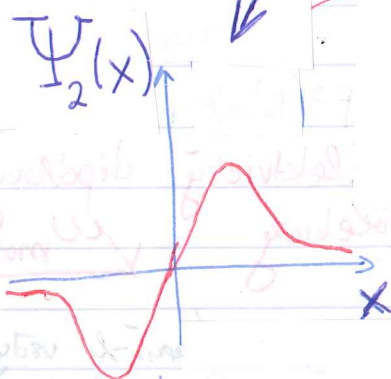


4.4

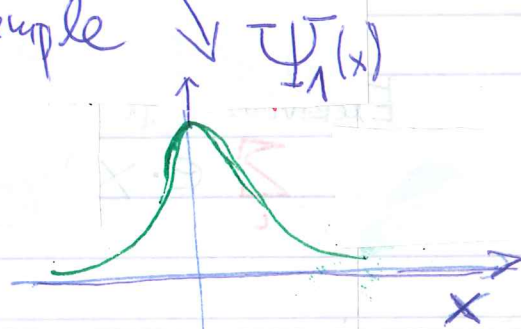
SELECTION RULES

FOR VIBRATIONAL TRANSITIONS
IN THE HARMONIC APPROXIMATION

TRANSITION MOMENT $\mu_{v'v} = \int \Psi_{v'}^* \hat{\mu} \Psi_v dx \neq 0$



for example



? What would be the overlap between $\Psi_1(x)$ and $\Psi_2(x)$ without $\hat{\mu}$? **Zero!**

$\hat{\mu}$ = ELECTRIC DIPOLE MOMENT OPERATOR

- Describes interaction between the electric component of EM field AND molecular charge distribution

Nov 7/1

In the so-called DIPOLE APPROXIMATION,
 x-component of $\hat{\mu}$ can be written as:

$$\hat{\mu}_x = -E_x \cdot e \cdot x$$

for 1 electron

E_x : electric field intensity in x-direction
 e : elementary charge
 x : coordinate

For many electrons + nuclei in a molecule

$$e \cdot x \rightarrow \mu_{MOL} = \sum_{i=1}^N e \cdot x_i$$

substitute with N

charge at position x due to particle i (= nucleus or electron)

μ_{MOL} = MOLECULAR DIPOLE MOMENT

to particle i (= nucleus or electron)

depends on R_{A-B} i.e. changes with the vibration

Using Taylor expansion, we can express

μ_{MOL} as:

DIPOLE MOMENT

PERMANENT

$$\mu_{MOL} = \mu_0 + \frac{1}{1!} \left(\frac{d\mu}{dx} \right)_{x=0} \cdot x + \frac{1}{2!} \left(\frac{d^2\mu}{dx^2} \right)_{x=0} \cdot x^2 + \dots$$

Nov 7/2

Let us insert μ_{MOL} in the expression for the transition moment:

$$\mu_{n'n'} = \int \Psi_{n'}^* \mu_{\text{MOL}} \Psi_n dx \neq 0$$

$$\mu_{n'n'} = \int \Psi_{n'}^* \left[\mu_0 + \frac{1}{1!} \left(\frac{d\mu}{dx} \right)_{x=0} x + \frac{1}{2!} \left(\frac{d^2\mu}{dx^2} \right)_{x=0} x^2 + \dots \right] \Psi_n dx$$

General expression for $\Psi_n, \Psi_{n'}$?

