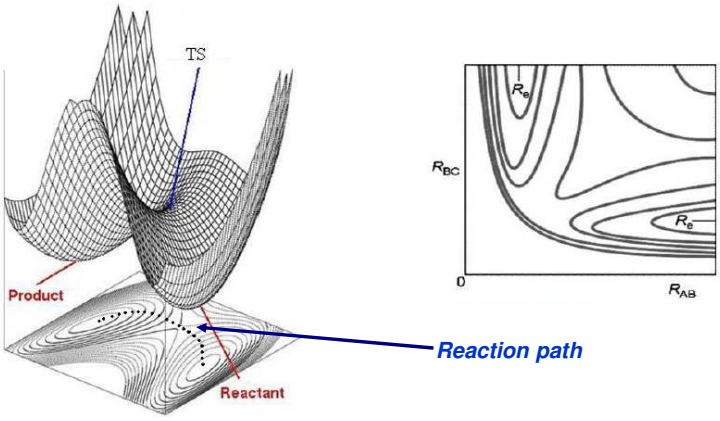
MOLÈCULES

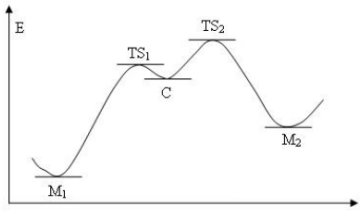
J. Planelles

UNIVERSITAT JAUME·I

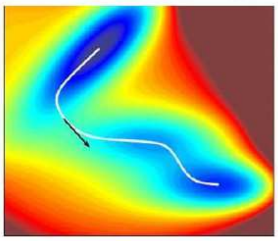
Chemical reactivity $H_2 + H \rightarrow H + H_2$



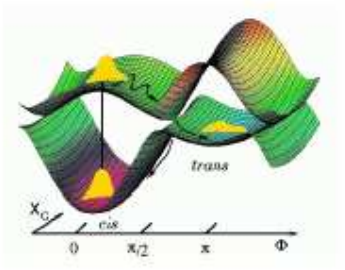
Chemical reactivity



Reaction path

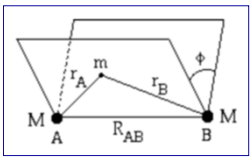


Energy hypersurface



Retinal: vision mechanism

Born-Oppenheimer approximation



H_2^+ molecule

$$\hat{\mathcal{H}} = -\frac{1}{2}\nabla^2 - \frac{1}{2}\frac{m}{M}\nabla_A^2 - \frac{1}{2}\frac{m}{M}\nabla_B^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R_{AB}}$$

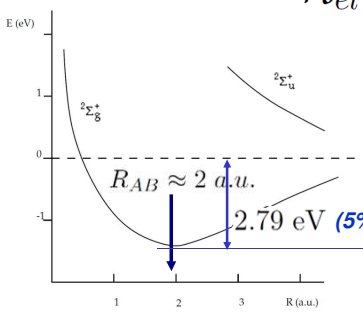
Frozen nuclei: $\hat{\mathcal{H}}_{el} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R_{AB}}$

Kinetic energy of nuclei: $\hat{T}_N = -\frac{1}{2}\frac{m}{M}(\nabla_A^2 + \nabla_B^2) \equiv -\frac{1}{2}\frac{m}{M}\nabla_N^2$

Total Hamiltonian: $\hat{\mathcal{H}} = \hat{\mathcal{H}}_{el}(R, r) + \hat{T}_N(R)$

Frozen nuclei:

$$\hat{\mathcal{H}}_{el}(R,r)\,\Phi_R(r) = E_{el}(R)\,\Phi_R(r)$$



Burrau 1926, see J.Chem. Educat 79 (2002) 127

(5% error)

Are nuclei frozen ?
… NO!

