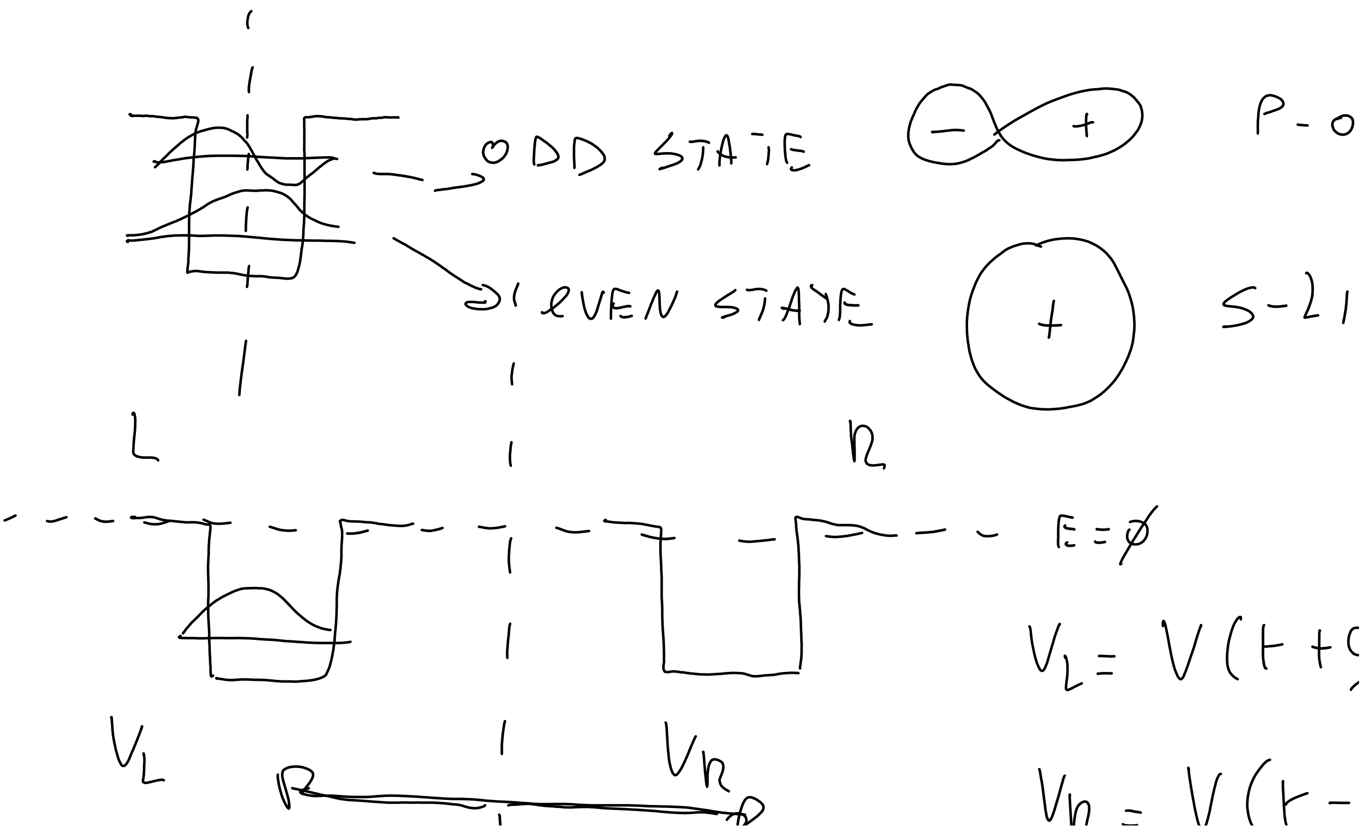
Linear Combination of Atomic Orbitals

martedì 29 ottobre 2024 17:15

Linear Combination of Atomic Orbitals

"*You don't understand any electronic structure property if you can't explain it in a 2x2* (matrix) *problem*" Manuel Cardona

- Linear combination of atomic orbitals: the LCAO approximation
- Formation of bonding and anti-bonding levels: on-site and overlap integrals
- Löwdin orthogonalization of atomic wavefunctions
- Matrix formalism of the Schrödinger equation
- Example: energy level of three coupled quantum wells



