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SEOUL NATIONAL UNIVERSITY
Department of Chemistry

Jiho Son

Physical Chemistry 2

Lecture 6. The Harmonic Oscillator (1)

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paradichlorobenzene1724@gmail.com
kadryjh1724@snu.ac.kr

Topics in Lecture 6

Harmonic Oscillator (single topic!)

In Atkins' *Physical Chemistry* (11th ed.),

7E Vibrational motion

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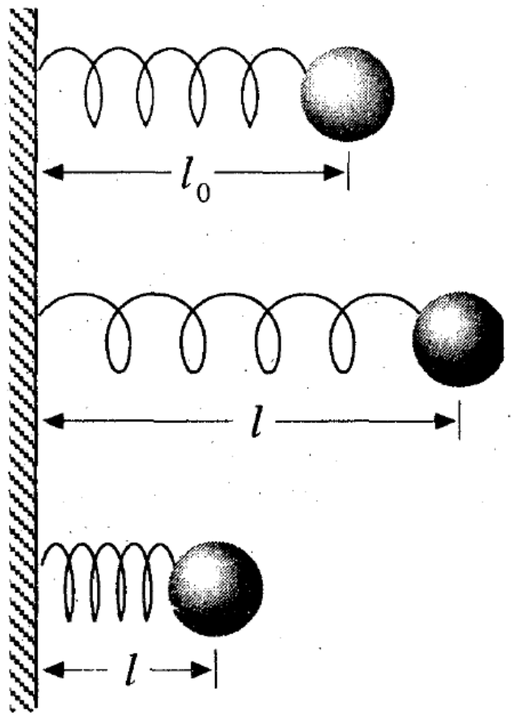
Hooke's law

Consider a mass *m* connected to a wall by a spring. Suppose that the only force is due to the spring. Then the restoring force follows *Hooke's law*:



$$F = -k(l - l_0) = -kx$$

where *x* is the displacement from the equilibrium. Then, Newton's equation with a Hooke's law force is

$$m\frac{d^2x}{dt^2} = -kx, \qquad m\frac{dx^2}{dt^2} + kx = 0$$

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x = -\omega^2 x$$

$$x(t) = c_1 \sin \omega t + c_2 \cos \omega t$$

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Hooke's law

Let's apply appropriate boundary conditions. For here: $x(0) = A, v(0) = \dot{x}(0) = 0.$

$$x(0) = c_2 = A,\ \dot{x}(0) = \omega c_1 = 0 \implies x(0) = A\cos\omega t$$

The force is related to potential energy.

$$F = -\frac{dV}{dx} \implies V = \frac{1}{2}kx^2$$

Then, the total energy is

$$E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 = \frac{1}{2}mA^2\omega^2\cos^2\omega t + \frac{1}{2}m\omega^2 \cdot A^2\sin^2\omega t = \frac{1}{2}m\omega^2A^2 = \frac{1}{2}kA^2$$

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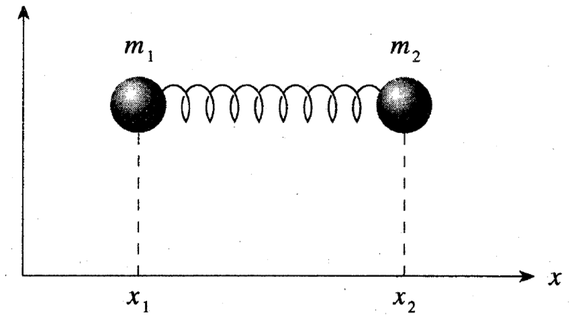
Reduced mass

Our main interest is *vibrational motion* of *diatomic molecules*. For polyatomic molecules, we need to consider *molecular symmetry* to analyze the vibration.



In diatomic molecules, two atoms vibrate relatively. In this case, it is convenient to introduce *center-of-mass coordinate*.

$$m_1\frac{d^2x_1}{dt^2} = k(x_2 - x_1 - l_0), \quad m_2\frac{d^2x_2}{dt^2} = -k(x_2 - x_1 - l_0)$$

$$X = \frac{m_1x_1 + m_2x_2}{M}, \quad M = m_1 + m_2 \implies M\frac{d^2X}{dt^2} = 0$$

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Reduced mass

The motion of two-body system must depend upon only the relative separation.

$$x = x_2 - x_1 - l_0$$

$$\frac{d^2x_2}{dt^2} - \frac{d^2x_1}{dt^2} = -\left(\frac{k}{m_1} + \frac{k}{m_2}\right)(x_2 - x_1 - l_0)$$

If we let

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

Then we have simplified equation of motion: separated COM and internal motion.

$$\mu \frac{d^2x}{dt^2} + kx = 0$$

We call μ *reduced mass*.

