

# Chapter 14

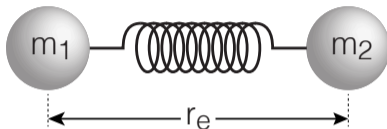
## Vibrational Motion of Molecules

P. J. Grandinetti

Chem. 4300

## Diatomic Molecule Vibration

Harmonic oscillator is model for small vibrations of molecules as well as other systems in physics and chemistry.



Model bond as spring that acts as restoring force whenever two atoms are squeezed together or pulled away from equilibrium position.

Kinetic and potential energy operators are

$$\hat{K} = \frac{\hat{p}^2}{2\mu} \quad \text{and} \quad \hat{V}(x) = \frac{1}{2} \kappa_f \hat{x}^2$$

$x = r - r_e$  and  $\mu$  is reduced mass

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

# Schrödinger equation for harmonic oscillator

Insert Kinetic and Potential Energy operators

$$\hat{H}\psi(x) = (\hat{K} + \hat{V})\psi(x) = -\frac{\hbar^2}{2\mu} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2}\kappa_f x^2 \psi(x) = E\psi(x)$$

Defining  $k^2 = \frac{2\mu E}{\hbar^2}$  and  $\alpha^4 = \frac{\mu\kappa_f}{\hbar^2}$  and substituting above, the Schrödinger equation becomes

$$\frac{d^2\psi(x)}{dx^2} + (k^2 - \alpha^4 x^2)\psi(x) = 0$$

- This ODE doesn't have simple solutions like particle in infinite well.
- Harmonic oscillator potential becomes infinitely high as  $x$  goes to  $\infty$
- Wave function is continuous and single valued over  $x = -\infty$  to  $\infty$ .

## Schrödinger equation for harmonic oscillator

Notice at large values of  $|x|$  one can approximate ODE:

$$\frac{d^2\psi(x)}{dx^2} + (k^2 - \alpha^4 x^2)\psi(x) = 0 \quad \text{at large } |x| \text{ becomes } \frac{d^2\psi(x)}{dx^2} - \alpha^4 x^2 \psi(x) \approx 0$$

With solutions

$$\psi(x) \sim Ae^{\pm\alpha^2 x^2/2} \quad \text{but only accept } \psi(x) \sim Ae^{-\alpha^2 x^2/2} \quad \text{as physical}$$

Don't forget, these are NOT solutions for all  $x$  — only large  $|x|$

However, in light of this asymptotic solution, we further define

$$\xi = \alpha x \quad \text{and} \quad \psi(x)dx = \chi(\xi)d\xi$$

to transform Schrödinger equation into

$$\frac{d^2\chi(\xi)}{d\xi^2} + \left( \frac{k^2}{\alpha^2} - \xi^2 \right) \chi(\xi) = 0$$

## Schrödinger equation for harmonic oscillator

We expect solution to this ODE to have asymptotic limits

$$\lim_{|\xi| \rightarrow \infty} \chi(\xi) = Ae^{-\xi^2/2}$$

We propose a general solution

$$\chi(\xi) = A H(\xi) e^{-\xi^2/2}$$

Substituting into ODE gives

$$\frac{d^2 H(\xi)}{d\xi^2} - 2\xi \frac{dH(\xi)}{d\xi} + 2nH(\xi) = 0 \quad \text{where} \quad n = \frac{k^2}{\alpha^2} - 1$$

9 out of 10 math majors recognize this as *Hermite's differential equation*

Its solutions are the *Hermite polynomials*.

Only solutions with  $n = 0, 1, 2, \dots$  are physically acceptable for harmonic oscillator.