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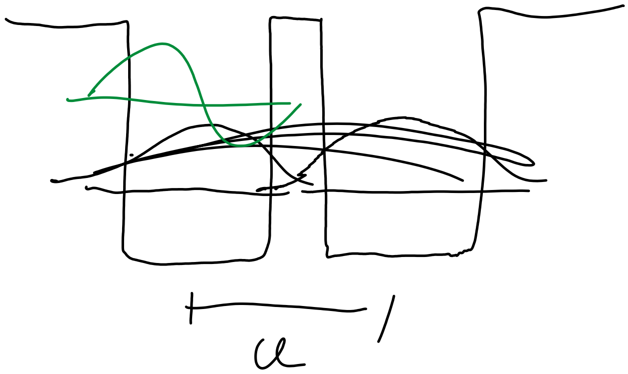
STARTING POINT
ISOLATED QW

$$(T+V)\phi_s = \varepsilon_s \phi_s$$

PROBLEM



SOLUTION $\rightarrow \psi = a_L$

$$\phi_L = \phi_s\left(r + \frac{a}{2}\right) \quad \phi$$

$$(T + V_L + V_R)(a_L \phi_L + a_R \phi_R) = E(a_L \phi_L$$

EIGEN VECTOR

EIGEN VALU

$$\int \phi_L^* \left[(T+V_L+V_R)(a_L\phi_L + a_R\phi_R)\right] dr = \int$$

$$\begin{cases} \langle \phi_L | T + V_L + V_R | a_L \phi_L + a_R \phi_R \rangle = \langle \phi_L | \\ \langle \phi_R | T + V_L + V_3 | a_L \phi_L + a_R \phi_R \rangle = \langle \phi_R | E \end{cases}$$

① $\langle \phi_L | T + V_L | a_L \phi_L \rangle = a_L \langle \phi_L \, \varepsilon_s \, \phi_L \rangle =$

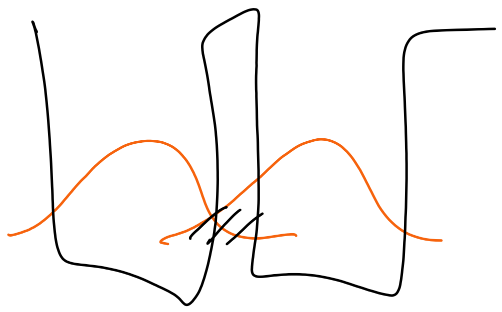
② $\langle \phi_L | V_R | a_L \phi_L \rangle = a_L \langle \phi_L | V_R | \phi_L \rangle$

$\Rightarrow \beta = -\langle \phi_L | V_R | \phi_L$

ON-SITE OVERLAP

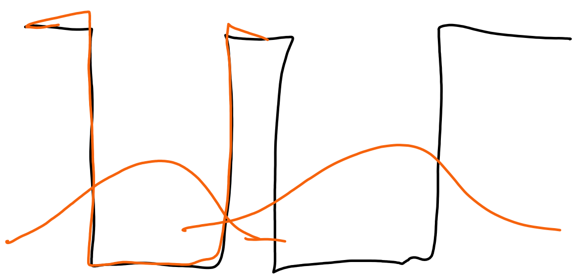
(3) $\underline{\langle \phi_L | T + V_R | a_R \phi_R \rangle} = a_R \langle \phi_L | \varepsilon_s | \phi_R$

$= a_R \varepsilon_s \langle \phi_s | \phi$



$\alpha =$ NON ORTHOGO FACTOR

(4) $\langle \phi_L | V_L | a_R \phi_R \rangle = a_R \langle \phi_L | V_L | \phi_R \rangle$



OVERLAP INTEGRA

$\gamma = -\langle \phi_L | V_L | \phi$

$\gamma > 0$

$\langle \phi_L | E | a_L \phi_L + a_R \phi_R \rangle = a_L E \langle \phi_L |$

$+ a_R E \langle \phi_L |$

(1) (2) (3) (4)

$$a_L \varepsilon_s - a_L \beta + a_R \varepsilon \partial - a_R \gamma = a_L E + a_R$$

$$\begin{cases} a_L(\varepsilon - \beta) + a_R(\partial \varepsilon - \gamma) = E a_L + a_R E \\ a_L(\partial \varepsilon - \gamma) + a_R(\varepsilon - \beta) = E a_R + a_L E \end{cases}$$

$$\partial = \emptyset$$

$$\begin{cases} a_L(\varepsilon - \beta) - \gamma a_R = E a_L \\ -a_L \gamma + a_R(\varepsilon - \beta) = E a_R \end{cases}$$

