Chapter 4
The Harmonic Oscillator

The one-dimensional harmonic oscillator

- Classical-Mechanical Treatment
- Quantum-Mechanical Treatment
The one-dimensional harmonic oscillator: Classical treatment

Illustration showing a classical particle mass $m$ attached to a spring and constrained to move in one dimension. The displacement of the particle from its equilibrium position is $x$. The box drawn with a broken line indicates a closed system.

\begin{align*}
F &= ma \\
F_x &= -kx \\
-kx &= m \frac{d^2 x}{dt^2} \\
x &= A \sin \left(2\pi vt + b\right) \\
\nu &= \frac{1}{2\pi} \left(\frac{k}{m}\right)^{1/2}
\end{align*}

\begin{align*}
y''(x) + \omega^2 y(x) &= 0 \\
y &= A \cos cx + B \sin cx \\
y &= D \sin (cx + \epsilon)
\end{align*}
The one-dimensional harmonic oscillator: Classical treatment

\[
F_x = -\frac{\partial V}{\partial x}, \quad F_y = -\frac{\partial V}{\partial y}, \quad F_z = -\frac{\partial V}{\partial z}
\]

\[
F_x = -\frac{dV}{dx} = -kx
\]

\[
V = \int kxdx = \frac{1}{2}kx^2 + C,
\]

\[
V = \frac{1}{2}kx^2 \quad C = 0
\]

\[
V = 2\pi^2 \nu^2 m x^2
\]

\[
T = \frac{1}{2}m(\frac{dx}{dt})^2
\]

\[
E = T + V = \frac{1}{2}kA^2 = 2\pi^2 \nu^2 mA^2
\]

Classical probability density for an oscillating particle.

\[
x = A \sin(2\pi \nu t + b)
\]

\[
\frac{dx}{dt} = A \times 2\pi \nu \cos(2\pi \nu t + b)
\]
The one-dimensional harmonic oscillator: Quantum treatment

Hamiltonian function

\[ H(x, p) = \frac{p^2}{2m} + V(x) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 \]

Hamiltonian operator

\[ \hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + 2\pi^2\nu^2m.x^2 = -\frac{\hbar^2}{2m} \left( \frac{d^2}{dx^2} - \alpha^2 x^2 \right) \]

\[ \alpha \equiv 2\pi \nu m / \hbar \]

\[ \frac{d^2\psi}{dx^2} + (2mE\hbar^{-2} - \alpha^2 x^2)\psi = 0 \]

There are two procedures available for solving this differential equation.

1) The Frobenius or series solution method
2) The ladder operator procedure

1) The Frobenius or series solution method

A substitution that simplify the procedure is:

\[ \psi = e^{-\alpha x^2/2} f(x) \]

\[ \psi'' = e^{-\alpha x^2/2} \left( f'' - 2\alpha xf' - \alpha f + \alpha^2 x^2 f \right) \]

\[ \frac{d^2\psi}{dx^2} + (2mE\hbar^{-2} - \alpha^2 x^2)\psi = 0 \]

\[ f''(x) - 2\alpha xf'(x) + (2mE\hbar^{-2} - \alpha) f(x) = 0 \]
The one-dimensional harmonic oscillator: Quantum treatment

\[ f(x) = \sum_{n=0}^{\infty} c_n x^n \]

\[ f'(x) = \sum_{n=1}^{\infty} n c_n x^{n-1} = \sum_{n=0}^{\infty} n c_n x^n \]

\[ f''(x) = \sum_{n=2}^{\infty} n(n-1)c_n x^{n-2} \]

\[ = \sum_{j=0}^{\infty} (j+2)(j+1)c_{j+2} x^j = \sum_{n=0}^{\infty} (n+2)(n+1)c_{n+2} x^n \]

\[ f''(x) - 2\alpha x f'(x) + (2mEh^{-2} - \alpha) f(x) = 0 \]

\[ \sum_{n=0}^{\infty} (n+2)(n+1)c_{n+2} x^n - 2\alpha \sum_{n=0}^{\infty} n c_n x^n + (2mEh^{-2} - \alpha) \sum_{n=0}^{\infty} c_n x^n = 0 \]

Two term recursion relation. Thus, there is two arbitrary constants: \( c_0 \) and \( c_1 \)
The one-dimensional harmonic oscillator: Quantum treatment

