GEN 2016

(2) PART 1

osc. har. 2D . $K_x = K_y$

a) E ? i d ? dos nivells E + baixa ?

$E_{n_x n_y} = \left(\frac{1}{2}+v\right)h\nu + \left(\frac{1}{2}+v\right)h\nu$ A $n_x = n_y = 0 \rightarrow E_{00} = h\nu$ $\underline{d=1}$

$n_x = 0\ n_y = 1 \rightarrow E_{10} = E_{01} = 2h\nu$ $\underline{d=2}$

$n_x = 1\ n_y = 0$

$$\phi_{00}(x,y) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \cdot \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha y^2/2} = \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\frac{\alpha x^2+\alpha y^2}{2}}$$

$$\phi_{10}(x,y) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2} \cdot \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha y^2/2} = \left(\frac{4}{\pi^2}\right)^{1/4} x\alpha\, e^{-\frac{\alpha x^2+\alpha y^2}{2}}$$

$$\phi_{10}(x,y) = \alpha x \sqrt{\frac{2}{\pi}}\, e^{-(\alpha x^2+\alpha y^2)/2} \xrightarrow{r} \alpha r\cos\varphi \sqrt{\frac{2}{\pi}}\, e^{-\alpha r^2/2}$$

$$\phi_{01}(x,y) = \alpha y \sqrt{\frac{2}{\pi}}\, e^{-(\alpha x^2+\alpha y^2)/2} \quad \text{"} \quad (\sin\varphi)$$

$$\phi_{00}(x,y) = \sqrt{\frac{\alpha}{\pi}}\, e^{-(\alpha r^2\sin^2\theta\cos^2\varphi + \alpha r^2\sin^2\theta\sin^2\varphi)/2} = \sqrt{\frac{\alpha}{\pi}}\, e^{-\alpha r^2/2}$$

$\alpha r^2\sin^2\theta + \alpha r^2\sin^2\theta$

(1) ... (1)

$\hat{L}_z = 0$ ✗ → sí que ho és valor propi = 0.

$\hat{L}_z\varphi = -i\hbar\left(-\alpha r\sin\varphi\sqrt{\frac{\alpha}{\pi}}\, e^{-\alpha r^2/2}\right) - i\hbar$ $\alpha r\sin\varphi$. $\hat{L}_z\varphi_{10} = +i\hbar\,\varphi_{01}$; $\hat{L}_z\varphi_{01} = -i\hbar\,\varphi_{10}$ } NO!!

Juny 2015

$$N = \frac{1}{\sqrt{\sum |c_i|^2}} = \frac{1}{\sqrt{1+2+1}} = \frac{1}{2}$$

b) $\hat{H}$ ✓ → sí!!

~~L^2~~ ~~L_z~~

$l(l+1)$ $l=1$ →

[2] Juny 2013 àt H estat fonamental $\mu \approx m_e$

a) $|\psi|^2(a_0, \theta, \varphi)$: $\quad \phi_{1s}(r,\theta,\varphi) = \left(\frac{1}{\pi}\right)^{1/2} e^{-r/a_0}$ $\quad a_0 = 1$ u.a

$$\cancel{|\psi|^2 = \int_{-\infty}^{+\infty} \frac{1}{\pi} e^{-2a_0/a_0} dV = \frac{1}{\pi}\int_{-\infty}^{+\infty} r^2 e^{-2} dr \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\varphi}$$

$$\cancel{|\psi|^2 = \frac{2}{\pi}\int_0^{\infty} r^2 e^{-2} dr \,(4\pi) =}$$ No és una integral !!

$$|\psi|^2 = \left|\left(\frac{1}{\pi}\right)^{1/2} e^{-1}\right|^2 = \frac{1}{\pi} e^{-2} = \boxed{0{,}0430 \text{ u.a}}$$ ✓

b) p? $|\psi|^2 \uparrow$ $\quad |\psi|^2 \cancel{\times 1}$ $\quad$ No $\quad$ p va de 1, 0 $\quad |\psi|^2$ no!

$$\cancel{1 = \frac{1}{\pi} e^{-2r}} \; ; \quad \cancel{\ln 1 = \ln\left(\frac{1}{\pi}\right) - 2r}$$

Maxim de la funció : $|\psi|^2 = \frac{1}{\pi} e^{-2r}$ decreix !!