	$\lvert \phi_L \rangle$	$\lvert \phi_R \rangle$
$\langle \phi_L \rvert$	$\langle \phi_L \lvert H \rvert \phi_L \rangle$	$\langle \phi_L \lvert H \rvert \phi_R \rangle$
$\langle \phi_R \rvert$		

$$H = T + V_L$$

$$\begin{bmatrix} \varepsilon - \beta & -\gamma \\ -\gamma & \varepsilon - \beta \end{bmatrix} \begin{bmatrix} a_L \\ a_R \end{bmatrix} = E \begin{bmatrix} a_L \\ a_R \end{bmatrix}$$

EIGEN VALUE ENERGY, E

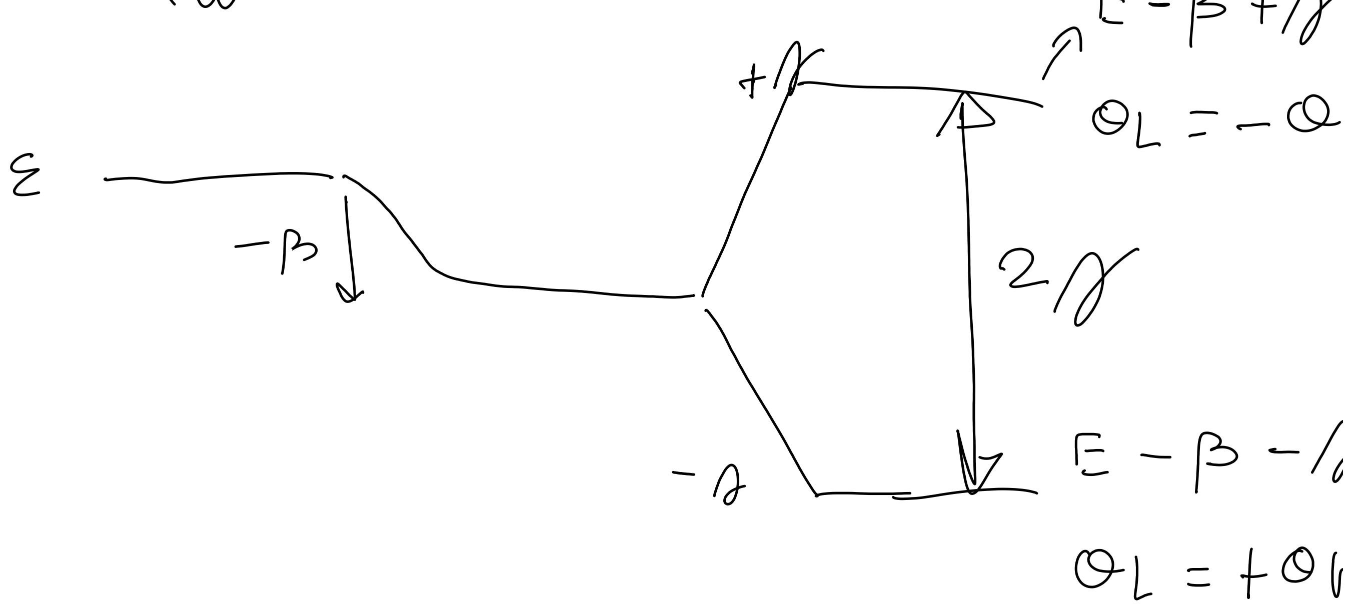
$$\det \begin{vmatrix} \varepsilon-\beta-E & -\gamma \\ -\gamma & \varepsilon-\beta-E \end{vmatrix} = \emptyset$$

