pmatrix} A_s \\ A_x \\ A_y \\ A_z \end{pmatrix}, H_0 = \begin{pmatrix} \epsilon_s & 0 & 0 & 0 \\ 0 & \epsilon_x & 0 & 0 \\ 0 & 0 & \epsilon_y & 0 \\ 0 & 0 & 0 & \epsilon_z \end{pmatrix}$$

$$H_1 = \begin{pmatrix} \gamma_{ss\sigma} & \gamma_{sp\sigma} & 0 & 0 \\ -\gamma_{sp\sigma} & \gamma_{pp\sigma} & 0 & 0 \\ 0 & 0 & \gamma_{pp\pi} & 0 \\ 0 & 0 & 0 & \gamma_{pp\pi} \end{pmatrix}$$