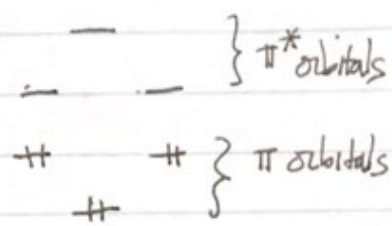
Comment on HW

Jahn-Teller theorem

If the highest occupied orbital of a molecule is degenate and contains an odd # of electrons the molecule will distort so as to remove the degeneracy.

Consider benzene (6-fold symmetry)



If you add an electron or remove an electron the molecule will distort so that the 6-fold symmetry is lost

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Hint for first HW problem.

I expect that it was obvious that I meant a distortion from square to rectangular

Note that for small δ the distortion approximately conserves area: $A = (a+\delta)(a-\delta) = a^2 - \delta^2$ | No linear term.

The key to the problem is the use of the Taylor series.

More on harmonic oscillator

$$\frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \alpha^2 x^2\right)\psi = 0$$

Try $\psi = e^{-bx^2}$; $\psi' = -2bx\, e^{-bx^2}$, $\psi'' = (-2b + 4b^2x^2)e^{-bx^2}$

$$\left(-2b + 4b^2x^2 + \frac{2mE}{\hbar^2} - \alpha^2x^2\right) e^{-bx^2} = 0$$

$\Rightarrow \frac{2mE}{\hbar^2} = 2b \Rightarrow E = \frac{1}{2}h\nu = \frac{1}{2}\hbar\omega$

and $4b^2 = \alpha^2 \Rightarrow b = \alpha/2$ $\therefore \psi = e^{-\alpha x^2/2}$

Now try $\psi = x e^{-bx^2}$, $\psi' = (1 - 2bx^2)e^{-bx^2}$, $\psi'' = (-2bx - 4bx + 4b^2x^3)e^{-bx^2}$

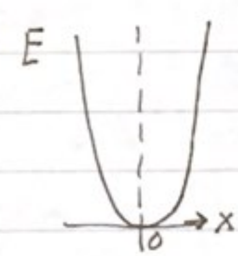
$$\left(-6bx + 4b^2x^3 + \frac{2mE}{\hbar^2}x - \alpha^2x^3\right) e^{-bx^2}$$

$\Rightarrow \frac{2mE}{\hbar^2} = 6b \Rightarrow E = \frac{3}{2}h\nu = \frac{3}{2}\hbar\omega$

and $4b^2 = \alpha^2 \Rightarrow \psi = x e^{-\alpha x^2/2}$

Now try $(ax^2 + c)e^{-bx^2}$

Then try $(ax^3 + cx)e^{-bx^2}$



What is the motivation for these guesses

The potential is symmetric about $x=0$.
Each higher energy solution has one more node than the level just below it.

So the levels will alternate even, odd, even, ... and as we go up in energy we need more nodes which $\Rightarrow$ a higher order polynomial.

Note that the wave function falls off as a Gaussian rather than as an exponential in the non-classical region.

Bra-Ket nomenclature

$|i\rangle = \psi_i$, where i is the quantum #

$\langle i|\hat{A}|j\rangle = \int \psi_i^* \hat{A} \psi_j \, d\tau$

If the functions ψ_i are from an eigenvalue problem they form a basis that spans the space.

$\langle i|j\rangle = \delta_{ij}$

Identity operator $1 = \sum_i |i\rangle\langle i|$

$\sum_i \sum_j |i\rangle\underbrace{\langle i|j\rangle}_{\delta_{ij}}\langle j| = \sum |i\rangle\langle i|$

$\sum_i |i\rangle\langle i|f\rangle$ projects f onto the various basis functions

Consider $\langle i|x^2|i\rangle$

we can always insert the identity operator

$\langle i|x^2|i\rangle = \langle i|x\,1\,x|i\rangle = \sum_j \langle i|x|j\rangle\langle j|x|i\rangle = \sum_j |\langle i|x|j\rangle|^2$

Consider $\sum_{j\neq 1} \langle 1|x|j\rangle\langle j|x|1\rangle$

$1 = |1\rangle\langle 1| + \sum_{j\neq 1} |j\rangle\langle j|$

So $\sum_{j\neq 1} \langle 1|x|j\rangle\langle j|x|1\rangle = \langle 1|x^2|1\rangle - \langle 1|x|1\rangle^2$