## First seven Hermite polynomials and approximate roots.

$n$	$H_n(y)$	Roots			
0	1				
1	$2y$	0			
2	$4y^2 - 2$	$\pm 0.707107$			
3	$8y^3 - 12y$	0	$\pm 1.224745$		
4	$16y^4 - 48y^2 + 12$	$\pm 0.5246476$	$\pm 1.650680$		
5	$32y^5 + 160y^3 + 120y$	0	$\pm 0.958572$	$\pm 2.020183$	
6	$64y^6 - 480y^4 + 720y^2 - 120$	$\pm 0.436077$	$\pm 1.335850$	$\pm 2.350605$	
7	$128y^7 - 1344y^5 + 3360y^3 - 1680y$	0	$\pm 0.816288$	$\pm 1.673552$	$\pm 2.65196$

## Harmonic Oscillator Wave Function

Normalized solutions to Schrödinger equation for harmonic oscillator are

$$\chi_n(\xi) = A_n H_n(\xi) e^{-\xi^2/2}, \quad \text{where} \quad A_n \equiv \frac{1}{\sqrt{2^n n! \pi^{1/2}}}$$

Condition that  $n$  only be integers leads to harmonic oscillator energy levels

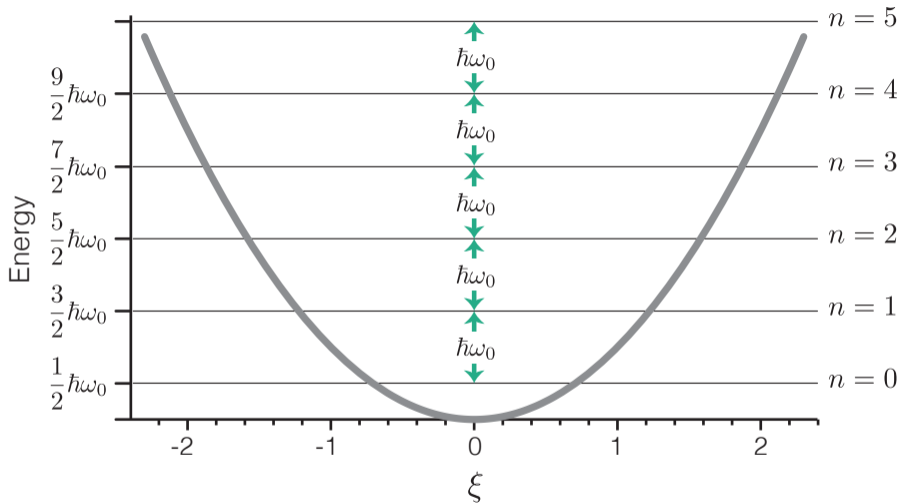
$$E_n = \hbar\omega_0(n + 1/2), \quad n = 0, 1, 2, \dots \quad \text{where} \quad \omega_0 = \sqrt{k_f/\mu}$$

Energy levels are equally spaced at intervals of  $\Delta E = \hbar\omega_0$ .

In spectroscopy, vibrational frequencies are given in terms of the *spectroscopic wavenumber*,

$$\tilde{\nu} = \frac{\omega_0}{2\pi c_0}$$

# Harmonic Oscillator Energy Levels



Ground state with  $n = 0$  has zero point energy of  $\frac{1}{2}\hbar\omega_0$ .



## Example

Calculate the vibrational energy level spacing for diatomic hydrogen molecule.

*From the Table 5.1 in text, we know that  $\tilde{\nu} = 4401 \text{ cm}^{-1}$  for the hydrogen molecule. Recalling that  $\tilde{\nu} = \omega/(2\pi c_0)$ , we calculate a spacing of*

$$\Delta E = \hbar\omega_0 = \hbar(2\pi c_0)\tilde{\nu} = \hbar(2\pi c_0)(4401 \text{ cm}^{-1}) = 87.423 \text{ zJ}.$$

## Example

Evaluate  $k_B T$  at room temperature,  $T = 298 \text{ K}$ , convert it to equivalent unit of  $\text{cm}^{-1}$ , and compare it to diatomic hydrogen molecule vibrational energy spacing.