$|\psi|^2 = \frac{1}{\pi}$!! L'única forma en que $\boxed{r=0}$ al (0,0).

c) $P(r < 2a_0) = P(r<2) = 1 - \underbrace{P(r \geq 2)}_{\text{millor!}}$

$$P(r \geq 2) = \int_2^{\infty} \frac{1}{\pi} e^{-2r} r^2 \, dr \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\varphi$$

$$P(r \geq 2) = 4 \int_2^{\infty} r^2 e^{-2r} dr = \frac{4 \cdot \cancel{2!}}{\cancel{2^3}} e^{-4}\left(1 + 4 + \frac{4 \cdot 4}{2!}\right)$$

$$= (1 + 4 + 8) e^{-4} = 13 e^{-4} = \underline{\underline{0{,}2381}}$$

$$P(r<2) = 1 - 0{,}2381 = \underline{\underline{0{,}762}}$$

d) P (prohibida)?

$E < V$

$$-\frac{z^2}{2n^2} < -\frac{z}{r} \rightarrow \frac{z}{2n^2} > \frac{1}{r}; \quad \text{si } n=1 \quad r > \frac{2}{z}$$

si $z = 1 \rightarrow r > 2$ prohibida !

Calcular abans! $P(r > 2) = 0{,}2381$

e) $\langle P_x \rangle$? $\langle U \rangle$? $\langle T \rangle$?

$$\langle P_x \rangle_{\Phi_{1s}} = \langle \Phi_{1s} | P_x \Phi_{1s} \rangle = \int_{-\infty}^{+\infty} \frac{1}{\sqrt{\pi}} e^{-r} \left(-i\hbar \frac{d}{dx}\right) \frac{1}{\sqrt{\pi}} e^{-r} \, dV$$

Polares / cartesianas !! $r = \sqrt{x^2 + y^2 + z^2}$

$$\langle P_x \rangle_{\Phi_{1s}} = \iiint_{-\infty}^{+\infty} \frac{1}{\pi} e^{-\sqrt{x^2+y^2+z^2}} \left(-i\hbar \frac{d}{dx}\right) e^{-\sqrt{x^2+y^2+z^2}} \, dx\,dy\,dz$$

Miramos si son simétricos!

impar

No es simétrica respecto a x !!

$$= \frac{1}{\pi}\iiint e^{-\sqrt{x^2+y^2+z^2}} \, -i\hbar \, e^{-\sqrt{x^2+y^2+z^2}} \left(\frac{2x}{2\sqrt{x^2+y^2+z^2}}\right) dx\,dy\,dz = 0$$

$$\langle U \rangle = \int_{?}^{+\infty} -\frac{1}{\pi} r \, e^{-2r} \cdot r^2 \, dr \int_0^{2\pi} \sin\theta \, d\theta \int_0^{\pi} d\varphi$$

$$\langle U \rangle = \frac{4\cancel{\pi}}{\cancel{\pi}} \int_0^{\infty} r^3 e^{-2r} \, dr = \frac{4 \cdot 3!}{-2^4} = -\frac{24}{24} = -1 \text{ hartree}$$

$\langle T \rangle$? saben que $E = -\frac{1}{2 \cdot 1^2} = -\frac{1}{2}$

$\hat{H} = \hat{T} + \hat{V}$; $\langle T \rangle = H - V = -\frac{1}{2} + 1 = \underline{\underline{1/2 \text{ hartree}}}$!!