Born-Oppenheimer approximation: $\Psi(R,r) = \Phi_R(r)\chi(R)$

$$\hat{\mathcal{H}}\,\Phi_R(r)\chi(R) \approx E\,\Phi_R(r)\chi(R)$$

$$\hat{\mathcal{H}}_{el}\Phi_R(r)\chi(R) + \hat{T}_N\chi(R)\Phi_R(r) \approx E\;\Phi_R(r)\chi(R)$$

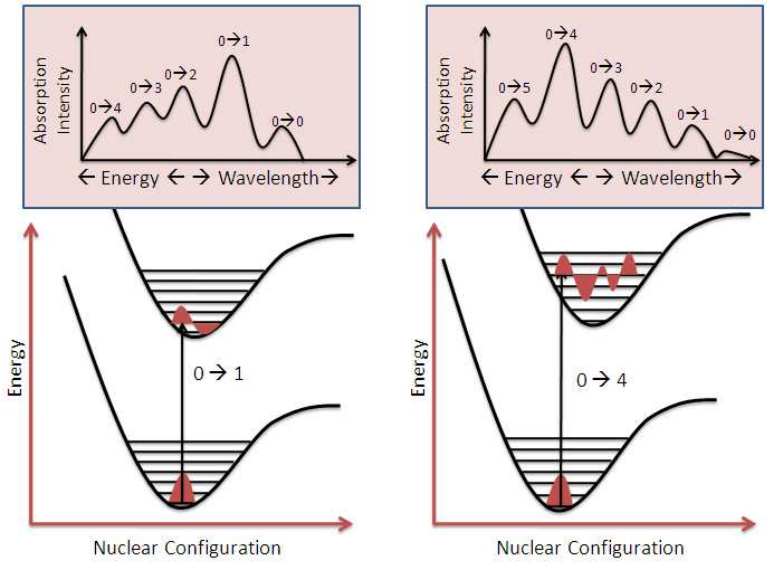
Left multiply by $\Phi_R(r)^*$ *and integrate the electronic coordinates:*

$$E_{el}(R)\chi(R)\langle\Phi_R(r)|\Phi_R(r)\rangle_r + \hat{T}_N\chi(R)\langle\Phi_R(r)|\Phi_R(r)\rangle_r \approx$$

$$\approx E\;\chi(R)\langle\Phi_R(r)|\Phi_R(r)\rangle_r$$

$$\longrightarrow\quad [\hat{T}_N + E_{el}(R)]\chi(R) \approx E\,\chi(R)$$

$E_{el}(R)$ *acts as a potential energy for the nuclei dynamics*



Hamiltonià Electrònic

$$\hat{\mathcal{H}} = -\frac{1}{2}\sum_{\mu}\nabla_{\mu}^{2} + \sum_{\mu>\nu}\frac{1}{r_{\mu\nu}} - \sum_{\mu,k}\frac{z_k}{r_{\mu k}}$$

$$\Psi(\tau_1, \tau_2 \cdots \tau_N) = \Phi(r_1, r_2 \cdots r_N)\Sigma(\sigma_1, \sigma_2 \cdots \sigma_N)$$

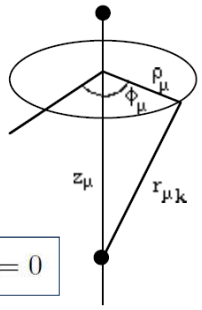
Aproximació IP

$$\hat{\mathcal{H}} = \underbrace{-\frac{1}{2}\sum_{\mu}\nabla_{\mu}^{2} - \sum_{\mu,k}\frac{z_k}{r_{\mu k}}}_{\hat{\mathcal{H}}_{\mathrm{IP}}} + \underbrace{\sum_{\mu>\nu}\frac{1}{r_{\mu\nu}}}_{\hat{\mathcal{H}}'}$$

Configuració electrònica $\sigma_g^2\,\sigma_u^2\,\pi_{xy}^3\cdots$ vs. àtoms $1s^2 2s^2 2p^3\cdots$

Molècules lineals

$$\hat{\mathcal{H}} = \underbrace{-\frac{1}{2}\sum_{\mu}\nabla^2_{\mu} + \sum_{\mu>\nu}\frac{1}{r_{\mu\nu}}}_{\hat{\mathcal{H}}_0} \underbrace{-\sum_{\mu,k}\frac{z_k}{r_{\mu k}}}_{\hat{\mathcal{H}}_1}$$



$$r_{\mu k} = \sqrt{z_\mu^2 + \rho_\mu^2} \qquad [\hat{\mathcal{H}}_1, \widehat{L^2}] \neq 0$$

$$\boxed{[\hat{\mathcal{H}}, \hat{L}_z] = 0}$$

$$\hat{L}_{z\mu} = \frac{\hbar}{i}\frac{\partial}{\partial\phi_\mu} \qquad [\hat{\mathcal{H}}_1, \hat{L}_z] = 0$$