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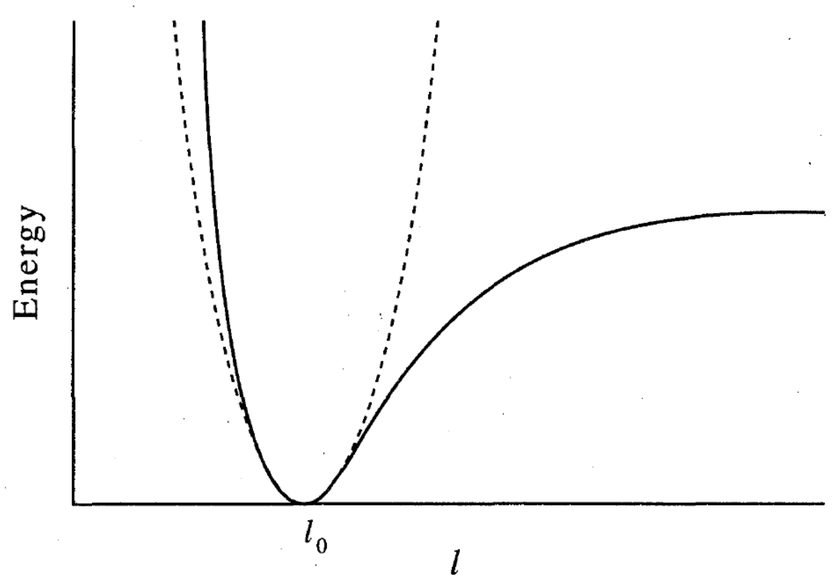
Harmonic potential

The harmonic oscillator potential may appear to be a terrible approximation to the experimental curve, note that it is a good approximation in the region of the minimum.



$$V(l) = V(l_0) + \left(\frac{dV}{dl}\right)_{l=l_0}(l - l_0) + \frac{1}{2!}\left(\frac{d^2V}{dl^2}\right)_{l=l_0}(l - l_0)^2 + \frac{1}{3!}\left(\frac{d^3V}{dl^3}\right)_{l=l_0}(l - l_0)^3 + \cdots$$

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QM treatment of HO

The Schrödinger equation for harmonic oscillator is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\frac{1}{2}kx^2\psi=E\psi$$

There are two ways to solve this: (1) algebraic method, (2) analytic method. In this lecture, we will try algebraic method, which involves *ladder operators*. Start from the Hamiltonian.

$$\hat{H}=\frac{\hat{p}^2}{2m}+\frac{1}{2}m\omega^2\hat{x}^2=\frac{\omega}{2}\left[\frac{\hat{p}^2}{m\omega}+m\omega\hat{x}^2\right]=\frac{\omega}{2}\left\{\left[\sqrt{m\omega}\hat{x}-\frac{i\hat{p}}{\sqrt{m\omega}}\right]\left[\sqrt{m\omega}\hat{x}+\frac{i\hat{p}}{\sqrt{m\omega}}\right]-i[\hat{x},\hat{p}]\right\}$$

$$=\frac{\omega}{2}\left(\sqrt{2\hbar}\hat{a}^\dagger\cdot\sqrt{2\hbar}\hat{a}-i[\hat{x},\hat{p}]\right)=\hbar\omega(\hat{a}^\dagger\hat{a}+\frac{1}{2})$$

Where $\hat{a}^\dagger$ and $\hat{a}$ are called *creation* and *annihilation* operators, respectively. Note that they are not hermitian; they are hermitian conjugate of each other.

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Ladder operators

Commutator of ladder operators

$$[a, a^\dagger] = \frac{1}{2\hbar}[\sqrt{m\omega}x + \frac{ip}{\sqrt{m\omega}}, \sqrt{m\omega}x - \frac{ip}{\sqrt{m\omega}}] = \frac{1}{2\hbar}(-2i[x, p]) = 1$$

We define *number operator*:

$$\hat{N} = \hat{a}^\dagger \hat{a}$$

Eigenstates of $\hat{H}$ are identical to eigenstates of $\hat{N}$, indeed. Moreover,

$$[N, a] = a^\dagger [a, a] + a[a^\dagger, a] = -a$$

$$[N, a^\dagger] = a^\dagger [a, a^\dagger] + a[a^\dagger, a^\dagger] = a^\dagger$$