Gen 2013

2. $\Psi(x,y) = \Phi_x(a)\,\Phi_y(a)$? Caixa □ área $= 4a_0^2$ $a = \sqrt{4a_0^2} = 2a_0$

E ?

$$\Psi(x,y) = \frac{2}{2a_0} \cdot \sin\frac{n\pi x}{2} \cdot \sin\frac{n\pi y}{2} = \sin\left(\frac{n_x \pi x}{2}\right)\sin\left(\frac{n_y \pi x}{2}\right) \quad x \in (0,a)\ y$$

$$E_{n_x n_y} = E_{n_y} + E_{n_y} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8ma^2}$$

$$E_{n_x n_y} = \frac{h^2}{8m\cdot 4}\left(n_x^2 + n_y^2\right) = \frac{h^2}{32m}\left(n_x^2 + n_y^2\right) \quad n = 1, 2, 3 \ldots$$

b) d ? E fonamental ? d ? E_1^0 ? $\hbar = \frac{h}{2\pi}$

$$E_{11} = \frac{h^2}{16m} \quad d = 1 \qquad E_{11} = \frac{h^2}{16m} = \frac{(\hbar 2\pi)^2}{\cancel{16}m} = \frac{\pi^2}{4m}$$

$$E_{21} = \frac{h^2}{32m}(4+1) = \frac{5h^2}{32m} = E_{12} \qquad d = 2$$

c) Si $\hat{H}' = b$ $\frac{1}{2}a_0 \leq x \leq 3/2\, a_0$; $\frac{1}{2}a_0 \leq y \leq 3/2\, a_0$

$$E_{11} = \langle \Phi_{xy} | \hat{H}\, \Phi_{xy} \rangle = \langle \Phi_{xy} | \hat{H}\, \Phi_{xy} \rangle + \langle \Phi_{xy} | \hat{H}'\, \Phi_{xy} \rangle$$

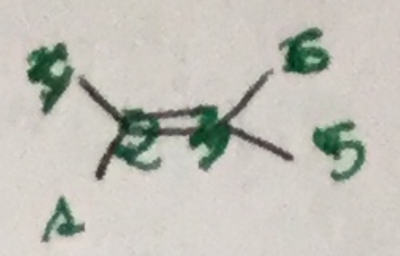
$$E_{11}' = \frac{h^2}{16m} + \int_{1/2}^{3/2}\int_{1/2}^{3/2} \sin\frac{\pi x}{2}\sin\frac{\pi y}{2} \cdot b \left| \sin\frac{\pi x}{2}\sin\frac{\pi y}{2}\right) dx\, dy$$

$$E_{11}' = \frac{h^2}{16m} + b \underbrace{\int_{1/2}^{3/2} \sin^2\frac{\pi x}{2}\,dx}_{0{,}8183} \underbrace{\int_{1/2}^{3/2} \sin^2\frac{\pi y}{2}\,dy}_{0{,}8183} \quad ??$$

GEN 2012

1

$H_2C=CH_2$



Etè

a) Objectiu: càlcul: optimitzar la geometria d'equilibri. Mètode RHF HF Roothan a geometria fija. De base mínima STO-3G

b)

1	H						
2	C	1	1,0				
3	C	2	1.3	1	120		
4	H	2	1,0	3	120	1	180
5	H	3	1,0	2	120	1	0
6	H	3	1,0	2	120	1	180

c) ${}_6C: 1s^2\,2s^2\,2p^2 \rightarrow \chi_{1s}, \chi_{2s}, \chi_{2px}, \chi_{2pz}, \chi_{2py} \quad \times 2 = 10$ OAs

${}_1H: 1s^1 \rightarrow \chi_{1s} \rightarrow 1\times4 = 4$ orbitals atòmics $+ 10 \Rightarrow 14$ OAs.