$$(\varepsilon-\beta-E)^2-\gamma^2=\emptyset \qquad \varepsilon-\beta-E=\pm$$

$$E=\varepsilon-\beta\mp\gamma$$

ISOLATED QW

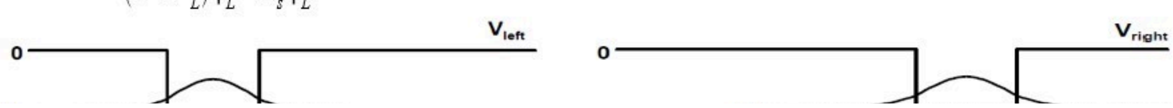
COUPLED QW

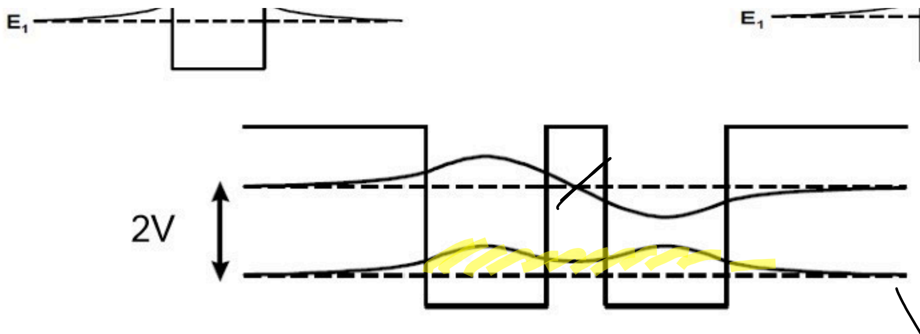


Linear combination of atomic orbitals - LCAO

In the LCAO approximation the problem of two interacting atoms (left and right) is solved by expressing the solution as a linear combination of the eigenfunction solving the single atom problem.

$$(T+V_L)\phi_L=E_s\phi_L \qquad (T+V_R)\phi_R=E_s\phi_R$$





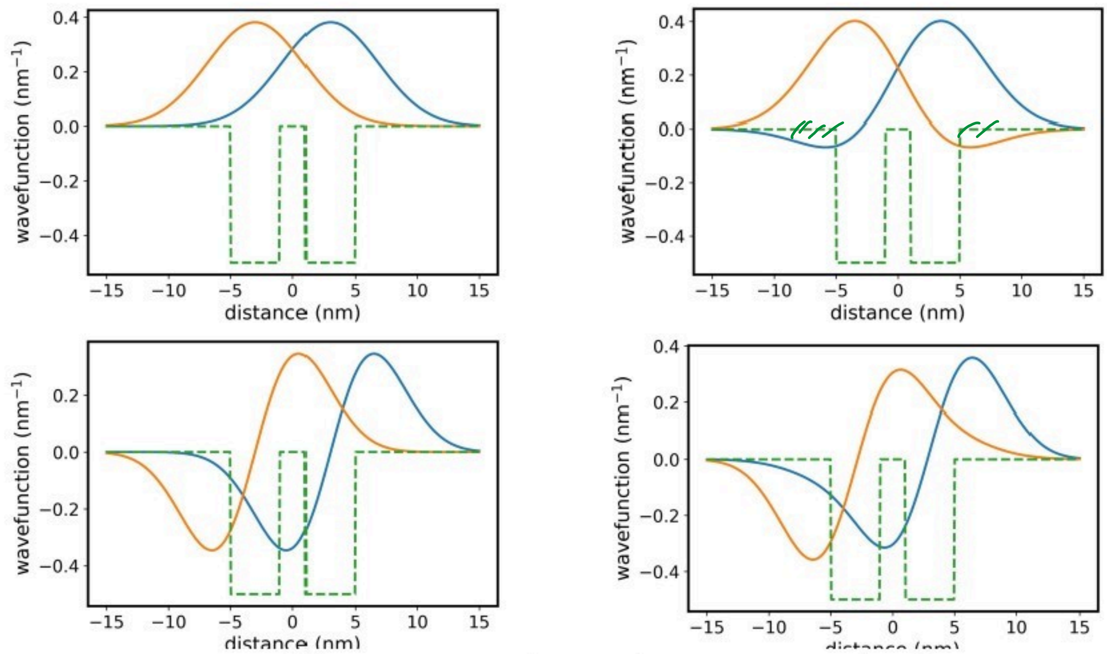
$\phi_L = -\phi_R$

$E = \varepsilon - \beta - \gamma$

$\phi_L = \phi_R$

$$(T+V_L+V_R)(a_L\phi_L+a_R\phi_R)=E(a_L\phi_L+a_R\phi_R)$$

Löwdin orthogonalization of s and p orbitals



$$\Phi_L^{orth} = \frac{1}{2}\left(\left(\frac{1}{\sqrt{1+\alpha}}+\frac{1}{\sqrt{1-\alpha}}\right)\phi_L+\left(\frac{1}{\sqrt{1+\alpha}}-\frac{1}{\sqrt{1-\alpha}}\right)\phi_R\right),$$

$$\Phi_R^{orth} = \frac{1}{2}\left(\left(\frac{1}{\sqrt{1+\alpha}}-\frac{1}{\sqrt{1-\alpha}}\right)\phi_L+\left(\frac{1}{\sqrt{1+\alpha}}+\frac{1}{\sqrt{1-\alpha}}\right)\phi_R\right).$$