etiquetatge

$\Lambda = 0 \pm 1 \pm 2 \ldots$

Orbitals $\sigma \quad \pi \quad \delta \cdots$

Termes $\Sigma \quad \Pi \quad \Delta \ldots$

Example càlcul termes

configuració π^2

$m_\ell(1)$	$m_S(1)$	$m_\ell(2)$	$m_S(2)$		M_L	M_S	símbol
1	1/2	-1	1/2		0	1	◦
1	1/2	1	-1/2		2	0	•
1	1/2	-1	-1/2		0	0	◦
-1	1/2	1	-1/2		0	0	◇
-1	1/2	-1	-1/2		-2	0	•
1	-1/2	-1	-1/2		0	-1	◦

$\diamond \rightarrow M_L = 0\ M_S = 0 \ \rightarrow M_L = 0\ S = 0$

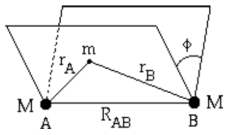
$\bullet \rightarrow M_L = \pm 2\ M_S = 0 \ \rightarrow M_L = \pm 2\ S = 0$

$\circ \rightarrow M_L = 0\ M_S = -1, 0, 1 \ \rightarrow M_L = 0\ S = 1$

Termes $^1\Sigma,\ ^1\Delta$ i $^3\Sigma$

Resolució variacional H_2^+

$$\psi = c_A\phi_A + c_B\phi_B$$



$$E(c_A, c_B) = \frac{\langle\psi|\hat{\mathcal{H}}|\psi\rangle}{\langle\psi|\psi\rangle}$$

$$E(c_A, c_B) = \frac{(c_A^2 + c_B^2)H_{AA} + 2c_Ac_BH_{AB}}{c_A^2 + c_B^2 + 2c_Ac_BS_{AB}}$$

$$\begin{bmatrix} (H_{AA} - E) & (H_{AB} - S_{AB}E) \\ (H_{AB} - S_{AB}E) & (H_{AA} - E) \end{bmatrix} = 0$$

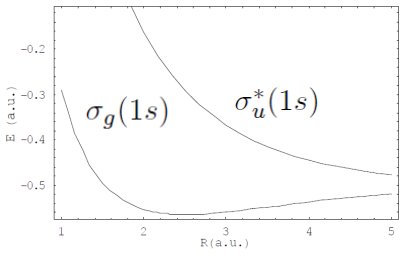
$\sigma_g(1s)$

$$E_\pm = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}} \qquad \psi_\pm = \frac{1}{\sqrt{2(1 \pm S_{AB})}}(1s_A \pm 1s_B)$$

$\sigma_u^*(1s)$

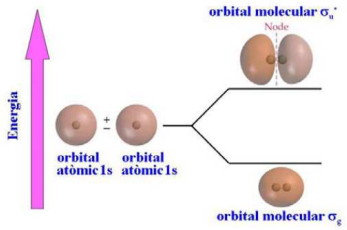
Resolució variacional H_2^+ (cont.)

$$\begin{aligned} S_{AB} &= e^{-R}\left(1 + R + \frac{R^2}{3}\right) \\ H_{AA} &= -\frac{1}{2} - \frac{1}{R}\left(1 - e^{-2R}(1+R)\right) \\ H_{AB} &= -\frac{S_{AB}}{2} - e^{-R}(1+R) \end{aligned}$$