*Equating  $k_B T$  to the energy associated with  $\tilde{\nu}$ ,*

$$\Delta E = \hbar\omega = \hbar(2\pi c_0)\tilde{\nu} = k_B T,$$

*gives*

$$\tilde{\nu} = k_B T / (\hbar(2\pi c_0)) = k_B(298 \text{ K}) / (\hbar(2\pi c_0)) = 207.12 \text{ cm}^{-1}.$$

## Harmonic Oscillator Wave Functions in terms of $x$

$$\chi_n(\xi) = A_n H_n(\xi) e^{-\xi^2/2}, \quad \text{where} \quad A_n \equiv \frac{1}{\sqrt{2^n n! \pi^{1/2}}}$$

Rewriting in terms of  $x$  gives

$$\psi_n(x) = N_n H_n(\alpha x) e^{-(\alpha x)^2/2} \quad \text{where} \quad N_n \equiv \sqrt{\alpha} A_n = \sqrt{\frac{\alpha}{2^n n! \pi^{1/2}}}$$

Lowest energy wave function has form of Gaussian function

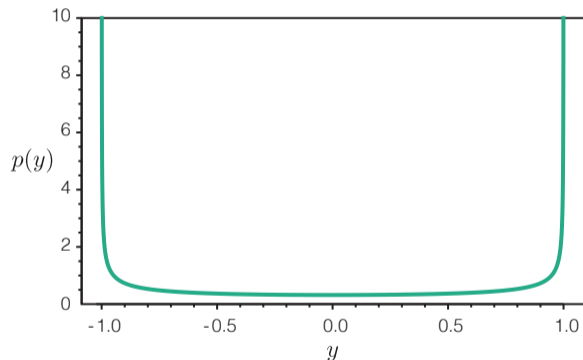
$$\psi_0(x) = \sqrt{\frac{\alpha}{\pi^{1/2}}} e^{-(\alpha x)^2/2}$$

and probability distribution that is Gaussian

$$\psi_0^*(x) \psi_0(x) = \frac{\alpha}{\sqrt{\pi}} e^{-(\alpha x)^2}$$

with standard deviation of  $\Delta x = 1/(\alpha\sqrt{2})$ .

## Maximum displacement of classical harmonic oscillator



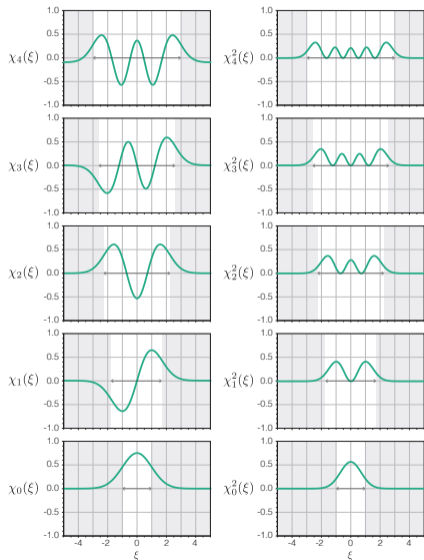
Recall: Maximum displacement of classical harmonic oscillator in terms of energy

$$x^{\max} = \frac{1}{\omega_0} \sqrt{\frac{2E}{m}}$$

Combined with  $E_n = \hbar\omega_0(n + 1/2)$  we obtain corresponding  $x^{\max}$ : classical turning point for each quantum oscillator state