Secular matrix for the LCAO approximation

	ϕ_L	ϕ_R
ϕ_L	$\epsilon-\beta-E$	$-\gamma$

$$\phi_R \quad \Big| \quad -\gamma \qquad \epsilon-\beta-E$$

$-\beta=\langle\phi_L|V_R|\phi_L\rangle$ On-site integral

$-\gamma=\langle\phi_L|V_L|\phi_R\rangle$ Off-site or overlap integral

Setting det=0 we obtain the energies of the bonding and anti-bonding levels

$$E=\epsilon-\beta\pm\gamma$$

Matrix formalism

2 QWs Hamiltonian

$$H=T+V_L+V_R$$

2 QWs Schrödinger equation

$$H(a_L\phi_L+a_R\phi_R)=E(a_L\phi_L+a_R\phi_R)$$

Schrödinger equation in matrix formalism

$$\begin{bmatrix}\langle\phi_L|H|\phi_L\rangle & \langle\phi_L|H|\phi_R\rangle\\ \langle\phi_R|H|\phi_L\rangle & \langle\phi_R|H|\phi_R\rangle\end{bmatrix}\begin{bmatrix}a_L\\ a_R\end{bmatrix}=E\begin{bmatrix}a_L\\ a_R\end{bmatrix}$$

Secular determinant

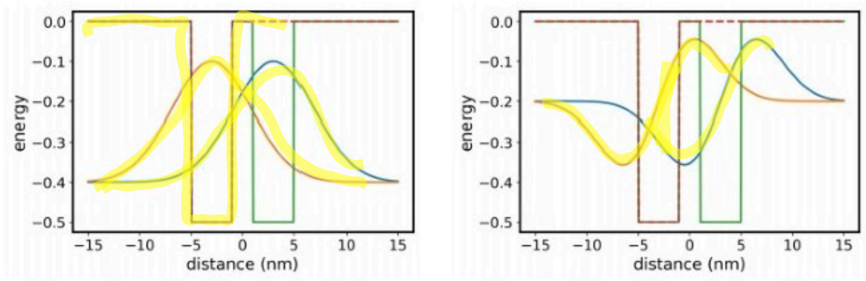
$$det\begin{bmatrix}\langle\phi_L|H|\phi_L\rangle-E & \langle\phi_L|H|\phi_R\rangle\\ \langle\phi_R|H|\phi_L\rangle & \langle\phi_R|H|\phi_R\rangle-E\end{bmatrix}=0$$

Overlap integral

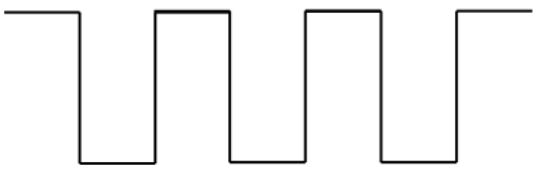
Overlap integral properties

- γ gets larger as the distance between the 2 QW is reduces
- $\gamma>0$ for even (s-type) orbitals

- $\gamma<0$ for odd (p-type) orbitals
- $|\gamma_s|>|\gamma_p|$ due to a better orbital overlap