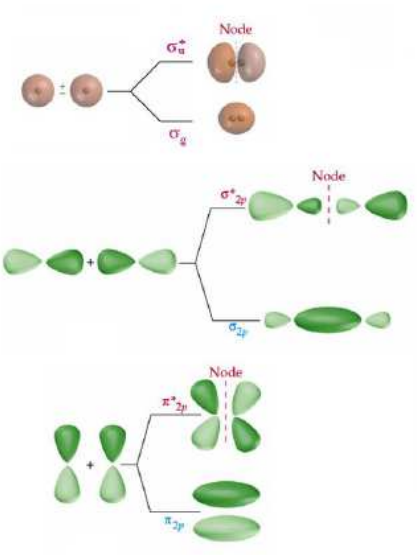
$R \approx 2.5\ a.u.$

$\Delta E = E_- - E_+ \approx 0.28\ a.u.$

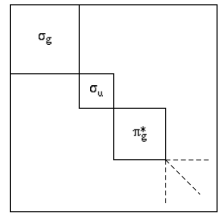


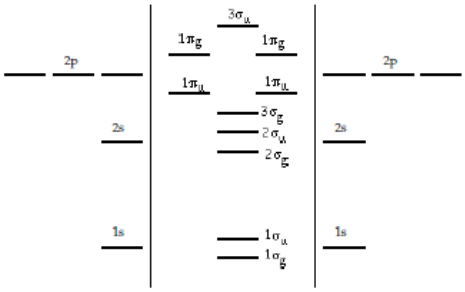
ORBITALS DE SIMETRIA

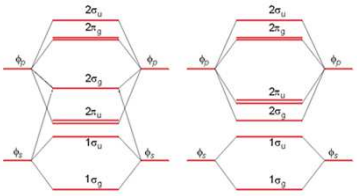
$$\sigma_g(1s) = 1s_A + 1s_B$$
$$\sigma_u(1s) = 1s_A - 1s_B$$
$$\sigma_g(2s) = 2s_A + 2s_B$$
$$\sigma_u(2s) = 2s_A - 2s_B$$
$$\dots$$
$$\sigma_g(2p_z) = 2p_{zA} - 2p_{zB}$$
$$\sigma_u(2p_z) = 2p_{zA} + 2p_{zB}$$
$$\dots$$
$$\pi_g(2p_x) = 2p_{xA} - 2p_{xB}$$
$$\pi_g(2p_y) = 2p_{yA} - 2p_{yB}$$
$$\pi_u(2p_x) = 2p_{xA} + 2p_{xB}$$
$$\dots$$



Resolució variacional H_2^+ (cont.)







Orbitals moleculares molècules Li_2-N_2 (esquerra) y O_2-F_2 (dreta)

Correlació electrònica: cas de l'H_2

$$\Psi(\tau_1,\tau_2) = \sigma_g(r_1)\sigma_g(r_2)\frac{1}{\sqrt{2}}[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)]$$

$$\sigma_g = \frac{1}{\sqrt{2(1+S)}}(s_A + s_B)$$

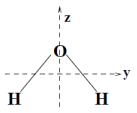
$$\begin{aligned}\Phi^{MO}(r_1,r_2) &= \frac{1}{2(1+S)}[\underbrace{s_A(r_1)s_A(r_2) + s_B(r_1)s_B(r_2)}_{\Phi_{ion}} + \\ &+ \underbrace{s_A(r_1)s_B(r_2) + s_B(r_1)s_A(r_2)}_{\Phi_{cov}}]\end{aligned}$$

$$\Psi = \Psi_{cov} + \Psi_{ion}$$

$$\begin{aligned}\Phi^{VB}(r_1,r_2) &= N\{[s_A(r_1)s_B(r_2) + s_B(r_1)s_A(r_2)] \times \\ &\times [\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)]\}\end{aligned}$$

$$\boxed{\Psi = \Psi_{cov} + \lambda\Psi_{ion}}$$

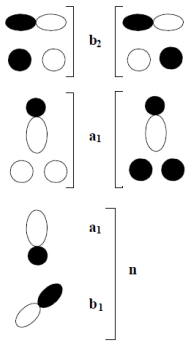
Mos en molècules poliatòmiques: el cas de l'aigua

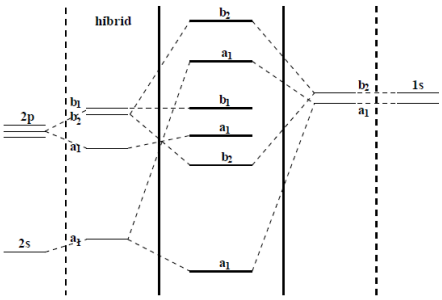


orbitals	C_2	σ_{xz}	σ_{yz}	Simetria
$2s$	1	1	1	a_1
$2p_z$	1	1	1	a_1
$2p_x$	-1	1	-1	b_1
$2p_y$	-1	-1	1	b_2

$$\phi_{a_1} = 1s(H_1) + 1s(H_2)$$

$$\phi_{b_2} = 1s(H_1) - 1s(H_2)$$





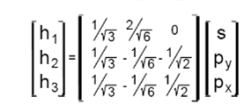
Enllaços de València: HOs

configuració dels àtoms en les molècules BF_3

$F\ 1s^2 2s^2 2p^5$ (fonamental)