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Ladder operators

Suppose we have an eigenstate $|n\rangle$ of $\hat{N}$ such that

$$\hat{N}|n\rangle = n|n\rangle$$

$$N(a|n\rangle) = (aN - a)|n\rangle = (n-1)(a|n\rangle)$$
$$N(a^\dagger|n\rangle) = (a^\dagger N + a^\dagger)|n\rangle = (n+1)(a^\dagger|n\rangle)$$

Note that $a|n\rangle$ and $a^\dagger|n\rangle$ are both eigenstate of $\hat{N}$. Therefore, for some constant *c*,

$$a|n\rangle \equiv c|n-1\rangle \implies |c|^2 = \langle n|a^\dagger a|n\rangle = n,\ \therefore\ a|n\rangle = \sqrt{n}|n-1\rangle$$

$$a^\dagger|n\rangle \equiv c|n+1\rangle \implies |c|^2 = \langle n|aa^\dagger|n\rangle = \langle n|a^\dagger a + 1|n\rangle = n+1,\ \therefore\ a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$$

Therefore, once we find one eigenstate, then other eigenstates can be found by acting ladder operators sequentially.

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Ladder operators

Since $\hat{H} = \hbar\omega(\hat{N} + \frac{1}{2})$ and $\hat{H}\,|n\rangle = \hbar\omega(n + \frac{1}{2})\,|n\rangle$ and Hamiltonian is bounded below,

$$\hat{a}^k\,|n\rangle = 0 \text{ for some } k$$

This indicates the *existence of ground state*. Here, k=n+1 and n is a integer, since

$$\hat{a}^{n+1}\,|n\rangle = \sqrt{n}\sqrt{n-1}\cdots\sqrt{n-n}\,\left|-1\right\rangle = 0$$

Conclusion Number operator has non-negative integer eigenvalue, and

$$E = \hbar\omega(n + \frac{1}{2}) \quad (n = 0,1,2,\ldots)$$

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Ladder operators

Classically, E=0 at x=0 and p=0. However, in quantum mechanics, such situation is impossible.
Even ground state has nonzero displacements and *zero point energy*.

$$|0\rangle$$
$$\downarrow$$
$$|1\rangle = \hat{a}^{\dagger}|0\rangle$$
$$\downarrow$$
$$|2\rangle = \frac{\hat{a}^{\dagger 2}}{\sqrt{2}}|0\rangle$$
$$\downarrow$$
$$\downarrow$$
$$\downarrow$$
$$|n\rangle = \frac{\hat{a}^{\dagger n}}{\sqrt{n!}}|0\rangle$$

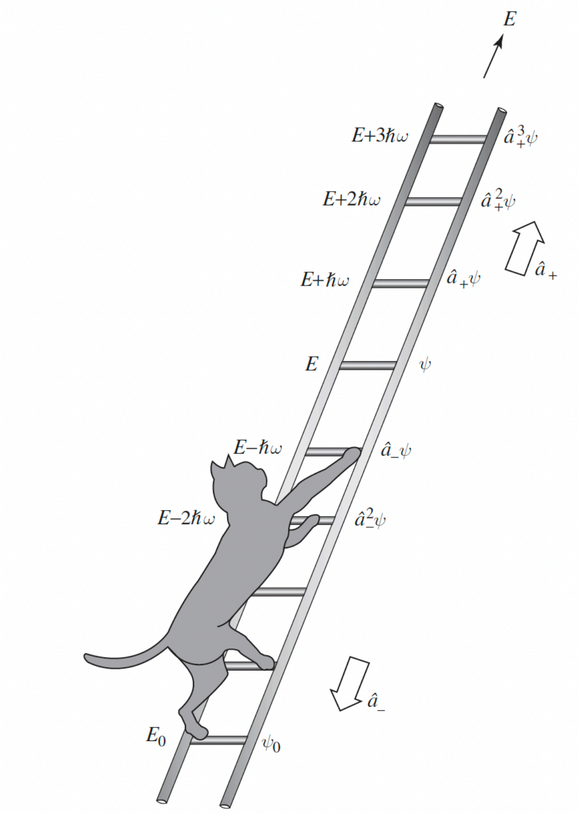

Figure 2.5: The "ladder" of states for the harmonic oscillator.

