Quantum Harmonic Oscillator

Chapter 13

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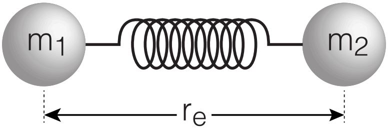
Kinetic and Potential Energy Operators

Harmonic oscillator well is model for small vibrations of atoms about bond 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

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

$x = r - r_e$ and μ is reduced mass

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

Force constants for selected diatomic molecules

Bond	κ_f/(N/m)	$\mu/10^{-28}$ kg	$\tilde{\nu}$/cm^{-1}	Bond length/pm
H_2	570	8.367664	4401	74.1
D_2	527	16.72247	2990	74.1
$H^{35}Cl$	478	16.26652	2886	127.5
$H^{79}Br$	408	16.52430	2630	141.4
$H^{127}I$	291	16.60347	2230	160.9
$^{35}Cl^{35}Cl$	319	290.3357	554	198.8
$^{79}Br^{79}Br$	240	655.2349	323	228.4
$^{127}I^{127}I$	170	1053.649	213	266.7
$^{16}O^{16}O$	1142	132.8009	1556	120.7
$^{14}N^{14}N$	2243	116.2633	2331	109.4
$^{12}C^{16}O$	1857	113.8500	2143	112.8
$^{14}N^{16}O$	1550	123.9830	1876	115.1
$^{23}Na^{23}Na$	17	190.8770	158	307.8
$^{23}Na^{35}Cl$	117	230.3282	378	236.1
$^{39}K^{35}Cl$	84	306.0237	278	266.7

Schrödinger equation for harmonic oscillator

Insert Kinetic and Potential Energy operators

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}\kappa_{\mathrm{f}} x^2\psi(x) = E\psi(x)$$

and defining $\quad k^2 = \dfrac{2\mu E}{\hbar^2}$ and $\alpha^4 = \dfrac{\mu\kappa_{\mathrm{f}}}{\hbar^2}$

so 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 ∞
- Wave function is continuous and single valued over $x = -\infty$ to ∞.

Schrödinger equation for harmonic oscillator

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

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

With solutions

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

But these are NOT solutions for all 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

$$\lim_{\xi \to \infty} \chi(\xi) = A e^{-\xi^2/2}$$

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 $n = 0, 1, 2, \ldots$ are physically acceptable for harmonic oscillator.

First seven Hermite polynomials and approximate roots.

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

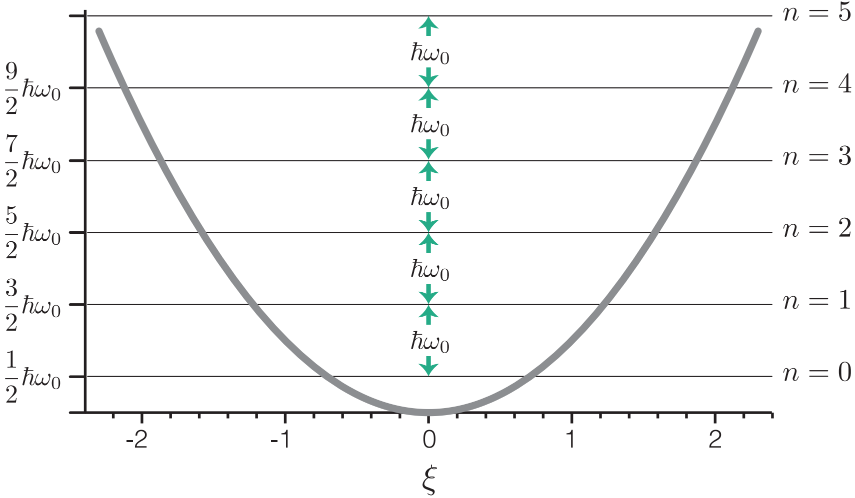
$$\boxed{E_n = \hbar\omega_0(n + 1/2), \quad n = 0, 1, 2, \ldots \quad \text{where} \quad \omega_0 = \sqrt{\kappa_\mathsf{f}/\mu}}$$

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

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

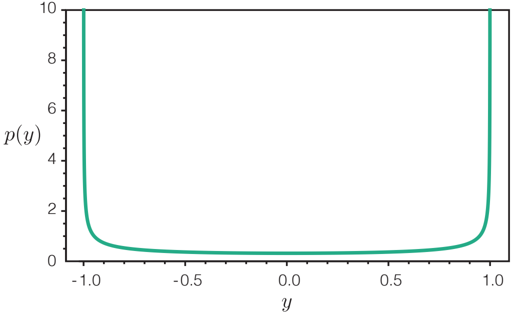
$$\tilde{\nu} = \frac{\omega_0}{2\pi c_0}$$