$B\ 1s^2 2s^2 2p^2$ (excitada)

$$\begin{bmatrix} h_1 \\ h_2 \\ h_3 \end{bmatrix} = \begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2} \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} \end{bmatrix} \begin{bmatrix} s \\ p_y \\ p_x \end{bmatrix}$$



orbital híbrid esquema

híbrids sp^2

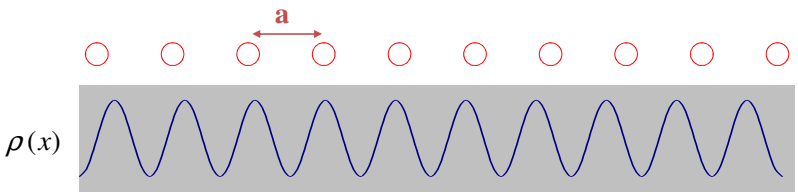
híbrids sp

híbrids sp^2

híbrids sp^3

$$\begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \begin{pmatrix} 2s \\ 2p_x \\ 2p_y \\ 2p_z \end{pmatrix}$$

Translational symmetry $[\hat{T}, \hat{H}] = 0$



$$\rho(x) = \rho(x + na) \Leftrightarrow |f(x)|^2 = |f(x + na)|^2 \Rightarrow f(x + na) = e^{i\phi} f(x)$$

$$f(x + na) = T_n f(x)$$

$$T_n = e^{i\,a\,n\,\hat{p}} = \sum_q \frac{(i\,a\,n)^q}{q!} \hat{p}^q$$

$$T_n f(x) = e^{ian\hat{p}} f(x) = \sum_q \frac{(ian)^q}{q!} (-i)^q \frac{d^q f}{dx^q} = f(x + an)$$

$\{T_n\} \rightarrow Translation\ \ Group \qquad [T_n, T_m] = 0 \rightarrow Abelian\ Group$

Eigenfunctions of the linear momentum are basis of T_n group irreps:

$$T_n e^{ikx} = e^{ian\hat{p}} e^{ikx} = e^{iank} e^{ikx}$$

	E	$\cdots$	T_n	$\cdots$	
$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\cdots$	$\vdots$
k	1	$\cdots$	e^{ikna}	$\cdots$	e^{ikx}
$\vdots$	$\vdots$	$\cdots$	$\vdots$	$\cdots$	$\vdots$

First Brillouin zone: $k \sim k' \rightarrow k' - k = K = \frac{2\pi}{a} : \ e^{iKa} = 1$

$\Gamma : \ k = 0, \quad k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$

Solving Schrödinger equation: Von-Karman BCs

Crystals are infinite... How are we supposed to deal with that?

We use periodic boundary conditions

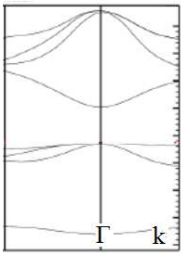
Group of translations:

$T_a \Psi_k(r) = e^{i k \cdot a} \Psi_k(r)$

$\Psi_k(-a/2) = e^{i\phi} \Psi_k(a/2), \quad \phi \in [-\pi, \pi]$

k is a quantum number due to translational symmetry

1rst Brillouin zone



We solve the Schrödinger equation for each k (or ϕ) *value:*

The plot $E_n(k)$ represents an energy band

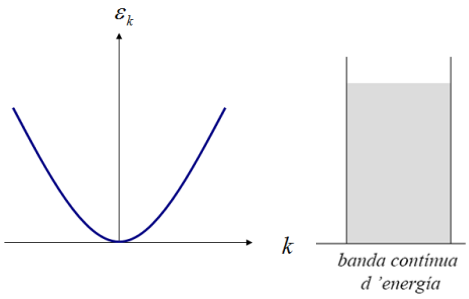
Band folded into the first Brillouin zone (flat potential)

$H = -\frac{\hbar^2}{2m}\nabla^2 \rightarrow \Psi = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}}$

ones viatgeres

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

$\varepsilon(k)$: **single parabola**

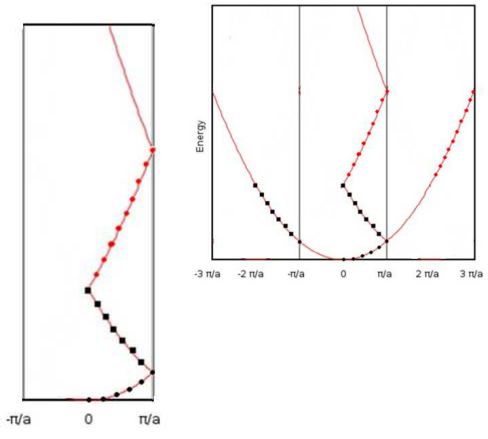


$$BC: \Psi_k(x+a) = e^{ika}\,\Psi_k(x)$$

$$k \sim k' \rightarrow k' - k = K = \frac{2\pi}{a}: \quad e^{iKa} = 1$$

folded parabola

Band folded into the first Brillouin zone (flat potential)