Three coupled QW



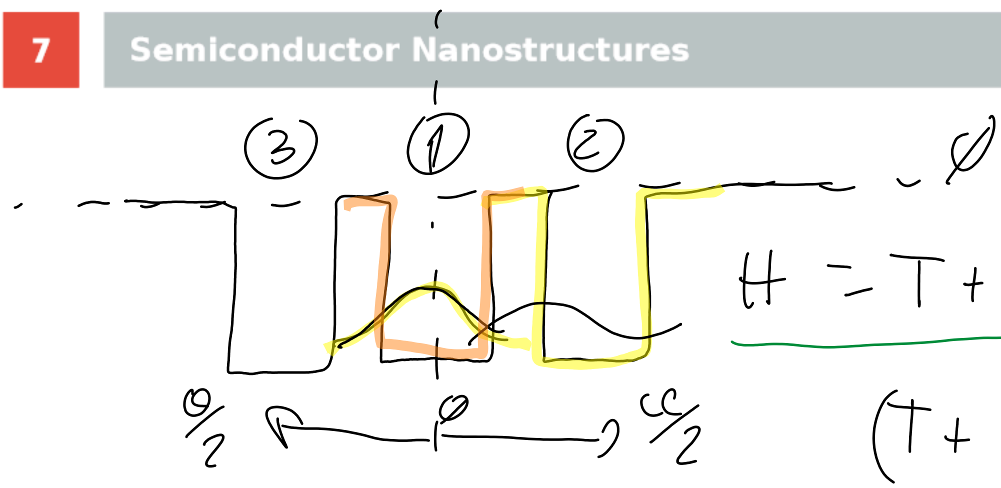
Assuming only near-neighbour interaction and setting all the on-site integral to zero

	ϕ_1	ϕ_2	ϕ_3
ϕ_1	$\epsilon-E$	$-\gamma$	$-\gamma$
ϕ_2	$-\gamma$	$\epsilon-E$	0
ϕ_3	$-\gamma$	0	$\epsilon-E$

$$E_1=\epsilon-\sqrt{2}\gamma$$

$$E_2=\epsilon$$

$$E_3=\epsilon+\sqrt{2}\gamma$$



$$H = T + V_1 + V_2 + V_3$$

$$(T + V_1)\,\phi_s = \varepsilon$$

$$\psi = a_1 \phi_1 + a_2 \phi_2 + a_3 \phi_3$$ $\phi_2 = \phi_1($

LÖWDIN METHOD $\phi_3 = \phi_1$

- near neighbour interaction
- β on-site integral $\approx \emptyset$

$$\begin{array}{cccc}
 & |\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle \\
\langle\phi_1 & \varepsilon - 2\beta & -\gamma & -\gamma \\
\langle\phi_2 & -\gamma & \varepsilon - \beta & 0 \\
\langle\phi_2 & -\gamma & 0 & \varepsilon - \beta
\end{array}$$

$$\langle\phi_2|H|\phi_1\rangle = \underbrace{\langle\phi_2|T+V_1|\phi_1\rangle}_{\varepsilon} + \underbrace{\langle\phi_1|V_2|\phi}_{-\beta}$$

$$\langle\phi_1|H|\phi_2\rangle = \underbrace{\langle\phi_1|V_1|\phi_2\rangle}_{-\gamma} + \underbrace{\langle\phi_1|T+V_2|\phi_2}_{\underline{\underline{\varepsilon}}\langle\phi_1|\phi_2\rangle = \emptyset}$$

$$\langle\phi_2|H|\phi_2\rangle = \underbrace{\langle\phi_2|T+V_2|\phi_2\rangle}_{\varepsilon} + \underbrace{\langle\phi_2|V_1|\phi_2}_{\beta}$$

$\varepsilon \qquad\qquad -\beta$

$$\langle \phi_2 | H | \phi_3 \rangle = \langle \phi_2 | T + V_3 | \phi_3 \rangle + \langle \phi_2 | V_1$$

$$\varepsilon \langle \phi_2 | \phi_3 \rangle \qquad\qquad \emptyset$$

$$\parallel$$

$$\emptyset$$

$\beta \approx \emptyset$

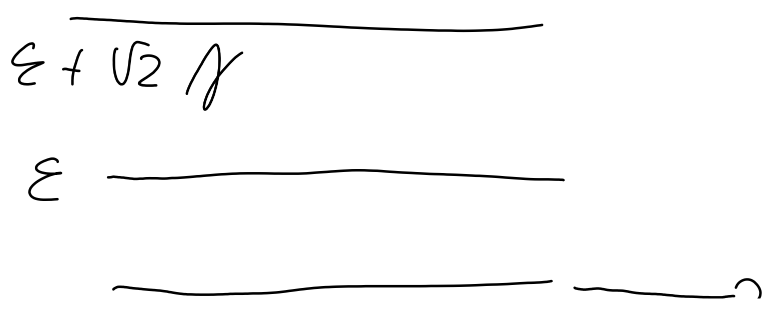
$E \to ?$

$$\det \begin{vmatrix} \varepsilon - E & -\gamma & -\gamma \\ -\gamma & \varepsilon - E & 0 \\ -\gamma & 0 & \varepsilon - E \end{vmatrix} = \emptyset$$

$$(\varepsilon - E)^3 - 2\gamma^2(\varepsilon - E) = \emptyset \qquad\qquad \varepsilon =$$

$$(\varepsilon - E)\left((\varepsilon - E)^2 - 2\gamma^2\right) = \emptyset \qquad\qquad E :$$