$$\xi_n^{\max} = \alpha x_n^{\max} = \sqrt{2n + 1}$$

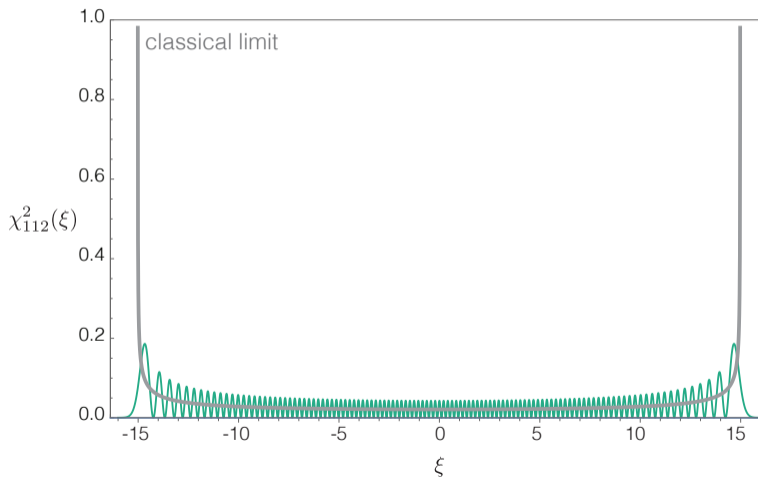
# Harmonic Oscillator Wave Functions



- $n$ th oscillator state has  $n$  nodes.
  - ▶ Wave function changes sign at roots of the Hermite polynomials.
- Note similarities and differences with 1D infinite well.
  - ▶  $n$ th oscillator state corresponds to  $(n + 1)$ th infinite well state.
- Tiny horizontal arrows represent classical oscillator displacement range for same energy.
  - ▶ Gray represents classically excluded region,  $\xi > \xi_n^{\max}$
  - ▶ Finite potential leads to wave function penetration into classically excluded region, i.e., tunneling.

## Classical Oscillator Turning Points

As  $n$  increases probability density function approaches that of classical harmonic oscillator displacement probability (gray line) shown with the  $n = 112$  oscillator



## (Avoiding) Integrals involving Hermite polynomials

Hermite polynomials with even  $n$  are even functions while those with odd  $n$  are odd functions. Keep this in mind when evaluating integrals.

### Example

Calculate  $\langle x \rangle$  for harmonic oscillator wave function.

Starting with integral

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) \hat{x} \psi_n(x) dx = \int_{-\infty}^{\infty} x \psi_n^*(x) \psi_n(x) dx,$$

- Note that  $\psi_n$  are real, so  $\psi_n^*(x) = \psi_n(x)$ .
- Since  $\psi_n(x)$  is either even or odd depending on whether  $n$  is even or odd, respectively, then product,  $\psi_n^*(x)\psi_n(x) = \psi_n(x)\psi_n(x)$  is always even.
- Therefore  $x\psi_n^2(x)$  is always odd and we obtain  $\langle x \rangle = 0$ .

## (Avoiding) Integrals involving Hermite polynomials

### Example

Calculate  $\langle p \rangle$  for harmonic oscillator wave function.

Calculate

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) \hat{p} \psi_n(x) dx = -i\hbar \int_{-\infty}^{\infty} \psi_n(x) \frac{\partial \psi_n(x)}{\partial x} dx.$$

- The derivative of an odd function is even
- The derivative of an even function is odd
- Integrand is product of even and odd functions
- Thus, integrand is odd function
- and therefore integral is zero, that is,  $\langle p \rangle = 0$ .

## (Avoiding) Integrals involving Hermite polynomials

Another useful result for avoiding integrals involving the Hermite polynomials is

$$A_m A_n \int_{-\infty}^{\infty} H_m(\xi) H_n(\xi) e^{-\xi^2} d\xi = \delta_{m,n}$$

where  $\delta_{m,n}$  is the *Kronecker delta function* defined as

$$\delta_{mn} = \begin{cases} 0 & \text{if } m \neq n, \\ 1 & \text{if } m = n. \end{cases}$$

Hermite polynomials also obey two useful recursion relations

$$H_{n+1}(\xi) - 2\xi H_n(\xi) + 2n H_{n-1}(\xi) = 0$$

and

$$\frac{dH_n(\xi)}{d\xi} = 2n H_{n-1}(\xi)$$



## Example

Using Hermite polynomials recursion relations to show that  $\langle x \rangle = 0$ .

Since  $\xi = \alpha x$  this is identical to  $\langle \xi \rangle = 0$ .