1rst Brillouin zone

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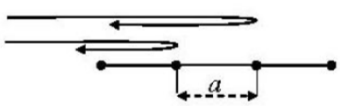
$$BC: \Psi_k(x+a) = e^{ika}\,\Psi_k(x)$$

$$k \sim k' \rightarrow k' - k = K = \frac{2\pi}{a}: \quad e^{iKa} = 1$$

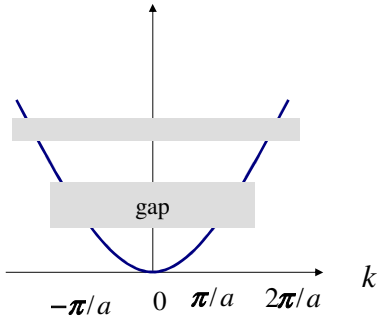
folded parabola

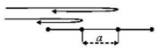
Bragg difraction

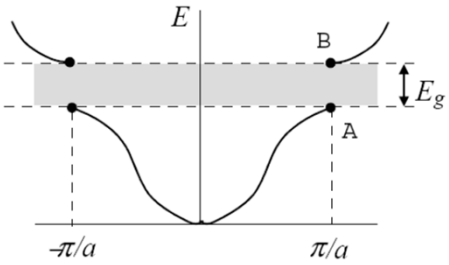


$$\lambda = \frac{2a}{n}, \quad n = 1, 2, 3, \ldots$$

$$k = \frac{\pi}{a}\, n$$







$$\Psi_1 = \sqrt{\frac{1}{L}}(e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x}) = \frac{2i}{\sqrt{L}} \sin\frac{\pi}{a}x$$

$$\Psi_2 = \sqrt{\frac{1}{L}}(e^{i\frac{\pi}{a}x} - e^{-i\frac{\pi}{a}x}) = \frac{2}{\sqrt{L}} \cos\frac{\pi}{a}x$$

ones estacionàries degenerades

operador de pertorbació $\hat{\mathcal{H}}' = V(x) = V_0 \cos(\frac{2\pi}{a}x)$

$$det|\hat{H}'_{jk} - \delta_{jk}\, E_n^{(1)}| = 0$$

In[5]:= $\frac{2}{a}\int_{-a/2}^{a/2} \text{Sin}\left[\frac{\pi}{a}x\right] \text{Sin}\left[\frac{\pi}{a}x\right] V0\, \text{Cos}\left[2\frac{\pi}{a}x\right] dx$

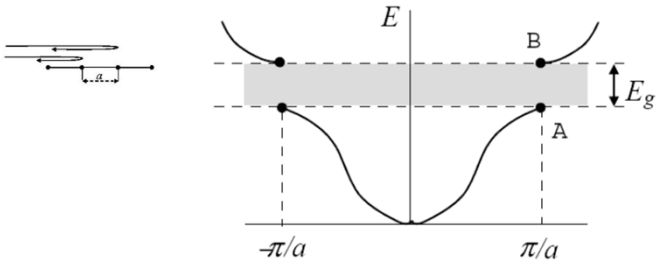
Out[5]= $-\frac{V0}{2}$

In[7]:= $\frac{2}{a}\int_{-a/2}^{a/2} \text{Cos}\left[\frac{\pi}{a}x\right] \text{Cos}\left[\frac{\pi}{a}x\right] V0\, \text{Cos}\left[2\frac{\pi}{a}x\right] dx$

Out[7]= $\frac{V0}{2}$

In[6]:= $\frac{2}{a}\int_{-a/2}^{a/2} \text{Sin}\left[\frac{\pi}{a}x\right] \text{Cos}\left[\frac{\pi}{a}x\right] V0\, \text{Cos}\left[2\frac{\pi}{a}x\right] dx$

