Chapter 13
Quantum Harmonic Oscillator

P. J. Grandinetti

Chem. 4300
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

\[ \hat{K} = \frac{\hat{p}^2}{2\mu} \quad \text{and} \quad \hat{V}(x) = \frac{1}{2} \kappa x^2 \]

\( x = r - r_e \) and \( \mu \) is reduced mass

\[ \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \]
<table>
<thead>
<tr>
<th>Bond</th>
<th>$k_f/(\text{N/m})$</th>
<th>$\mu/10^{-28}\text{ kg}$</th>
<th>$\tilde{\nu}/\text{cm}^{-1}$</th>
<th>Bond length/pm</th>
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<tbody>
<tr>
<td>H$_2$</td>
<td>570</td>
<td>8.367664</td>
<td>4401</td>
<td>74.1</td>
</tr>
<tr>
<td>D$_2$</td>
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<td>74.1</td>
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<tr>
<td>H$^{35}\text{Cl}$</td>
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<td>16.26652</td>
<td>2886</td>
<td>127.5</td>
</tr>
<tr>
<td>H$^{79}\text{Br}$</td>
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<td>16.52430</td>
<td>2630</td>
<td>141.4</td>
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<tr>
<td>H$^{127}\text{I}$</td>
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<td>16.60347</td>
<td>2230</td>
<td>160.9</td>
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<tr>
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<td>290.3357</td>
<td>554</td>
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<tr>
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<td>240</td>
<td>655.2349</td>
<td>323</td>
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<tr>
<td>$^{127}\text{I}^{127}\text{I}$</td>
<td>170</td>
<td>1053.649</td>
<td>213</td>
<td>266.7</td>
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<tr>
<td>$^{16}\text{O}^{16}\text{O}$</td>
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<td>132.8009</td>
<td>1556</td>
<td>120.7</td>
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<tr>
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<td>116.2633</td>
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<td>306.0237</td>
<td>278</td>
<td>266.7</td>
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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:

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

at large $|x|$ becomes

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

With solutions

$$\psi(x) \sim Ae^{\pm \alpha^2 x^2/2}$$

but only accept

$$\psi(x) \sim Ae^{-\alpha^2 x^2/2}$$

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

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

We propose a general solution

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

Substituting into ODE gives

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

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.

<table>
<thead>
<tr>
<th>n</th>
<th>$H_n(y)$</th>
<th>Roots</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$2y$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>$4y^2 - 2$</td>
<td>$\pm 0.707107$</td>
</tr>
<tr>
<td>3</td>
<td>$8y^3 - 12y$</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>$16y^4 - 48y^2 + 12$</td>
<td>$\pm 0.5246476$</td>
</tr>
<tr>
<td>5</td>
<td>$32y^5 + 160y^3 + 120y$</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>$64y^6 - 480y^4 + 720y^2 - 120$</td>
<td>$\pm 0.436077$</td>
</tr>
<tr>
<td>7</td>
<td>$128y^7 - 1344y^5 + 3360y^3 - 1680y$</td>
<td>0</td>
</tr>
</tbody>
</table>
Harmonic Oscillator Wave Function

Normalized solutions to Schrödinger equation for harmonic oscillator are

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

Condition that \( n \) only be integers leads to harmonic oscillator energy levels

\[ E_n = \hbar \omega_0 (n + 1/2), \quad n = 0, 1, 2, \ldots \]  
where  
\[ \omega_0 = \sqrt{\kappa f/\mu} \]

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

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

\[ \tilde{v} = \frac{\omega_0}{2\pi c_0} \]
Harmonic Oscillator Energy Levels

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

Energy

-2
-1
0
1
2

$n = 5$
$n = 4$
$n = 3$
$n = 2$
$n = 1$
$n = 0$

Energy Levels

$\frac{9}{2}\hbar\omega_0$
$\frac{7}{2}\hbar\omega_0$
$\frac{5}{2}\hbar\omega_0$
$\frac{3}{2}\hbar\omega_0$
$\frac{1}{2}\hbar\omega_0$

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Chapter 13: Quantum Harmonic Oscillator
Recall: 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 \( x_{\text{max}} \): classical turning point for each oscillator state

\[
\xi_{n}^{\text{max}} = \alpha x_{n}^{\text{max}} = \sqrt{2n + 1}
\]
Harmonic Oscillator Wave Functions

- $n$th oscillator state has $n$ nodes.
  - approximate roots of the Hermite polynomials in earlier slide.

- 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, $\xi > \xi_{n}^{\text{max}}$
  - 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.
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.
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 $\Delta x = 1/(\alpha \sqrt{2})$. 

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Chapter 13: Quantum Harmonic 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 \( n \), 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 \( \langle x \rangle = 0 \).
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
(Avoiding) Integrals involving Hermite polynomials

Another useful result for avoiding integrals involving the Hermite polynomials is

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

Hermite polynomials also obey two useful recursion relations

\[
H_{n+1}(\xi) - 2\xi H_n(\xi) + 2nH_{n-1}(\xi) = 0
\]

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

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

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

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

$$= \frac{1}{2} \int_{-\infty}^{\infty} H_n H_{n+1} e^{-\frac{\xi^2}{2}} d\xi + n \int_{-\infty}^{\infty} H_n H_{n-1} e^{-\frac{\xi^2}{2}} d\xi$$

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

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

$$\hat{a}_+ \hat{a}_- = \frac{\mu \omega_0}{2\hbar} \left( \hat{x}^2 + \frac{i\hat{p} \hat{x} - \hat{x} \hat{p}}{\mu \omega_0} + \frac{\hat{p}^2}{\mu^2 \omega^2} \right) = \frac{1}{\hbar \omega_0} \left( \frac{\hbar \omega_0}{2\mu} + \frac{\mu \omega_0^2 \hat{x}^2}{2} \right) + \frac{i}{2\hbar} (\hat{\chi} \hat{p} - \hat{p} \hat{\chi})$$

Recognizing the commutator in the last term we obtain

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

and obtain

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

Both $\hat{\chi}$ and $\hat{a}_+ \hat{a}_-$ have same $\psi_n(x)$ as eigenstates. We further define the number operator as

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

and

$$\hat{\chi} = \hbar \omega_0 \left( \hat{N} + \frac{1}{2} \right)$$
Creation and Annihilation Operators

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

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

and

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

Then we can write

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

We just learned that energy of $\hat{a}_+ \psi_n$ is $\hbar \omega_0$ higher than $E$, 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 \( \psi_0(x) \).

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

Check that

\[
\frac{\hbar \alpha^2}{\mu \omega} = \frac{\hbar}{\mu \omega} \left( \frac{\mu \kappa_f}{\hbar^2} \right)^{1/2} = \left( \frac{\mu \kappa_f}{\mu \omega} \right)^{1/2} = \left( \frac{\mu}{\kappa_f} \right)^{1/2} = 1
\]

Thus we obtain

\[
\psi_1(x) = \frac{\alpha^{3/2}}{\sqrt{2} \pi^{1/4}} 2 x e^{-\alpha^2 x^2/2} = \frac{\alpha^{1/2}}{\sqrt{2} \pi^{1/4}} \left( 2 \alpha x \right) e^{-\alpha^2 x^2/2}
\]

Although tedious you can find all Hermite polynomials this way.