$\gamma > 0$

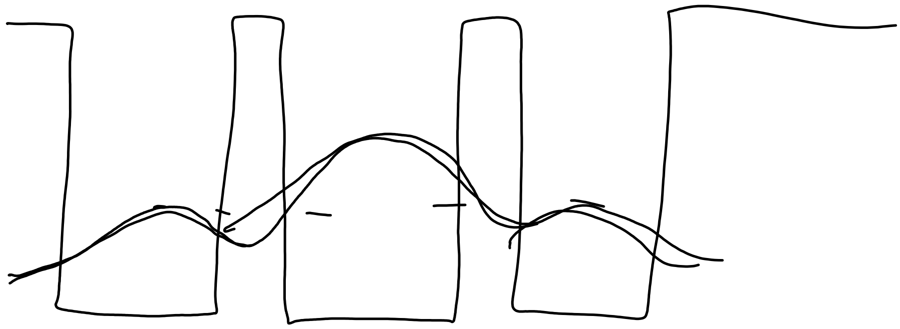


$\varepsilon - \sqrt{2}\gamma$

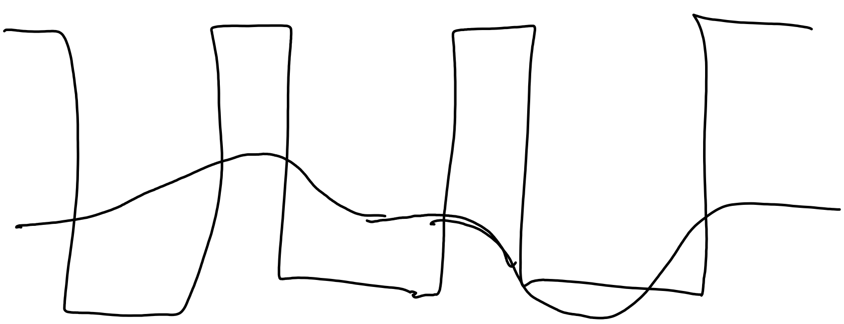
$$\begin{bmatrix} \varepsilon & -\gamma & -\gamma \\ -\gamma & \varepsilon & 0 \\ -\gamma & 0 & \varepsilon \end{bmatrix} \begin{bmatrix} \theta_1 \\ \theta_2 \\ \theta_3 \end{bmatrix} = E \begin{bmatrix} \theta_1 \\ \theta_2 \\ \theta_3 \end{bmatrix}$$

$E = \varepsilon - \sqrt{2}\gamma \qquad \theta_2 = \theta_3 \qquad \theta_1 = \sqrt{2}\,\theta$

$\cancel{\theta_1^2 + \theta_2^2 + \theta_3^2 = 1}$



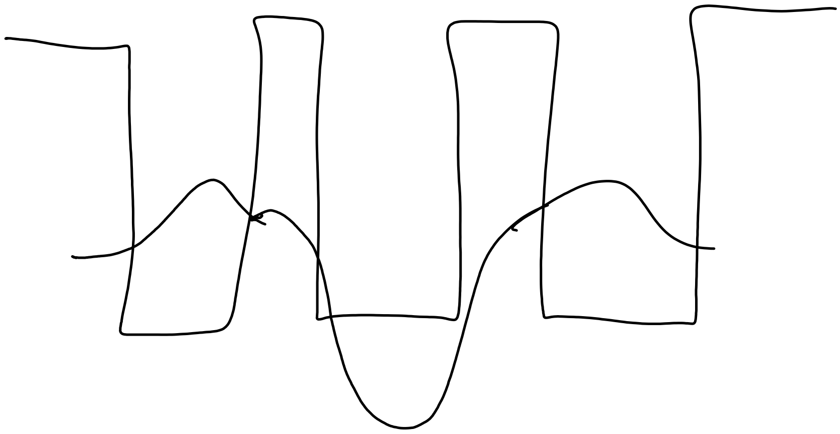
$E = \varepsilon \qquad \theta_2 = -\theta_3 \qquad \theta_1 = \emptyset$