Start with

$$\langle \xi \rangle = A_n A_m \int_{-\infty}^{\infty} (H_n e^{-\xi^2/2}) \xi (H_n e^{-\xi^2/2}) d\xi = A_n A_m \int_{-\infty}^{\infty} H_n \xi H_n e^{-\xi^2} d\xi$$

Using recursion relation we find

$$\xi H_n = \frac{1}{2} H_{n+1} + n H_{n-1},$$

Substituting back into our integral we obtain

$$\begin{aligned} \langle \xi \rangle &= A_n A_m \int_{-\infty}^{\infty} H_n \left( \frac{1}{2} H_{n+1} + n H_{n-1} \right) e^{-\xi^2} d\xi \\ &= \frac{1}{2} A_n A_m \int_{-\infty}^{\infty} H_n H_{n+1} e^{-\xi^2} d\xi + n A_n A_m \int_{-\infty}^{\infty} H_n H_{n-1} e^{-\xi^2} d\xi \end{aligned}$$

Since  $n \neq n \pm 1$ , both integrals are zero and thus  $\langle \xi \rangle = 0$ .

# Polyatomic Molecule Vibration

## Polyatomic Molecule Vibration

Hamiltonian operator describing vibrational motion of polyatomic molecule is

$$\hat{H} = V_e + \frac{1}{2} \sum_i^{3N-6} \left( \hat{Q}_i^2 + \lambda_i \hat{Q}_i^2 \right)$$

Leave it as exercise to show that

$$\hat{Q}_i = -i\hbar \frac{\partial}{\partial Q_i}$$

Hamiltonian becomes

$$\hat{H}_{\text{vib}} = \sum_i^{3N-6} \left( -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \lambda_i \hat{Q}_i^2 \right) = \sum_i^{3N-6} \hat{H}_i$$

Dropped  $V_e$ , as it does not affect eigenfunctions. It is constant added to  $E_{\text{vib}}$ .

$$\hat{H}_{\text{vib}} \psi_{\text{vib}} = E_{\text{vib}} \psi_{\text{vib}}$$

## Polyatomic Molecule Vibration

$$\hat{H}_{\text{vib}} = \sum_i^{3N-6} \left( -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \lambda_i \hat{Q}_i^2 \right) = \sum_i^{3N-6} \hat{H}_i$$

Since the Hamiltonian is sum of contributions, and each contribution depends on only one normal mode coordinate, solution to Schrödinger equation is product of wave functions for each normal mode,

$$\psi_{\text{vib}} = \psi_1(Q_1) \psi_2(Q_2) \dots \psi_{3N-6}(Q_{3N-6}) = \prod_i^{3N-6} \psi_i(Q_i)$$

where

$$\hat{H}_i \psi_i(Q_i) = E_i \psi_i(Q_i)$$

Total energy is sum of eigenvalues of each  $\hat{H}_i$ : 
$$E_{\text{vib}} = \sum_i^{3N-6} E_i$$

## Polyatomic Molecule Vibration

Summary: solving Schrödinger wave equation for polyatomic molecule vibrations involves solving  $3N - 6$  wave equations for each normal mode coordinate, each given by

$$\hat{H}_i \psi_i(Q_i) = -\frac{\hbar^2}{2} \frac{\partial^2 \psi_i(Q_i)}{\partial Q_i^2} + \frac{1}{2} \lambda_i \hat{Q}_i^2 \psi_i(Q_i) = E_i \psi_i(Q_i)$$