Out[6]= 0



$$\Psi_1 = \sqrt{\frac{1}{L}}(e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x}) = \frac{2i}{\sqrt{L}}\sin\frac{\pi}{a}x$$
$$\Psi_2 = \sqrt{\frac{1}{L}}(e^{i\frac{\pi}{a}x} - e^{-i\frac{\pi}{a}x}) = \frac{2}{\sqrt{L}}\cos\frac{\pi}{a}x$$

ones estacionàries degenerades

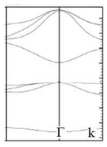
operador de pertorbació $\hat{\mathcal{H}}' = V(x) = V_0\cos(\frac{2\pi}{a}x)$

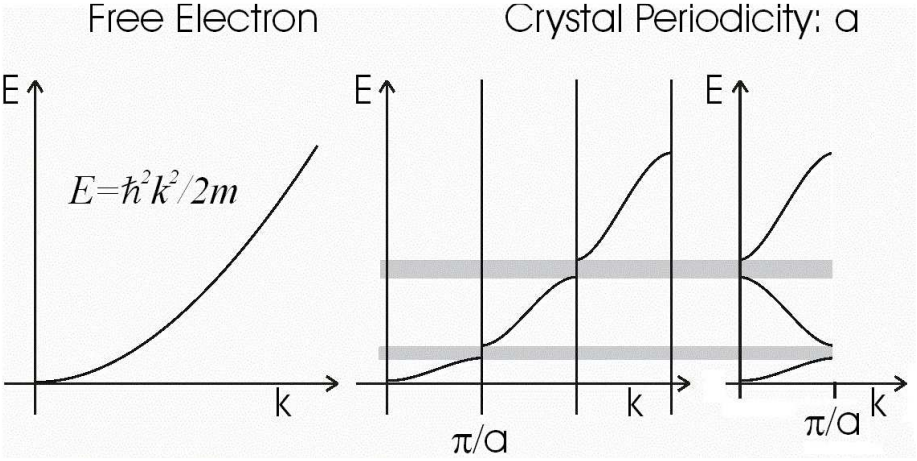
$det|\hat{H}'_{jk} - \delta_{jk}\, E_n^{(1)}| = 0 \qquad \hat{H}'_{11} = V_0/2 \quad \hat{H}'_{22} = -V_0/2 \quad \hat{H}'_{12} = \hat{H}'_{21} = 0$

$$\Longrightarrow E^{(1)} = \pm V_0/2.$$

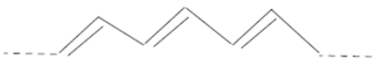
gap d'energia $\Delta E = V_0$

$$\left(\frac{p^2}{2m}+V_c(x)\right)\Psi_k(x)=\varepsilon_k\,\Psi_k(x)$$





Formació d'una banda combinant orbitals



$$D_N(x)=\begin{vmatrix} x & 1 & 0 & 0 & 0 & \dots \\ 1 & x & 1 & 0 & 0 & \dots \\ 0 & 1 & x & 1 & 0 & \dots \\ 0 & 0 & 1 & x & 1 & \dots \\ 0 & 0 & 0 & 1 & x & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{vmatrix}$$

canvi $x = 2\cos\theta$

$$D_1(x) = x \;= 2\cos\theta \;= \frac{\sin 2\theta}{\sin\theta}$$

$$D_2(x) = \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = x^2 - 1 = 4\cos^2\theta - 1$$

$$\frac{\sin 3\theta}{\sin\theta} = \frac{\sin\theta\cos 2\theta + \cos\theta\sin 2\theta}{\sin\theta} = \cos 2\theta + 2\cos^2\theta = 4\cos^2\theta - 1 = D_2$$

$$D_3(x) = xD_2(x) - D_1(x) = x(x^2-1) - x = x^3 - 2x = \frac{\sin 4\theta}{\sin\theta}$$

.....

$$D_N = \frac{\sin(N+1)\theta}{\sin\theta}$$

$$D_N = \frac{\sin(N+1)\theta}{\sin\theta}$$

$$D_N = 0 \Rightarrow (N+1)\theta = n\pi \Rightarrow \theta = \frac{\pi}{N+1}n,\ n = 1, 2, 3...N.$$

$$x = 2\cos\frac{\pi}{N+1}n,\ n = 1, 2, 3...N$$

$$E = \alpha - 2\beta\cos\frac{\pi}{N+1}n,\ n = 1, 2, 3...N$$