If $c_1 = 0$

$$\psi = e^{-\alpha x^2/2} f(x) = e^{-\alpha x^2/2} \sum_{n=0,2,4,...}^\infty c_n x^n = e^{-\alpha x^2/2} \sum_{l=0}^\infty c_{2l} x^{2l}$$

If $c_0 = 0$

$$\psi = e^{-\alpha x^2/2} \sum_{n=1,3,...}^\infty c_n x^n = e^{-\alpha x^2/2} \sum_{l=0}^\infty c_{2l+1} x^{2l+1}$$

The general solution:

$$\psi = A e^{-\alpha x^2/2} \sum_{l=0}^\infty c_{2l+1} x^{2l+1} + B e^{-\alpha x^2/2} \sum_{l=0}^\infty c_{2l} x^{2l}$$

We now must see if the boundary conditions on the wave function lead to any restrictions on the solution.

How the two infinite series behave for large $x$:

$$c_{n+2} = \frac{\alpha + 2\alpha n - 2mEh^{-2}}{(n+1)(n+2)} c_n$$

$$n = 2l$$

$$c_{2l+2} = \frac{\alpha + 4\alpha l - 2mEh^{-2}}{(2l+1)(2l+2)} c_{2l}$$
The one-dimensional harmonic oscillator: Quantum treatment

Assuming that for large values of x the later terms are the dominant ones:

\[ \frac{c_{2l+2}}{c_{2l}} \approx \frac{4\alpha l}{(2l)(2l)} = \frac{\alpha}{l} \]

For \( n = 2l + 1 \)

\[ \frac{c_{2l+3}}{c_{2l+1}} \approx \frac{\alpha}{l} \]

The one-dimensional harmonic oscillator: Quantum treatment

\[ e^z = \sum_{n=0}^{\infty} \frac{z^n}{n!} = 1 + z + \frac{z^2}{2!} + \cdots \]

\[ e^{\alpha x^2} = 1 + \alpha x^2 + \cdots + \frac{\alpha^l x^{2l}}{l!} + \frac{\alpha^{l+1} x^{2l+2}}{(l+1)!} + \cdots \]

\[ \frac{\alpha^{l+1}}{(l+1)!} \div \frac{\alpha^l}{l!} = \frac{\alpha}{l+1} \sim \frac{\alpha}{l} \quad \text{For large } l \]
The one-dimensional harmonic oscillator: Quantum treatment

For large $x$:

Each series goes as $e^{ax^2}$, $\Psi$ goes as $e^{ax^2/2}$

If we could somehow break off the series after a finite number of terms, then the factor $e^{-ax^2/2}$ would ensure that $\psi$ went to zero as $x$ became infinite.

How?

If the coefficient for $c_v (n=v)$ become zero, then $c_{v+2}$, $c_{v+4}$, ... vanishes

$$c_{n+2} = \frac{\alpha + 2nv - 2mEh^{-2}}{(n+1)(n+2)} c_n$$

The one-dimensional harmonic oscillator: Quantum treatment

$$n = v$$

$$\alpha + 2nv - 2mEh^{-2} = 0$$

$$2mEh^{-2} = (2v + 1)2\pi vmh^{-1}$$

$$E = (v + \frac{1}{2})h\nu, \quad v = 0, 1, 2, \ldots$$

$$E_n = (n + \frac{1}{2})h\omega, \quad \text{with } n = 0, 1, 2, 3, \ldots$$
The one-dimensional harmonic oscillator: Quantum treatment

\[ V(x) = \frac{1}{2} m \omega^2 x^2 \]

For values of E that differ from above mentioned equation, \( \psi \) is not quadratically integrable

\[ E_n = \frac{1}{2} \hbar \omega \]

\[ E_1 = \frac{3}{2} \hbar \omega \]

\[ E_2 = \frac{5}{2} \hbar \omega \]

\[ E_0 = \frac{1}{2} \hbar \omega \]

Zero point energy \( \neq 0 \)