$$\Psi_n(x) = A_n e^{-\frac{x^2}{2}} H_n(x)$$

$X = \sqrt{\frac{m\omega}{\hbar}} x$
vibrat. displacement

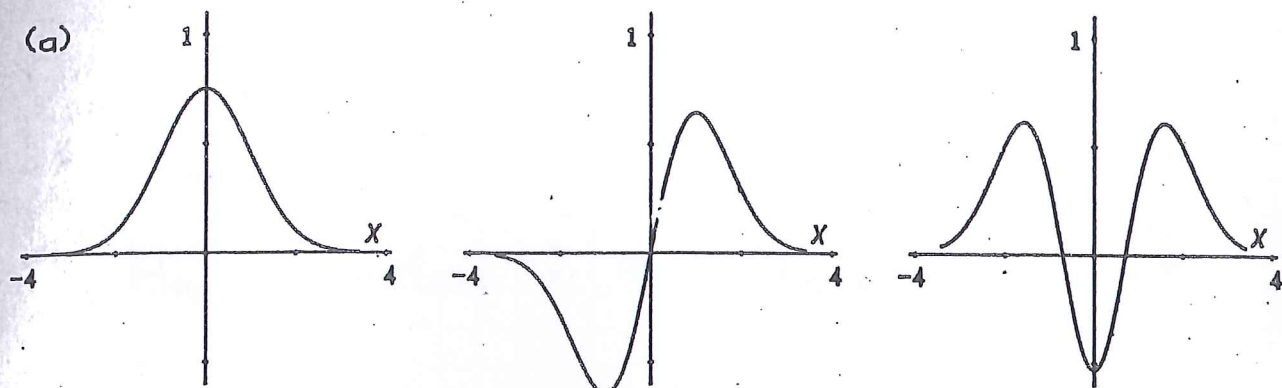
NORMALIZATION CONSTANT SOLUTION FOR $n=0$ HERMITIAN POLYNOMIAL IN X

TABLE OF HERMITIAN POLYNOMIALS

$H_n(x)$ for $n = 0, 1, 2, 3, 4, 5$

$H_0(x) = 1$
$H_1(x) = 2x$
$H_2(x) = 4x^2 - 2$
$H_3(x) = 8x^3 - 12x$
$H_4(x) = 16x^4 - 48x^2 + 12$
$H_5(x) = 32x^5 - 160x^3 + 120x$

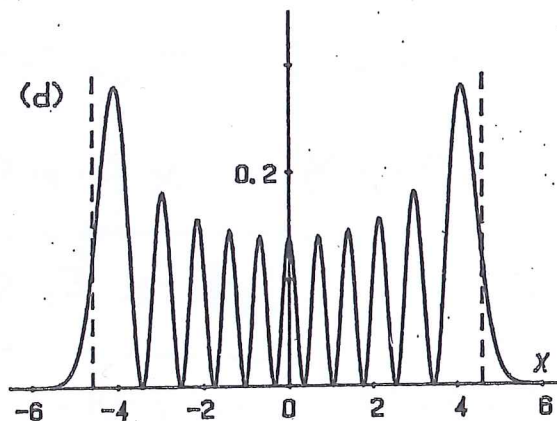
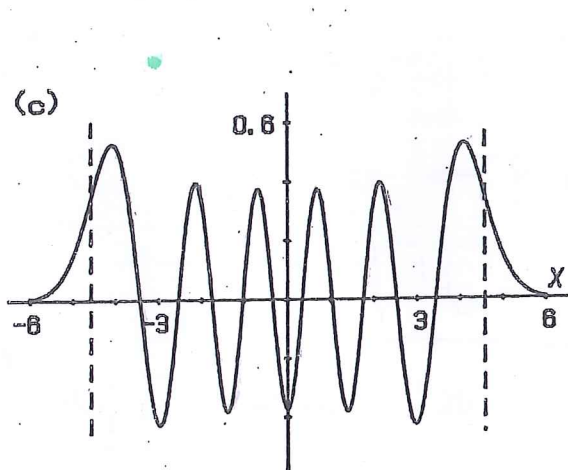
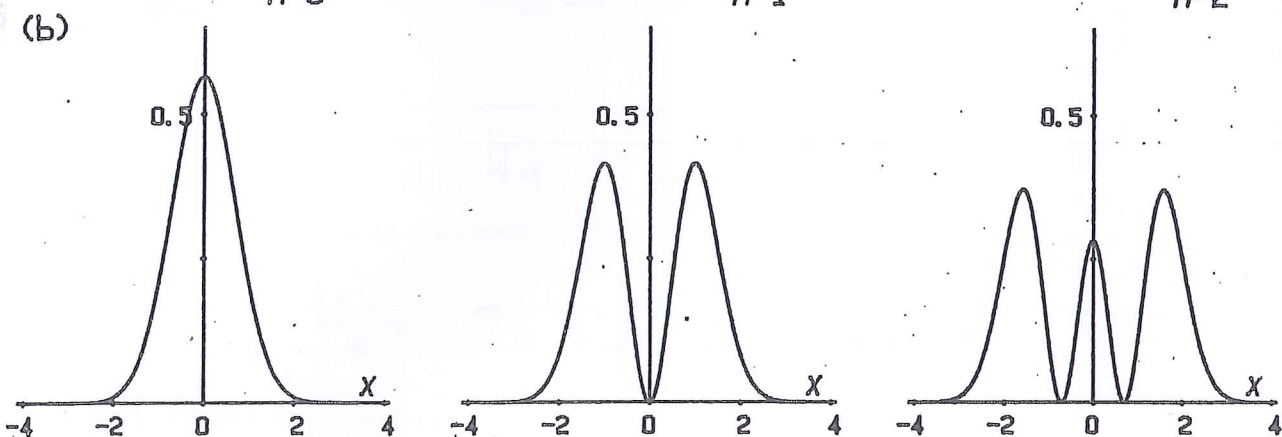
How do the Ψ_n look like?



