Let us translate this to the 3D case - ~~[illegible]~~ can we know the coordinate along x and the momentum along ~~[illegible]~~ y for a particle, with arbitrary precision?

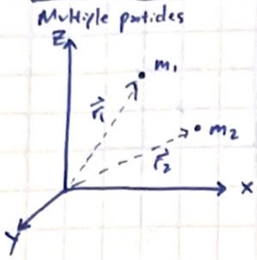
$$[\hat{x}, \hat{p}_y]\psi = x(-i\hbar \tfrac{d}{dy}\psi) - (-i\hbar \underbrace{(\tfrac{d}{dy} x y)}_{\to\, x \frac{d}{dy} y})$$

$\hookrightarrow x \frac{d}{dy}y$, since y ~~[illegible]~~ is independent of x.

$$\therefore [\hat{x}, \hat{p}_y]\psi = x(-i\hbar \tfrac{d}{dy}\psi) + i\hbar x \tfrac{d}{dy}y = 0$$ Yes, it is possible

1 particle

Multiple particles



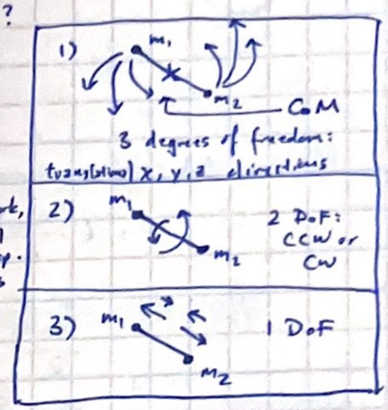
Particles 1 and 2 (m_1 and m_2) both have 3 degrees of freedom (movement in xyz directions) so total of 6 degrees of freedom when particles move independently of each other.

→ What if the particles are bound by a chemical bond?

Three types of motion to consider:

1) Movement about the center of mass (CoM)
2) Movement associated with rotation (CW or CCW)
3) Vibrational movement

For our model to work, we must assume that all types of motion are indep. of each other. This does not often reflect reality, where variables may affect each other.



Therefore total energy, E:

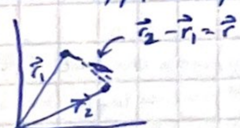
$$E = \overset{\text{(Kinetic energy)}}{E_{tr}} + E_{vib} + E_{rot}$$

When the energies are independent of each other, we can multiply their wave functions together:

$$\Psi = (\Psi_{tr})(\Psi_{vib})(\Psi_{rot})$$

Translational energies → Vibrational Energies

By definition $\vec{r}_{com} = \dfrac{\vec{r}_1 \cdot m_1 + \vec{r}_2 \cdot m_2}{m_1 + m_2} = \dfrac{\vec{r}_1 m_1 + \vec{r}_2 m_2}{M}$. We ~~[illegible]~~ use the reduced mass, μ, to represent vibrational and rotational motion: $\mu = \dfrac{m_1 \cdot m_2}{m_1 + m_2}$, and $\vec{r} = \vec{r}_2 - \vec{r}_1$:



Then for each mass $\mu = m_1\left(\dfrac{m_2}{m_1+m_2}\right) + m_2\left(\dfrac{m_1}{m_1+m_2}\right)$. Consider for example, H_2.

Each H atom is the same mass, and therefore $\mu = 1\left(\frac{1}{2}\right)$ a.m.u. $= \frac{1}{2}$ a.m.u.

$\hookrightarrow \frac{1}{2}(1.7 \times 10^{-27}\ kg)$

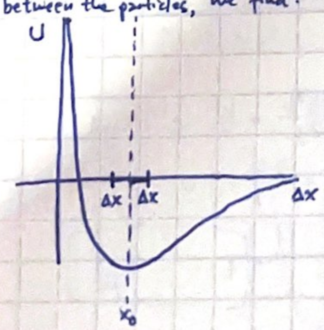
Consider H-Cl: What is the reduced mass? ~~[illegible]~~?

$$\mu = 1\left(\frac{35}{36}\right)\text{a.m.u.} = \left(\frac{35}{36}\right)\text{a.m.u.} = \frac{35}{36}(1.7 \times 10^{-27}\ kg).$$

Relation to Vibrational Energy:

We have translational energy defined as $\frac{p^2}{2\mu}$, where μ is used in place of m to simplify our two body problem to a one-body problem. The total energy is now $E = \frac{p^2}{2\mu} + E_{vib} + E_{rot}$.