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The one-dimensional harmonic oscillator: Quantum treatment

\[ c_{n+2} = \frac{\alpha + 2\alpha n - 2mE\hbar^{-2}}{(n+1)(n+2)} c_n \]

\[ E = (v + \frac{1}{2})\hbar \nu \]

\[ c_{n+2} = \frac{2\alpha(n-v)}{(n+1)(n+2)} c_n \]

\[ \psi_v = \begin{cases} e^{-\alpha x^2/2}(c_0 + c_2 x^2 + \cdots + c_v x^v) \\ e^{-\alpha x^2/2}(c_1 x + c_3 x^3 + \cdots + c_v x^v) \end{cases} \]

For values of \( E \) that differ from above mentioned equation, \( \psi \) is not quadratically integrable
In the region around $x = 0$, the three curves nearly coincide. For $|a^{1/2}x| > 3$, the $E/h\nu = 0.500$ curve nearly coincides with the $x$ axis.

why is $E_0 \neq 0$?
Even and odd functions

**Even functions:**

**Definition:** \( f(-x) = f(x) \)

**Example:**

\[ x^2, \quad e^{-bx^2} \]

\((-x)^2 = x^2\)
\[ e^{-b(-x)^2} = e^{-bx^2} \]

\[ \int_{-a}^{+a} f(x) \, dx = 2 \int_{0}^{a} f(x) \, dx \]

**Odd functions:**

**Definition:** \( g(-x) = -g(x) \)

**Example:** \( x, \ 1/x, \ xe^{x^2} \cdot \)

\[ \int_{-a}^{+a} g(x) \, dx = 0 \]
The Harmonic-Oscillator Wave Functions

$$\psi_e = \begin{cases} 
  e^{-\alpha x^2/2} (c_0 + c_2 x^2 + \cdots + c_e x^e) & \text{even} \\
  e^{-\alpha^2/2} (c_1 x + c_3 x^3 + \cdots + c_e x^e) & \text{odd}
\end{cases}$$

Normalization:
\begin{align*}
\psi_0 &= c_0 e^{-\alpha x^2/2} & \text{even} \\
1 &= \int_{-\infty}^{\infty} |c_0|^2 e^{-\alpha x^2} \, dx = 2|c_0|^2 \int_{0}^{\infty} e^{-\alpha x^2} \, dx \\
\psi_0 &= (\alpha/\pi)^{1/4} e^{-\alpha x^2/2}
\end{align*}

Exercise: complete the normalization of $\psi_0$ wave function.

The Harmonic-Oscillator Wave Functions

$$\psi_v = e^{-\alpha x^2/2} (c_1 x + c_3 x^3 + \cdots + c_v x^v)$$

$$\psi_1 = c_1 x e^{-\alpha x^2/2}$$

Normalization

$$\psi_1 = (4\alpha^3/\pi)^{1/4} x e^{-\alpha x^2/2}$$
The Harmonic-Oscillator Wave Functions

\[ \psi_v = e^{-\alpha x^2/2} (c_0 + c_2 x^2 + \ldots + c_v x^v) \]
\[ c_{n+2} = \frac{2\alpha (n-v)}{(n+1)(n+2)} c_n \]
\[ c_2 = \frac{2\alpha(-2)}{1 \cdot 2} \quad c_0 = -2\alpha c_0 \]
\[ \psi_2 = c_0 (1 - 2\alpha x^2) e^{-\alpha x^2/2} \]
\[ \psi_v = (\alpha/4\pi)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2} \]

The one-dimensional harmonic oscillator: Quantum treatment

2) The ladder operator procedure

\[ \psi_v(x) = (2^v v!)^{-1/2} \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} H_v(\alpha^{1/2} x) \]
\[ H_n(z) = (-1)^n e^{z^2} \frac{d^n e^{-z^2}}{dz^n} \]
\[ z H_n(z) = n H_{n-1}(z) + \frac{1}{2} H_{n+1}(z) \]

Example:
Obtain the the Hermite polynomials for \( n = 0 \) to \( n = 10 \), and normalized \( \psi_1 \) to \( \psi_5 \)

\[ H_0 = 1, \quad H_1 = 2z, \quad H_2 = 4z^2 - 2, \quad H_3 = 8z^3 - 12z \]
The classically allowed (-a ≤ x ≤ a) and forbidden (x < -a and x > a) regions for the harmonic oscillator.