$n=0$

$n=1$

$n=2$



(a) Wavefunctions $\Psi_n(x)$, $n=0,1,2$ + (b) Corresponding probability densities, $\Psi_n^2(x)$. On y axis, (a) $(\hbar/m\omega)^{1/4} \Psi_n(x)$ and (b) $(\hbar/m\omega)^{1/2} \Psi_n^2(x)$ is displayed.

(c) Wavefunction $(\hbar/m\omega)^{1/4} \Psi_{10}(x)$, (d) Probability density $(\hbar/m\omega)^{1/2} \Psi_{10}^2(x)$

Nov 7th/14

Let us insert $\Psi_{\nu'}(x)$ and $\Psi_{\nu}(x)$ into $\mu_{\nu'\nu}$ keeping just first 2 terms of μ_{MOL} (=approximation)

$$\mu_{\nu'\nu} \equiv \int A_{\nu'} e^{-\frac{x^2}{2}} H_{\nu'}(x) \left[\mu_0 + \left. \left(\frac{d\mu}{dx} \right) \cdot x \right]_{x=0} A_{\nu} e^{-\frac{x^2}{2}} H_{\nu}(x) dx$$

$$\mu_{\nu'\nu} = A_{\nu'} A_{\nu} \mu_0 \underbrace{\int e^{-\frac{x^2}{2}} H_{\nu'}(x) \cdot e^{-\frac{x^2}{2}} H_{\nu}(x) dx}_{=0} +$$

Since $\Psi_{\nu'}(x)$ is always orthogonal to $\Psi_{\nu}(x)$ for $\nu' \neq \nu$

$$+ A_{\nu'} A_{\nu} \left(\frac{d\mu}{dx} \right)_{x=0} \int e^{-\frac{x^2}{2}} H_{\nu'}(x) \cdot x \cdot e^{-\frac{x^2}{2}} H_{\nu}(x) dx$$

must

overlap

with $e^{-\frac{x^2}{2}} H_{\nu}(x)$

↓

From table of $H_{\nu}(x)$ it can be

shown that $\nu'' = \nu \pm 1$

MOLECULAR DIPOLE MOMENT MUST CHANGE WITH THE VIBRATION

(\Rightarrow) TRANSITION FORBIDDEN

FOR HOMONUCLEAR DIATOMICS BUT ALLOWED e.g. for $\text{O}=\text{C}=\text{O}$ BENDING

2 BASIC SELECTION RULES FOR VIBRATIONAL TRANSITIONS IN THE HARMONIC APPROXIMATION.

Nov 7th / 15