E_{vib} can be represented as a potential, U, between the two particles: Representing the U as a function of Δx between the particles, we find:



If we assume that amplitudes of vibration are small, we can find ~~the~~ 2nd express the resting potential as a taylor approximation:

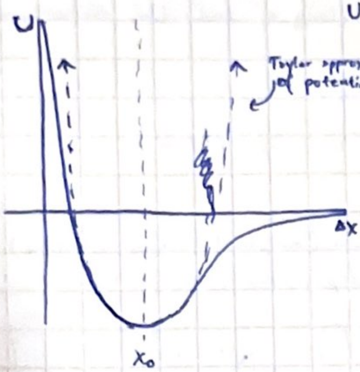
$$U(x) = U(x_0 + \Delta x):$$

$$= U(x_0) + \frac{d}{dx}U\Big|_{x=x_0} \cdot \Delta x + \frac{1}{2}\frac{d^2}{dx^2}U\Big|_{x=x_0} \cdot \Delta x^2 + \ldots$$

At x_0, $\frac{d}{dx}U = 0$:

$$= U(x_0) + \tfrac{1}{2}\frac{d^2}{dx^2}U\Big|_{x=x_0} \cdot \Delta x^2 + \ldots$$ Let $\frac{d^2}{dx^2}U = k$. Then

$$= U(x_0) + \underbrace{\tfrac{1}{2}k(\Delta x)^2}_{\text{Mass on a spring (Hooke's Law)}} + \ldots$$



Using our connection to springs, we see that

$$U(x) = U(x_0) + \tfrac{1}{2}k\Delta x^2 + \dots \longrightarrow$$

We will ignore the Δx^3, Δx^4 terms as they will be very small, and our parabolic estimation is sufficient at this point.

Just to verify that potential is indeed represented by Hooke's law, we see:

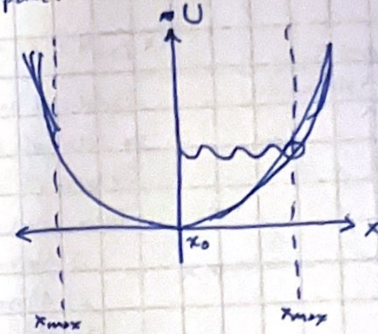
$$F = -\frac{dU}{d\Delta x}, \quad U(x) = \underset{\text{constant}}{U_0} + \tfrac{1}{2}k\Delta x^2.$$

$$F = -k\Delta x, \text{ Hooke's law:}$$

We can shift $x_0 \to 0$ and therefore $\Delta x \to x$ in our estimation:

$$\Delta x = \Delta x_{max}\cos(\omega t), \text{ where } \omega = \sqrt{\frac{k}{\mu}}$$

We see harmonic oscillation



At x_{max}, **ALL** energy is potential energy. Therefore,

$$E = k\frac{(x_{max})^2}{2}, \text{ and } x_{max} = \pm\sqrt{\frac{2E}{k}}.$$

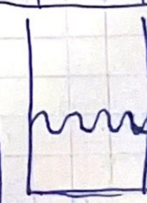
$$\omega_{ho} = \sqrt{\frac{k}{\mu}}$$

$$\nu_{ho} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

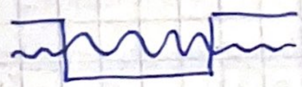
and we can substitute this expression in TISE:

$$\hat{H}\psi = E\psi, \quad \underbrace{-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\psi}_{K} + \underbrace{\frac{k}{2}x^2\psi}_{U} = E\psi$$

Similar to our solution of particle in a box with both infinite and finite box height lengths:



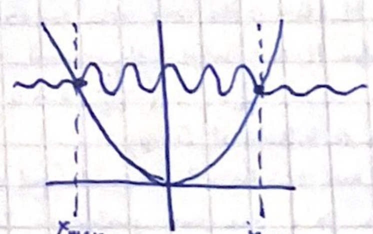
Infinite



Finite

(Has some level of penetrance)

For our potential model:



The potentials are not infinitely high, therefore there will be some penetrance.

