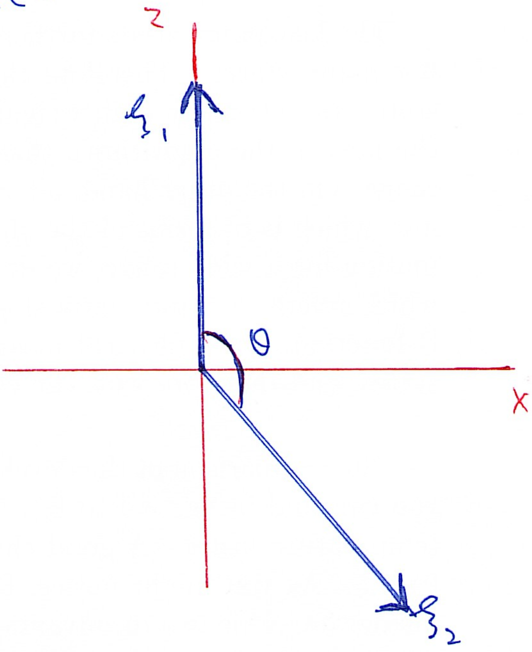
SQ30

The four hybrid orbitals:

$$\xi_i = a_i\psi_{2s} + b_i\psi_{2p_x} + c_i\psi_{2p_y} + d_i\psi_{2p_z}, \text{ where } i = 1,2,3,4.$$

Before doing the real calculation, we can set:

- ξ_1 to point along the z-direction
- ξ_2 to lie on the x-z plane



Also, $a_i = \frac{1}{\sqrt{4}}$ for $i=1,2,3,4$

$$\therefore \xi_1 = \frac{1}{\sqrt{4}}\psi_{2s} + d_1\psi_{2p_z}$$

$$\xi_2 = \frac{1}{\sqrt{4}}\psi_{2s} + b_2\psi_{2p_x} + d_2\psi_{2p_z}$$

Apply normalization conditions,

for ξ_1,

$$\left(\frac{1}{\sqrt{4}}\right)^2 + d_1^2 = 1 \Rightarrow d_1 = \pm\frac{\sqrt{3}}{2}$$

take $\boxed{d_1 = +\frac{\sqrt{3}}{2}}$ since it points to +z-direction

for ξ_2,

$$\left(\frac{1}{\sqrt{4}}\right)^2 + b_2^2 + d_2^2 = 1 \Rightarrow b_2^2 + d_2^2 = \frac{3}{4} \quad \cdots \text{(I)}$$

Apply orthogonality conditions,

for ξ_1 and ξ_2,

$$\int \xi_1^* \xi_2 \, d\tau = 0$$

$$\Rightarrow \left(\frac{1}{\sqrt{4}}\right)^2 + d_1 d_2 = 0$$

$$\Rightarrow \boxed{d_2 = -\frac{\sqrt{3}}{6}}$$

put the result back to the normalization condition (I),

$\boxed{b_2 = +\frac{\sqrt{6}}{3}}$ (Choose +ve sign to have positive x component)

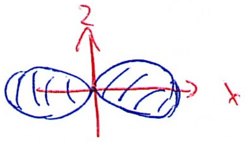
We now have

$$\xi_1 = \frac{1}{\sqrt{4}}\psi_{2s} + \frac{\sqrt{3}}{2}\psi_{2p_z}$$

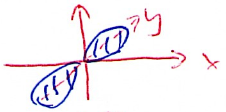
$$\xi_2 = \frac{1}{\sqrt{4}}\psi_{2s} + \frac{\sqrt{6}}{3}\psi_{2p_x} - \frac{\sqrt{3}}{6}\psi_{2p_z}$$

We can write a vector to represent the polarization of the wavefunction, with

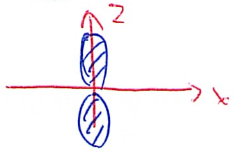
$\psi_{2p_x} \rightarrow \hat{x}$



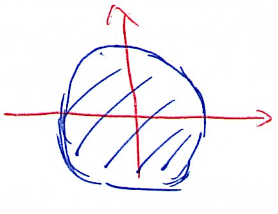
$\psi_{2p_y} \rightarrow \hat{y}$



$\psi_{2p_z} \rightarrow \hat{z}$



Note: ψ_{2s} has no direction since it looks like this:

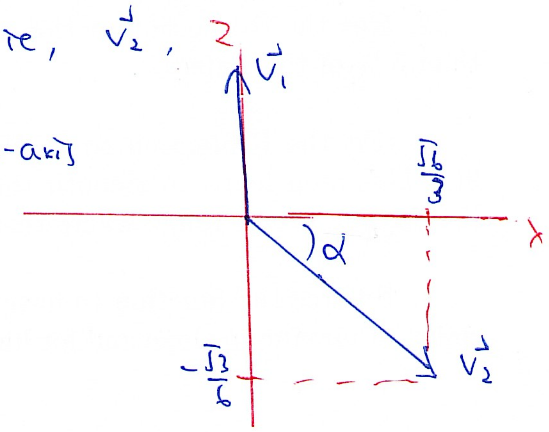


The vectors representing ξ_1 and ξ_2 are:

$\vec{v}_1 = d_1\hat{z} = \frac{\sqrt{3}}{2}\hat{z}$

$\vec{v}_2 = b_2\hat{x} + d_2\hat{z} = \frac{\sqrt{6}}{3}\hat{x} - \frac{\sqrt{3}}{6}\hat{z}$

(i) By observing the coeffs of ξ_2, ie, $\vec{v}_2$, the angle α between the vector and the x-axis can be found to be:



$$\tan\alpha = \frac{\left(\frac{\sqrt{3}}{6}\right)}{\left(\frac{\sqrt{6}}{3}\right)} = \frac{1}{2\sqrt{2}}$$

$\Rightarrow \alpha \simeq 19.5°$.

$\therefore$ The angle between ξ_1 and ξ_2 is $90° + 19.5° = 109.5°$

(ii) The angular dependence of ψ_{2p_x} and ψ_{2p_z} can be written separately such that:

$$\psi_{2p_x} = \sin\theta\cos\phi \quad R_{2p}(r)$$

$$\psi_{2p_z} = \cos\theta \quad R_{2p}(r)$$

(Note: $R_{2p}(r)$ is different from what we see in hydrogen atom)

$$\therefore \xi_2 = \frac{1}{\sqrt{4}}\psi_{2s} + \frac{\sqrt{6}}{3}\sin\theta\cos\phi\, R_{2p}(r) - \frac{\sqrt{3}}{6}\cos\theta\, R_{2p}(r)$$

We would like to find the value of θ, such that ξ_2 attains its maximum (to which direction the wavefunction points to)

Set $$\frac{\partial \xi_2}{\partial\theta} = \left(\frac{\sqrt{6}}{3}\cos\theta\cos\phi + \frac{\sqrt{3}}{6}\sin\theta\right) R_{2p}(r) = 0$$

Since ξ_2 lies on x-z plane,

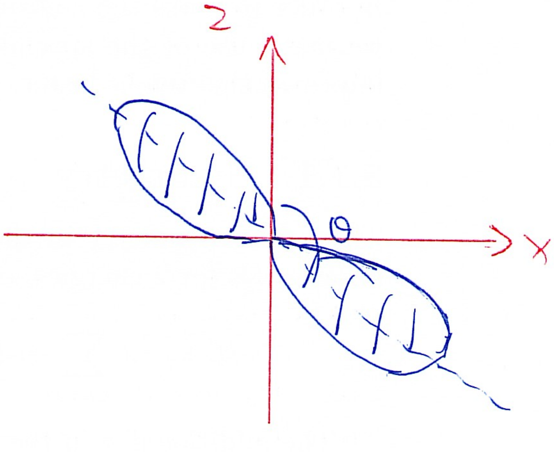
put $\phi = 0$,

$\therefore$ The equation becomes:

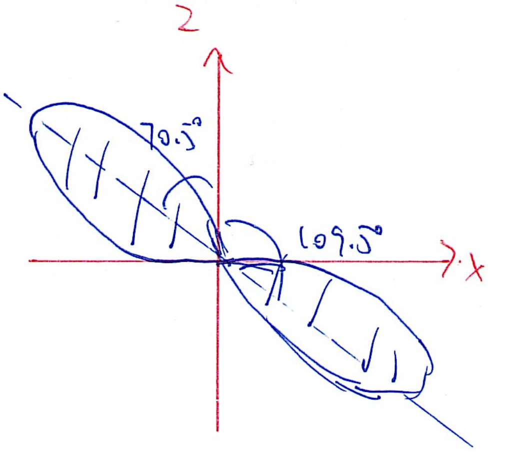
$$\frac{\sqrt{6}}{3}\cos\theta + \frac{\sqrt{3}}{6}\sin\theta = 0$$

$$\Rightarrow \quad \tan\theta = -2\sqrt{2}$$

$$\theta = -70.5^\circ.$$



This is equivalent to the wavefunction points to $\theta = 180^\circ - 70.5^\circ = 109.5^\circ$ //



SQ31

(a)
$$f_{n=0} = \frac{e^{-\hbar\omega/2kT}}{\sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\hbar\omega/kT}}$$

$$= \frac{1}{\sum_{n=0}^{\infty} e^{-n\hbar\omega/kT}}$$

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r} \quad \text{for } |r|<1$$

$$= \left[\frac{1}{1-e^{-\hbar\omega/kT}}\right]^{-1}$$

$$= 1 - e^{-\hbar\omega/kT}$$

(b)
$$\nu = \frac{1}{\lambda} = 299094 \text{ m}^{-1}$$

$$\omega = \frac{2\pi c}{\lambda} = 5.638 \times 10^{14} \text{ s}^{-1}$$

$$f_0 = 1 - e^{-\hbar\omega/kT} \approx 0.9999994$$

(c)
$$\mu = \left[\frac{1}{m_H} + \frac{1}{m_{Cl}}\right]^{-1} = 1.6273 \times 10^{-27} \text{ kg}$$

$$k = \mu\omega^2 = 517.231 \text{ kg s}^{-2}$$

$m_H = 1.00784\,u$

$m_{Cl} = 35.453\,u$

$1u = 1.66054 \times 10^{-27}$ kg

SQ 32

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(a) The third term, i.e. the rotational levels are:

$$E_l = \frac{l(l+1)\hbar^2}{2I}.$$

By the selection rule that $\Delta l = \pm 1$, the spectral line between an l state and an $l+1$ state has the energy:

$$E_{l+1} - E_l = \frac{\hbar^2}{2I}\left[(l+1)(l+2) - l(l+1)\right] = \frac{\hbar^2}{I}(l+1).$$

Similarly, the spectral line between an $l+1$ state and an $l+2$ state has the energy:

$$E_{l+2} - E_{l+1} = \frac{\hbar^2}{I}(l+2).$$

Then the spacing between spectral lines is:

$$\frac{\hbar^2}{I}(l+2) - \frac{\hbar^2}{I}(l+1) = \frac{\hbar^2}{I},$$

which is a constant, i.e. an equal spacing for all spectral lines.

(b) The equally spaced lines has a separation of frequency

$$f = 6.350 \times 10^{11}\ \mathrm{Hz}.$$

The moment of inertia I is calculated by:

$$\frac{\hbar^2}{I} = hf$$

$$\Rightarrow I = \frac{\hbar}{2\pi f}. \quad [1]$$

And if we treat the diatomic molecule by the method of center of mass, the moment of inertia I is:

$$I = \mu R_0^2, \quad [2]$$

where R_0 is the bond length and μ is the reduced mass:

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{1 \times 35}{1 + 35}\ \mathrm{amu} \approx 1.624 \times 10^{-27}\ \mathrm{kg}.$$

Then by equations [1] and [2],

$$R_0 = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{\hbar}{2\pi f \mu}} \approx 1.28\ \mathring{A}.$$