Rearranging this wave function to

$$\frac{\partial^2 \psi_i(Q_i)}{\partial Q_i^2} + \left( \frac{2E_i}{\hbar^2} - \frac{\lambda_i}{\hbar^2} \hat{Q}_i^2 \right) \psi_i(Q_i) = 0$$

and defining

$$k_i^2 = \frac{2E_i}{\hbar^2}, \quad \text{and} \quad \alpha_i^4 = \frac{\lambda_i}{\hbar^2}$$

obtain wave equation in same form as diatomic molecule

$$\frac{d^2 \psi_i(Q_i)}{dQ_i^2} + (k_i^2 - \alpha_i^4 Q_i^2) \psi_i(Q_i) = 0$$

## Polyatomic Molecule Vibration

$$\frac{d^2\psi_i(Q_i)}{dQ_i^2} + (k_i^2 - \alpha_i^4 Q_i^2)\psi_i(Q_i) = 0$$

Solutions have same form as diatomic molecule

$$\psi_{i,n}(Q_i) = N_{n_i} H_{n_i}(\alpha_i Q_i) e^{-(\alpha_i Q_i)^2/2}, \quad \text{where} \quad N_{i,n} = \sqrt{\alpha_i} A_{n_i} = \sqrt{\frac{\alpha_i}{2^{n_i} n_i! \pi^{1/2}}}$$

where  $n_i$  is vibrational quantum number for  $i$ th normal mode.

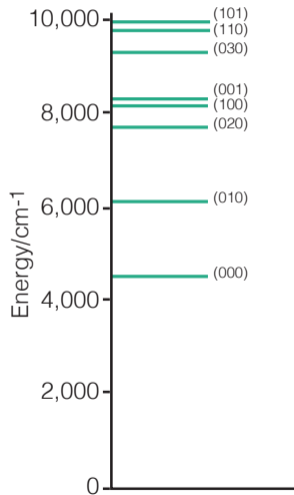
Energy of each normal mode is given by

$$E_{i,n} = \hbar\omega_i(n_i + 1/2), \quad n_i = 0, 1, 2, \dots \quad \text{where} \quad \omega_i = \sqrt{\lambda_i}$$

Total energy is given by

$$E_{\text{vib}} = \sum_i^{3N-6} \hbar\omega_i(n_i + 1/2)$$

# Water Vibrational Energy Levels



- Ground state energy, with  $n_i = 0$  for all normal modes, is

$$E_{\text{vib}}^{\circ} = \frac{1}{2} \hbar \sum_i^{3N-6} \omega_i$$

- Zero-point energy can be considerable in polyatomic molecule.
- Water molecule, ( $n_1 = 0, n_2 = 0, n_3 = 0$ ) ground state energy is
  - ▶  $E_{\text{vib}}^{\circ} = 8.939 \times 10^{-20} \text{ J}$  or  $E_{\text{vib}}^{\circ}/(hc_0) = 4,500 \text{ cm}^{-1}$
- *Fundamental energy levels* have all normal mode quantum numbers of zero except one, which has a value of 1.
- *Overtone energy levels* have all normal mode quantum numbers of zero except one, which has a value greater than 1.
- *Combination energy levels* have two or more non-zero quantum numbers.

# Creation and Annihilation Operators



## Creation and Annihilation Operators

- Small oscillations in potential well can be approximated as harmonic oscillator
- Describes situations from molecular vibration to nuclear structure.
- Quantum field theory starting point–basis of quantum theory of light.

Consider harmonic oscillator Hamiltonian written in form

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} \mu \omega_0^2 \hat{x}^2$$

Define two non-hermitian operators

$$\hat{a}_+ = \sqrt{\frac{\mu\omega_0}{2\hbar}} \left( \hat{x} - i \frac{\hat{p}}{\mu\omega_0} \right) \quad \text{and} \quad \hat{a}_- = \sqrt{\frac{\mu\omega_0}{2\hbar}} \left( \hat{x} + i \frac{\hat{p}}{\mu\omega_0} \right)$$

called Creation and Annihilation operators, respectively.