Normalization:

$$\int P\,dx = 1.$$

(discuss later)

Solve Schrödinger's

Before, we had just considered

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$$

where $\psi = ce^{ikx}$

However, in the case that $\hat{H}\psi = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\psi + \frac{kx^2}{2}\psi = E\psi$, ce^{ikx} can no longer be a solution to the differential equation since $\frac{kx^2}{2}\psi$ does not distribute out:

Suppose then that $\boxed{\psi = ce^{bx^2}}$

$$\frac{d}{dx}\psi = 2xbce^{bx^2}$$

$$\frac{d^2}{dx^2}\psi = 2bce^{bx^2} + 4b^2cx^2e^{bx^2}$$

This term will compensate for the $\frac{kx^2}{2}$ term.

Now we can solve for Schrödinger's equation:

$$\hat{H}\psi = -\frac{\hbar^2}{2\mu}\left(2bce^{bx^2} + 4b^2cx^2e^{bx^2}\right) + \frac{kx^2}{2}\left(ce^{bx^2}\right) = E\psi$$

$$-\frac{\hbar^2}{2\mu}\left[2b + 4b^2x^2\right]\left[\cancel{ce^{bx^2}}\right] + \frac{kx^2}{2}\left[\cancel{ce^{bx^2}}\right] = E\left(\cancel{ce^{bx^2}}\right)$$

$$-\frac{\hbar^2}{2\mu}\left(2b + 4b^2x^2\right) + \frac{kx^2}{2} = E,$$

$$-\frac{\hbar^2}{2\mu}(2b) - \frac{\hbar^2}{2\mu}(4b^2x^2) + \frac{kx^2}{2} = E$$

Isolate x

$$-\frac{\hbar^2}{2\mu}(4b^2x^2) + \frac{kx^2}{2} = E + \frac{\hbar^2}{2\mu}(2b)$$

$$\underbrace{x^2\left(-\frac{4\hbar^2 b}{2\mu} + \frac{k}{2}\right)}_{\text{Depends on } x} = \underbrace{E + \frac{2\hbar^2 b}{2\mu}}_{\text{Does not depend on } x}$$

→ The only time this can be true is if they = 0.

$$\therefore -\frac{4\hbar^2 b}{2\mu} + \frac{k}{2} = 0 \text{ and}$$

$$E + \frac{\hbar^2 b}{\mu} = 0.$$

$$\boxed{E = -\frac{\hbar^2 b}{\mu}}$$

Since we see $E = -\frac{\hbar^2 b}{\mu}$, b <u>must</u> be negative since $\hbar^2$ and μ cannot be negative, and E cannot be negative, with potential energy already accounted for.

The other term: $-\frac{4b^2\hbar}{2\mu} + \frac{k}{2} = 0$, $\therefore$ $\frac{k}{2} = \frac{4b^2\hbar}{2\mu}$, $b^2 = \frac{k\mu}{4\hbar^2}$, $b = \pm\sqrt{\frac{k\mu}{4\hbar^2}}$

Recall that b <u>must</u> be negative to make physical sense.

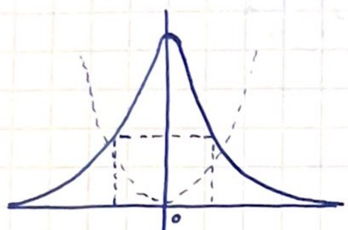
Now we can relate both to energy, E:

$$E = -\frac{\hbar^2}{\mu}(b) = -\frac{\hbar^2}{\mu}\left(-\sqrt{\frac{k\mu}{4\hbar^2}}\right)$$

$$E = \frac{\hbar^{\cancel{2}}}{\mu}\frac{\sqrt{k\mu}}{2\cancel{\hbar}} = \frac{1}{2}\hbar\frac{\sqrt{k\mu}}{\mu} = \frac{1}{2}\hbar\overbrace{\sqrt{\frac{k}{\mu}}}^{\omega_{HO}} = \boxed{\frac{1}{2}\hbar\omega_{HO}} = \frac{1}{2}h\nu_{HO},$$ when $n=0$