Harmonic Oscillator Energy Levels



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

Maximum displacement of classical harmonic oscillator



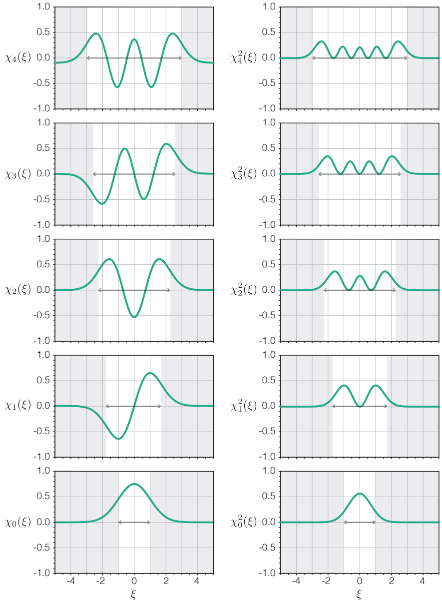
Maximum displacement of classical harmonic oscillator in terms of energy

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

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

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

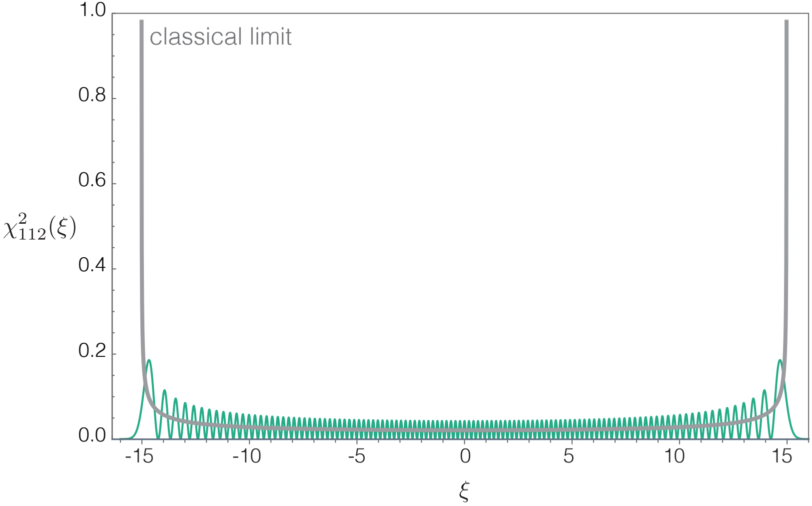
Harmonic Oscillator Wave Functions



- nth oscillator state has n nodes.
- approximate roots of the Hermite polynomials in earlier slide.
- Note similarities and differences with infinite well.
- nth 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, $\xi > \xi_n^{\text{max}}$
- Finite potential leads to wave function penetration into classically excluded region.

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



Web App - 1D QM simulation of single bound particle

Link here: 1D Quantum Wells

- 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.

Harmonic Oscillator Wave Functions

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

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 $\Delta x = 1/(\alpha\sqrt{2})$.

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 ψ_n are real, so $\psi_n^*(x) = \psi_n(x)$.
- Since $\psi_n(x)$ is either even or odd depending on whether n, 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 $\langle x \rangle = 0$.

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, $\langle p \rangle = 0$.

Integrals involving Hermite polynomials

A useful integral involving the Hermite polynomials is

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

Hermite polynomials also obey two useful recursion relations

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

and

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

Example

Using the recursion relations above show that $\langle x \rangle = 0$.
Since $\xi = \alpha x$ this is identical to $\langle \xi \rangle = 0$.
Start with

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

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

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

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

Creation and Annihilation Operators

- Nearly every 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

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

We now define two non-hermitian operators

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

Creation and Annihilation Operators

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

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

and rearrange to

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

Recognizing the commutator in the last term we obtain

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

and obtain

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

Creation and Annihilation Operators

Both $\hat{\mathcal{H}}$ and $\hat{a}_-\hat{a}_+$ have same $\psi_n(x)$ as eigenstates.

We further define the *number operator* as

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

and

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

Similarly you can show that

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

and identify $\hat{a}_-\hat{a}_+ = \hat{N} + 1$

Creation and Annihilation Operators

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

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

and

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

Then we can write

$$\hat{\mathcal{H}}\psi' = \hat{\mathcal{H}}(\hat{a}_+\psi_n) = \hat{a}_+\left(\hat{\mathcal{H}} + \hbar\omega_0\right)\psi_n = \hat{a}_+\left(E + \hbar\omega_0\right)\psi_n = \left(E + \hbar\omega_0\right)(\hat{a}_+\psi_n)$$

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

Effect of $\hat{a}_+$ on ψ_n is to change it into ψ_{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 ψ_n turns it into ψ_{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

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

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 ψ_0

Since

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

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 $(\mu\omega_0/\hbar) = \sqrt{\mu\kappa_{\mathsf{f}}/\hbar^2} = \alpha^2$

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 ψ_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 ψ_0 we can use $\hat{a}_+$ to generate all higher energy eigenstates.

Example

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

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

Check that

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

Thus we obtain

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

Although tedious you can find all Hermite polynomials this way.