14 OAs $\rightarrow$ 14 OMs $\times 2 (\alpha$ i $\beta) =$ ~~28 files~~ $\rightarrow$ 16 files $\times$ 16 col.

$6+6+4 = 16\ e^- \rightarrow /2 \rightarrow$ 8 OMs ocupats + 6 virtuals

8 OMs ocupats $\times 2 \rightarrow \boxed{16\times16}$ o $\boxed{16\ e^-}$ nº e^- determina files & col

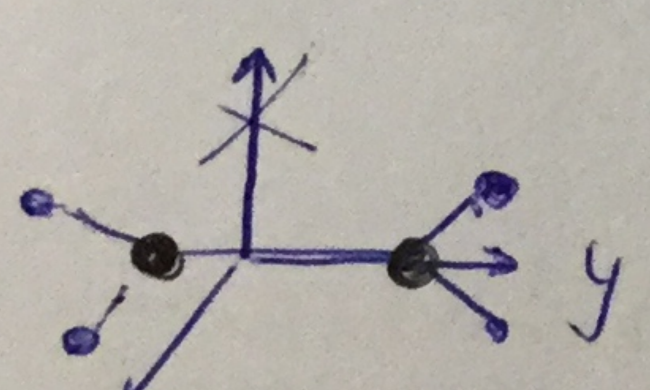
d) 8 OMs ocupados y 6 OMs virtuales.

e)

Plano ~~xz~~

OM 1 (s) $\rightarrow \sigma$
2 (s) $\rightarrow \sigma$
3 s/z $\rightarrow \sigma$
4 s/z $\rightarrow \sigma$
5 $\rightarrow \sigma$
6 $\rightarrow \sigma$
7 $\rightarrow \sigma$
8 $\rightarrow \pi$ (y)
9 y $\rightarrow \pi$
10 σ

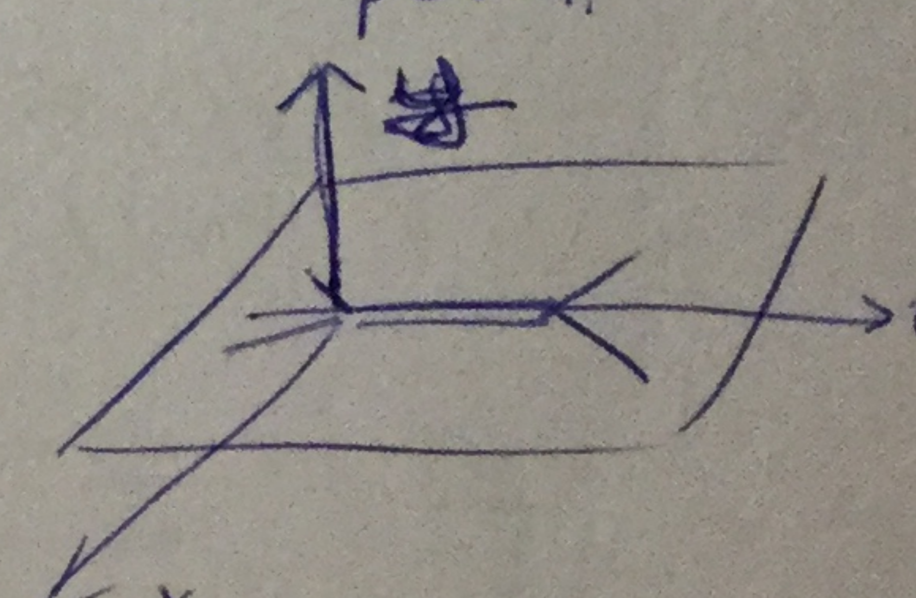
2py (C)