## Creation and Annihilation Operators

Calculate product  $\hat{a}_+\hat{a}_-$

$$\hat{a}_+\hat{a}_- = \frac{\mu\omega_0}{2\hbar} \left( \hat{x}^2 + \frac{i\hat{x}\hat{p} - i\hat{p}\hat{x}}{\mu\omega_0} + \frac{\hat{p}^2}{\mu^2\omega_0^2} \right) = \frac{1}{\hbar\omega_0} \underbrace{\left( \frac{\hat{p}^2}{2\mu} + \frac{\mu\omega_0^2\hat{x}^2}{2} \right)}_{\hat{H}} + \frac{i}{2\hbar} \underbrace{(\hat{x}\hat{p} - \hat{p}\hat{x})}_{[\hat{x},\hat{p}]=i\hbar}$$

Recognizing the commutator in the last term we obtain

$$\hat{a}_+\hat{a}_- = \frac{\hat{H}}{\hbar\omega_0} + \frac{i}{2\hbar}(i\hbar) = \frac{\hat{H}}{\hbar\omega_0} - \frac{1}{2}$$

and obtain

$$\hat{H} = \hbar\omega_0 \left( \hat{a}_+\hat{a}_- + \frac{1}{2} \right)$$

Both  $\hat{H}$  and  $\hat{a}_+\hat{a}_-$  have same  $\psi_n(x)$  as eigenstates. Define  $\hat{a}_+\hat{a}_-$  as the *Number operator*:

$$\hat{N} = \hat{a}_+\hat{a}_- \quad \text{where} \quad \hat{N}\psi_n(x) = n\psi_n(x)$$

and

$$\hat{H} = \hbar\omega_0 \left( \hat{N} + \frac{1}{2} \right)$$

## Creation and Annihilation Operators

Look at effect of applying  $\hat{a}_+$  on eigenstates of  $\hat{H}$ .

$$\text{If } \psi' = \hat{a}_+ \psi_n \text{ then } \hat{H}\psi' = \hat{H}(\hat{a}_+ \psi_n) = \underbrace{\hbar\omega_0 \left( \hat{a}_+ \hat{a}_- + \frac{1}{2} \right)}_{\hat{H}} (\hat{a}_+ \psi_n)$$

and

$$\hat{H}\psi' = \hbar\omega_0 \left( \hat{a}_+ \hat{a}_- \hat{a}_+ + \frac{1}{2} \hat{a}_+ \right) \psi_n = \hat{a}_+ \hbar\omega_0 \underbrace{\left( \hat{a}_- \hat{a}_+ + \frac{1}{2} \right)}_{\frac{\hat{H}}{\hbar\omega_0} + 1} \psi_n = \hat{a}_+ (\hat{H} + \hbar\omega_0) \psi_n$$

Then we can write

$$\hat{H}\psi' = \hat{H}(\hat{a}_+ \psi_n) = \hat{a}_+ (\hat{H} + \hbar\omega_0) \psi_n = \hat{a}_+ (E_n + \hbar\omega_0) \psi_n = (E_n + \hbar\omega_0) (\hat{a}_+ \psi_n)$$

We found that energy of  $\hat{a}_+ \psi_n$  is  $\hbar\omega_0$  higher than  $E_n$ , the energy of  $\psi_n$ .

**Effect of  $\hat{a}_+$  on  $\psi_n$  is to change it into  $\psi_{n+1}$  with  $E_{n+1} = E_n + \hbar\omega_0$**

## Creation (Raising) and Annihilation (Lowering) operators

- Similarly, one can show that  $\hat{a}_-$  applied to  $\psi_n$  turns it into  $\psi_{n-1}$ .
- $\hat{a}_+$  and  $\hat{a}_-$  are called *Creation and Annihilation operators*, respectively.
- $\hat{a}_+$  and  $\hat{a}_-$  are also called *Raising and Lowering operators*, respectively.
- Without proof, coefficients that maintain normalization of the wave functions when applying  $\hat{a}_\pm$  are

$$\hat{a}_+\psi_n = \sqrt{(n+1)}\psi_{n+1} \quad \text{and} \quad \hat{a}_-\psi_n = \sqrt{n}\psi_{n-1}$$