$E = \varepsilon + \sqrt{2}\gamma \qquad \theta_2 = \theta_3$

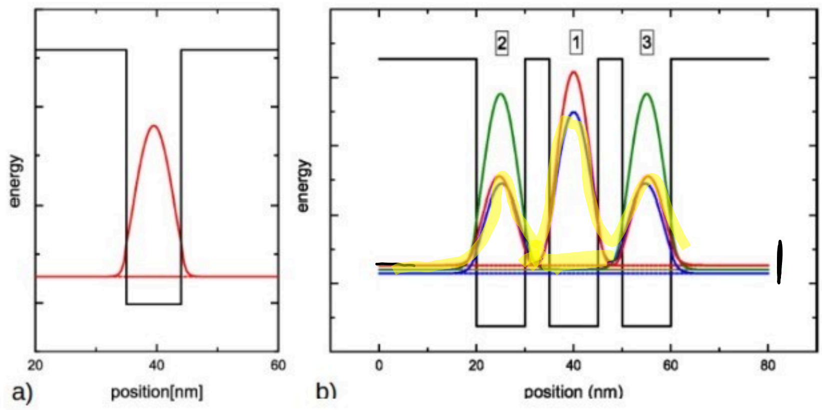
$\theta_2 = \theta_3$

$\theta_1 = -\sqrt{2}\,\theta_2$

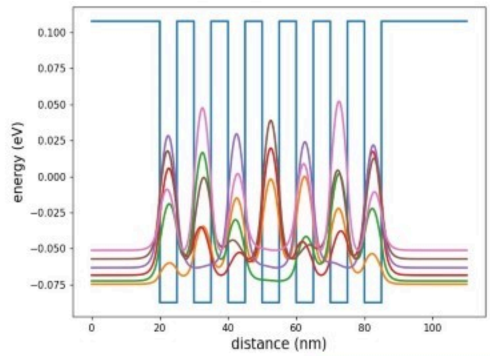


Three coupled QW

Squared wavefunctions for one, three and seven coupled quantum wells

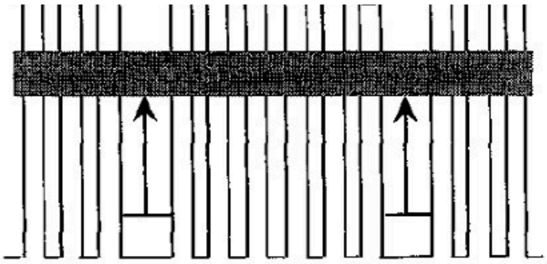


As the number of interacting QWs increases more and more levels are obtained. In the limit of infinite levels a “continuum” band is formed. This is true also if we consider only near-neighbour interaction.

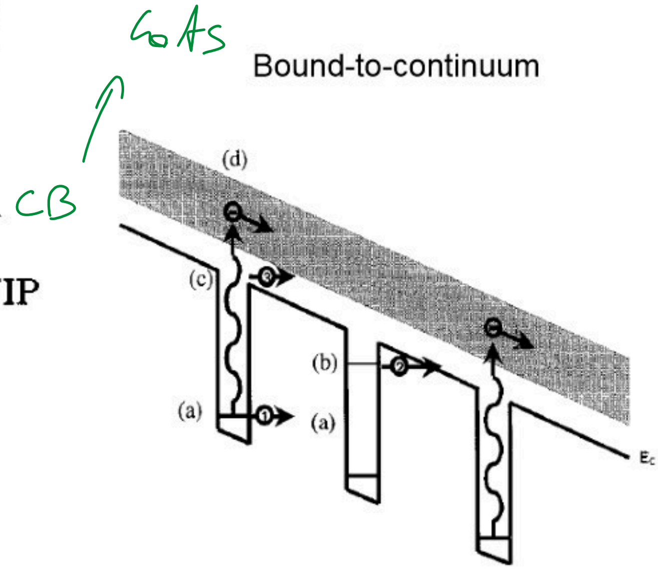


Application to intersubband photodetectors

Far-infrared photodetectors exploiting intersubband transitions



(c) Bound-to-Miniband (B-M) QWIP



Another application: the quantum cascade laser