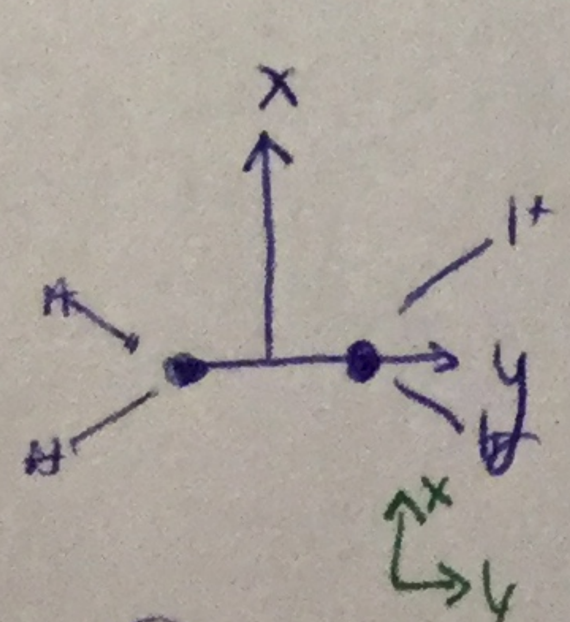


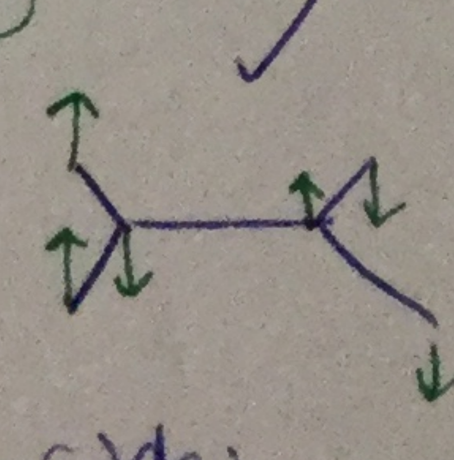
La única manera que la girar φ sea antisimetrica es si no está en el plano!!

↓

está plano xz





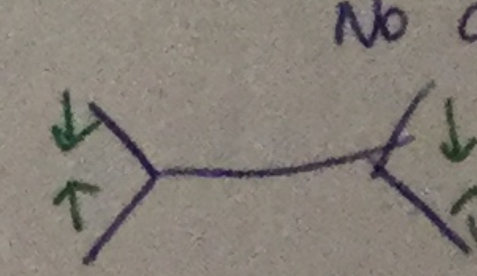


9

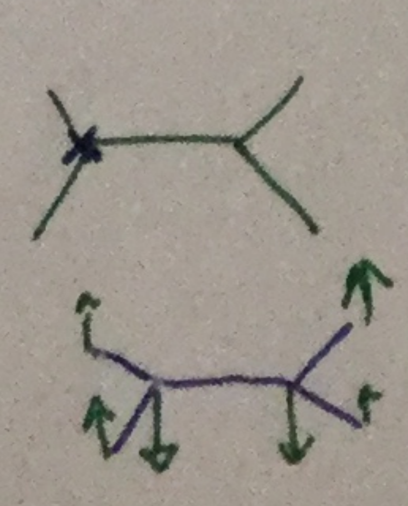
10

No activo

se anulan (flexión)



8



activo ie $p_q\left(\frac{d\mu}{dQ_8}\right) \neq 0$

2 $t=0 \rightarrow \Phi = N(\Phi_{2s} - \Phi_{2pz}) \rightarrow \Phi = \frac{1}{\sqrt{2}}(\Phi_{2s} - \Phi_{2pz})$

a) Sí que és estacionari pq $n=n=2 \rightarrow$ propi de $\hat{H}$

b) És pròpia de $\hat{L_z} \Rightarrow m=0$ i no és pròpia de $\hat{L}^2$ pq $l_{2s}=0$ $l_p=1$

c) $P = \sum C_i^2$ $\quad \hat{L}^2 = 2\hbar^2 = l(l+1)\hbar^2 \Rightarrow l=1$

$\boxed{P = 1/2} = 0{,}5$

$\Phi_{2pz} \left(\frac{z^5}{2^5\pi a^5}\right)^{1/2} r\cos\theta\, e^{-zr/2a} = \left(\frac{1}{2^5\pi}\right)^{1/\alpha} r\cos\theta\, e^{-r/2}$

d) $L_z \rightarrow 0$ only

e) $P(z>0) \Rightarrow z>0$

$P(z>0) = \int_0^\infty \Phi_{2pz}^2\, dV = \int_0^\infty \frac{1}{\sqrt{2}} \cancel{\Phi_{2s} + \frac{1}{\sqrt{2}}}\Phi_{2pz}\ dV$

$P(z>0) = \int_0^\infty \frac{z^5}{2^5\pi a^5} r^2\cos^2\theta\, e^{-2zr/2a}\, dV =$

$P(z>0) = \frac{z^5}{2^5\pi}\int_0^\infty r^2\cos^2\theta\, e^{-r}\, dV = \frac{1}{2^5\pi}\int_0^\infty r^2\cos^2\theta\, e^{-r} r^2 \sin\theta\, d\theta\, dr\, d\varphi$