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HO wavefunctions

Ground state wavefunctions are characterized by

$$\hat{a}\left|0\right\rangle = 0 = \frac{1}{2\hbar}\left(\sqrt{m\omega}x + \frac{ip}{\sqrt{m\omega}}\right)\left|0\right\rangle$$

$$0 = \sqrt{\frac{\hbar}{2m\omega}}\left(\frac{m\omega}{\hbar}x + \frac{d}{dx}\right)\psi_0, \quad \psi_0' = -\frac{m\omega}{\hbar}x \cdot \psi_0 \implies \psi_0(x) = C\exp\left[-\frac{m\omega}{2\hbar}x^2\right]$$

After normalization, all excited states can be obtained with $\hat{a}^\dagger$.

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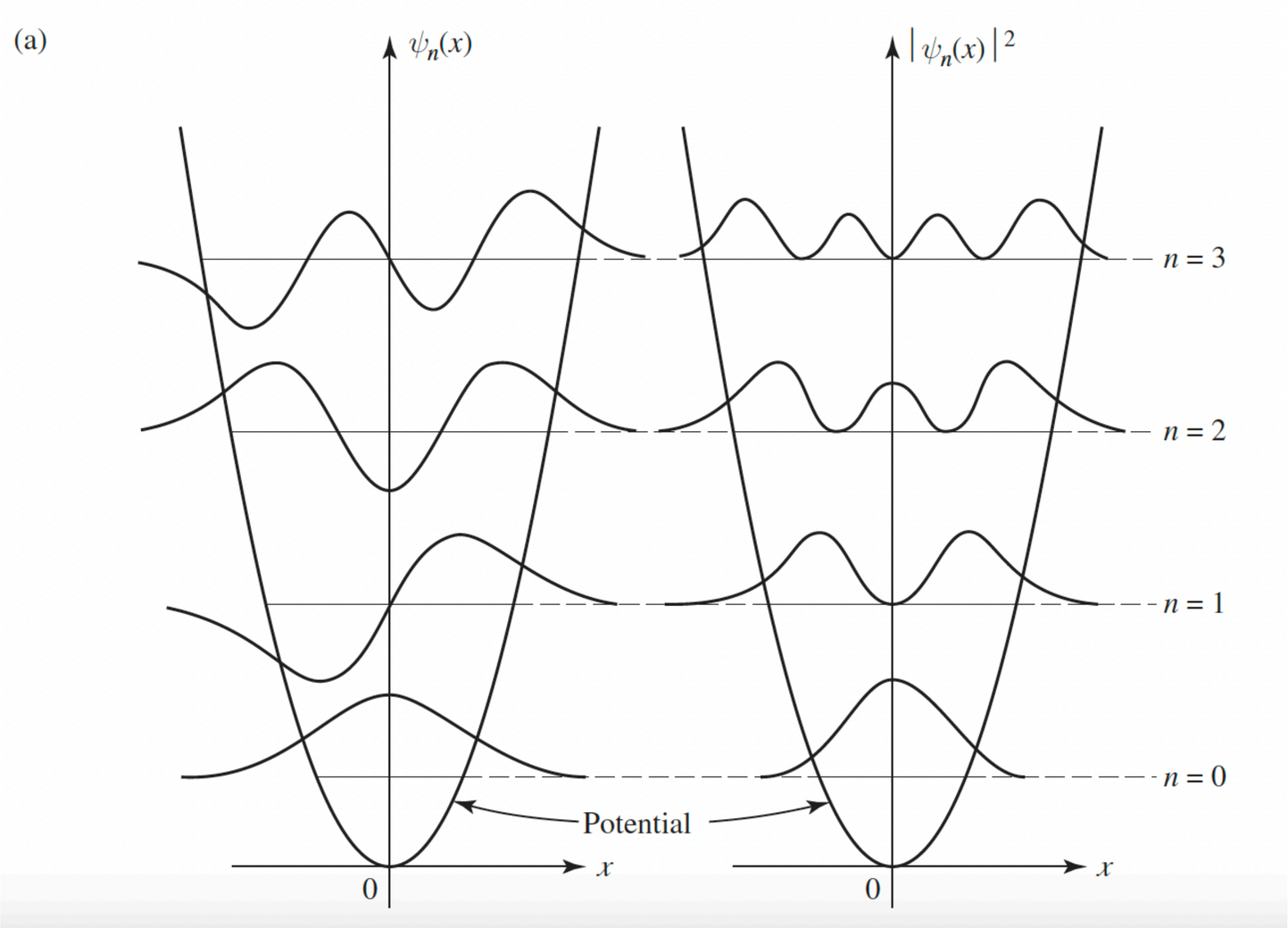
HO wavefunctions



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