Classically:

\[ E = T + V \]
\[ T \geq 0 \]
\[ E - V = T \geq 0 \]
\[ E \geq V \]

The Harmonic-Oscillator Wave Functions

In quantum mechanics:

\[ \hat{T} \Psi \neq cte \Psi \]
\[ \hat{V} \Psi \neq cte \Psi \]

We can not assign definite values to T and V

Stationary state wave functions

Classical equations: \( E = T + V \) and \( V \geq 0 \)
Quantum mechanics: \( E = <T> + <V> \) and \( <V> \geq 0 \)

So, in quantum mechanics \( <V> \leq E \), but we can not write \( V \leq E \)

A particle has some probability to be found in classically forbidden regions where \( V > E \)
For a harmonic oscillator stationary state

\[ E = (v + \frac{1}{2})\hbar \nu \]
\[ V = \frac{1}{2}kx^2 = 2\pi^2\nu^2mx^2 \]

\[ V \leq E \]
\[ 2\pi^2\nu^2mx^2 \leq (v + \frac{1}{2})\hbar \nu. \]
\[ x^2 \leq (v + \frac{1}{2})\hbar/2\pi^2\nu m = (2v + 1)/\alpha \quad \alpha = 2\pi\nu m/\hbar \]
\[ -(2v + 1)^{1/2} \leq \alpha^{1/2}x \leq (2v + 1)^{1/2} \]
The Harmonic-Oscillator Wave Functions

As we go to higher energy states $\psi$, $|\psi|^2$ tend to have maxima farther from origin

\[
V = \frac{1}{2} k x^2 \\
\langle V \rangle = \int_{-\infty}^{\infty} |\psi|^2 V \, dx
\]

\[
\langle T \rangle = -\left(\frac{\hbar^2}{2m}\right) \int_{-\infty}^{\infty} \psi^* \psi^\prime \, dx \\
\text{Integration by parts} \\
\langle T \rangle = \left(\frac{\hbar^2}{2m}\right) \int_{-\infty}^{\infty} |d\psi/dx|^2 \, dx
\]
Vibration of molecules

\[ \mu = \frac{m_1 + m_2}{m_1 + m_2} \]

\[ U = U(R) \]

Internal motion of diatomic molecule = vibration + rotation

Equilibrium vibrational frequency

\[ \nu_c = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \]

\[ R_e \equiv \text{equilibrium distance} \]

\[ k = \frac{d^2V}{dx^2} \]

\[ k = \frac{d^2U}{dR^2}\bigg|_{R=R_e} \]

\[ x \equiv R - R_e \]
Vibration of molecules

\[ E_{\text{vib}} = (v + \tfrac{1}{2})h\nu_e - (v + \tfrac{1}{2})^2h\nu_e \]

Unharmonicity constant \( \equiv \nu_e x_e > 0 \)

Selection rule \( \Delta v = 1 \)

For absorption or emission of electromagnetic radiation to occur, the vibration must change the molecule's dipole moment.

\[ \nu_{\text{light}} = (E_2 - E_1)/h \approx [(v_2 + \tfrac{1}{2})h\nu_e - (v_1 + \tfrac{1}{2})h\nu_e]/h \]

\[ = (v_2 - v_1)\nu_e = \nu_e \]

\( \Delta v = 2, 3, \ldots \) overtones, much weaker than \( \Delta v = 1 \)

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Vibration of molecules

\[ \nu_{\text{light}} = \nu_e - 2\nu_e x_e(v_1 + 1) \]

\[ \frac{N_i}{N_j} = \frac{g_i}{g_j} e^{-(E_i - E_j)/kT} \]

**Boltzmann distribution law**

\( E_i \) and \( E_j \) are the energies of levels \( i \) and \( j \), \( g_i \) and \( g_j \) are the degeneracies of levels \( i \) and \( j \), \( N_i \) and \( N_j \) are the populations of levels \( i \) and \( j \).

\( g_i = 1 \) for a nondegenerate level

\[ v = 0 \rightarrow 1 \]

\( (v = 0 \rightarrow 2, 0 \rightarrow 3, \ldots) \) Overton bands

\[ v = 1 \rightarrow 2, 2 \rightarrow 3 \]

Hot bands

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Vibration of molecules

\[ \tilde{\nu} \equiv \frac{1}{\lambda} = \frac{\nu}{e} \]

\[ E_{\text{vib}} = \sum_i (v_i + \frac{1}{2}) \hbar \nu_i \]  

For a polyatomic molecule