$P(z>0) = \frac{1}{\pi 2^5}\int_0^\infty r^4 e^{-r}\, dr \int_0^{\pi/2} \cos^2\theta \sin\theta \int_0^{2\pi} d\varphi$

$= \frac{2\pi}{2^5\pi} \cdot \frac{4!}{1^5} \cdot \int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta = \frac{24}{16}\int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta$

$= \frac{3}{2} \cdot \frac{1}{3} = 1/2$

$\hat{S}^2 = s(s+1)\hbar = 3/4\,\hbar$ $\quad P=1$

$s = 1/2$

$S_z = m_s\hbar = 1/2\,\hbar \Rightarrow 1/2 = P$

$= -1/2\,\hbar$ $\quad P = 1/2$

Gen 2013

2 Ψ : nivells caixa $\cancel{\square}$ àrea $= 4a_0^2$ $\square$ 0,0 $2a_0$

(x,y) $\square$

Area $= a \times b = a^2 = 4a_0^2 \rightarrow a = \sqrt{4a_0^2} = 2a_0$ $\quad l = 2a_0$

$\Phi(x,y) = \Phi_x(a)\,\Phi_y(b) = \Phi_x(a)\,\Phi_y(a)$

$\Phi_x(a) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad a \; x \in (0,a)$ $\qquad E_{n_x n_y} = E_{n_x} n_y$

$\Phi(x,y) = \frac{2}{2a_0} \sin\left(\frac{n\pi x}{2a_0}\right) \sin\left(\frac{n\pi y}{2a_0}\right) \quad a \; x \in (0,a) \Rightarrow \Phi = 2 \sin\left(\frac{n\pi x}{2}\right) \sin\left(\frac{n\pi y}{2a}\right)$

$E_{n_x n_y} = \cancel{\frac{n_x^2 n_y^2 h^2}{8^2 m^2}}$ $\qquad E_{n_x n_y} = \frac{h^2}{8m}\left(\frac{n_x^2 + n_y^2}{a^2}\right)$ $\quad n = 1, 2, 3 \ldots$

$E_{n_x n_y} = \frac{h^2}{32m}(n_x^2 + n_y^2)$

d ? $n = 1 \rightarrow E_{10} = \frac{h^2}{8ma} = E_{01}$ $\qquad d = 2 \rightarrow E_{10} = \frac{h^2}{16m}$

d ? $n = 2 \rightarrow E_{11} = \frac{2h^2}{8ma}$ $\qquad d = 1 \rightarrow E_{11} = \frac{h^2}{8m}$

c) $\hat{H}' = b \quad \frac{1}{2}a_0 \le x \le \frac{3}{2}a_0$ i $\frac{1}{2}a_0 < y \le \frac{3}{2}a_0$ $\qquad H' = 0$ resta

E'_{00} ? $\hat{H} = -\frac{h^2}{2m}\frac{d^2}{dx^2} - \frac{1}{2}kx^2 + b$ $\qquad$ Estat fonamental $n = 1$

$E = \langle \Phi_{(x,y)} | \hat{H} \Phi(x,y) \rangle = \frac{2}{a_0}\int_{1/2}^{3/2}\int_{1/2}^{3/2} \sin\left(\frac{n\pi x}{a_0}\right) \sin\left(\frac{n\pi y}{a_0}\right) \hat{H}\,\Phi \; dx\,dy$

$E' = \underbrace{\langle \Phi(x,y) | \hat{H}\Phi(x,y) \rangle}_{n=1} + \langle \Phi(x,y) | \hat{H}' \Phi(x,y) \rangle$

Suposem $E_{10} = E_{01}$

$E = \frac{h^2}{8ma} + \frac{2}{a_0}\int_{1/2}^{3/2}\int_{1/2}^{3/2} \sin\frac{\pi x}{a_0} \sin\frac{\pi y}{a_0} \, b \left(\sin\frac{\pi x}{a_0} \sin\frac{\pi y}{a_0}\right) dx\,dy$