## Fun trick with Creation and Annihilation operators

As we can't go any lower than  $n = 0$  we must have  $\hat{a}_-\psi_0 = 0$

We can use this to determine  $\psi_0$

Since

$$\hat{a}_-\psi_0 = \sqrt{\frac{\mu\omega_0}{2\hbar}} \left( \hat{x} + i\frac{\hat{p}}{\mu\omega_0} \right) \psi_0 = 0$$

Expanding and rearranging gives

$$\frac{d\psi_0}{dx} = -\frac{\mu\omega_0}{\hbar}x\psi_0$$

Integrating

$$\int \frac{d\psi_0}{\psi_0} = -\frac{\mu\omega_0}{\hbar} \int x dx$$

gives

$$\psi_0 = A_0 e^{(\mu\omega_0/\hbar)x^2/2}$$

Recalling  $(\mu\omega_0/\hbar) = \sqrt{\mu\kappa_f/\hbar^2} = \alpha^2$

gives

$$\psi_0 = A_0 e^{-\alpha^2 x^2/2} = A_0 e^{-\xi^2/2}$$

## Fun trick with Creation and Annihilation operators

Normalizing  $\psi_0$  with integral

$$\int_{-\infty}^{\infty} \psi_0^*(x)\psi_0(x)dx = \int_{-\infty}^{\infty} |A_0|^2 e^{-\alpha^2 x^2} dx = 1$$

gives

$$|A_0|^2 = \alpha/\sqrt{\pi}$$

so we have

$$\psi_0 = \frac{\alpha^{1/2}}{\pi^{1/4}} e^{-\alpha^2 x^2/2}$$

From  $\psi_0$  we can use  $\hat{a}_+$  to generate all higher energy eigenstates.

## Example

Use  $\hat{a}_+$  to generate  $\psi_1(x)$  from  $\psi_0(x)$ .

$$\psi_1 = \hat{a}_+ \psi_0 = \underbrace{\left[ \frac{\alpha}{\sqrt{2}} \left( \hat{x} - i \frac{\hat{p}}{\mu\omega_0} \right) \right]}_{\hat{a}_+} \underbrace{\frac{\alpha^{1/2}}{\pi^{1/4}} e^{-\alpha^2 x^2/2}}_{\psi_0} = \frac{\alpha^{3/2}}{\sqrt{2}\pi^{1/4}} \left[ 1 + \frac{\hbar\alpha^2}{\mu\omega_0} \right] x e^{-\alpha^2 x^2/2}$$

Check that

$$\frac{\hbar\alpha^2}{\mu\omega_0} = \frac{\hbar}{\mu\omega_0} \left( \frac{\mu\kappa_f}{\hbar^2} \right)^{1/2} = \frac{(\mu\kappa_f)^{1/2}}{\mu\omega_0} = \frac{(\mu\kappa_f)^{1/2}}{\mu} \left( \frac{\mu}{\kappa_f} \right)^{1/2} = 1$$

Thus we obtain

$$\psi_1(x) = \frac{\alpha^{3/2}}{\sqrt{2}\pi^{1/4}} 2x e^{-\alpha^2 x^2/2} = \underbrace{\frac{\alpha^{1/2}}{\sqrt{2}\pi^{1/4}}}_{A_1} \underbrace{(2\alpha x)}_{H_1(\alpha x)} e^{-\alpha^2 x^2/2}$$

Although tedious you can find all Hermite polynomials this way.

# Web App - 1D QM simulation of single bound particle

Link here: [1D Quantum Wells](#)

Web app instructions:

- Solves Schrödinger equation and shows solutions.
- Default is infinite square well (zero everywhere inside, infinite at edges).
- Top is graph of potential and horizontal lines show energy levels.
- Below is probability distribution of particle's position, oscillating back and forth in a combination of two states.
- Below particle's position is graph of momentum.
- Bottom set of phasors show magnitude and phase of lower-energy states.
- To view state, move mouse over energy level on potential graph.
- To select a single state, click on it.
- Select single state by picking one phasor at bottom and double-clicking.
- Click on phasor and drag value to modify magnitude and phase to create combination of states.
- Select different potentials from Setup menu at top right.