Consider the wave function $\psi = ce^{bx^2}$ again: since $b = -\frac{\sqrt{k\mu}}{2\hbar}$, we substitute to get:

$$\psi = ce^{\left(-\frac{\sqrt{k\mu}}{2\hbar}\right)x^2}.$$ Let $\frac{\sqrt{\mu k}}{\hbar} = a$: $\psi = ce^{-\frac{a}{2}x^2}$, which corresponds to a <u>gaussian curve</u>.



We have just solved the quantum mechanical oscillator:

Since $E = \frac{1}{2}\hbar\omega_{HO} = nh\nu_{HO}$, and $\nu_{HO} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ and $\omega_{HO} = \sqrt{\frac{k}{\mu}}$

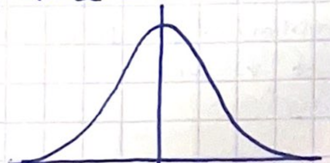
Then $E_n = nh\left(\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$

$E_n = n\hbar\sqrt{\frac{k}{\mu}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$

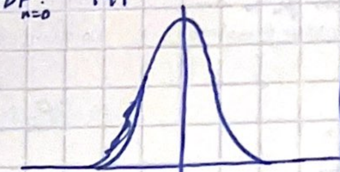
$$\boxed{E_n = (n+\tfrac{1}{2})\hbar\sqrt{\frac{k}{\mu}} = (n+\tfrac{1}{2})\hbar\omega_{HO} = (n+\tfrac{1}{2})h\nu_{HO}.}$$

Graphically, we can plot the wave function and its PDF:

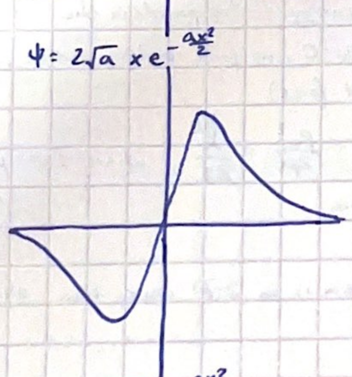
For $n=0$, $\psi = ce^{-\frac{ax^2}{2}}$



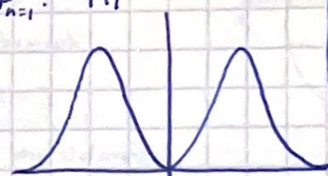
$PDF_{n=0}$: $|\psi|^2$



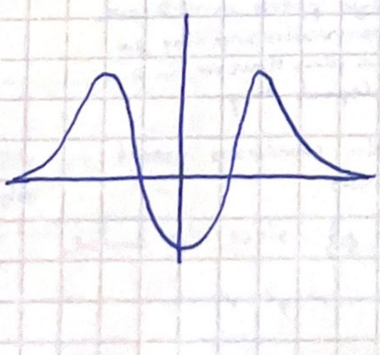
For $n=1$, $\psi = 2\sqrt{a}\,xe^{-\frac{ax^2}{2}}$



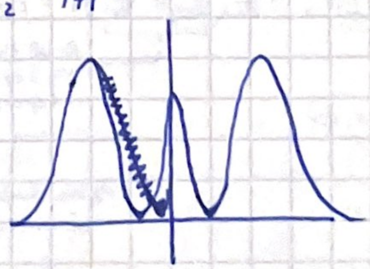
$PDF_{n=1}$: $|\psi|^2$



For $n=2$, $\psi = 2(2ax^2-1)e^{-\frac{ax^2}{2}}$



$PDF_{n=2}$ $|\psi|^2$



Follows the rule:

$\psi_n(x) = \underbrace{A_n H_n(\sqrt{a}\,x)}_{=c} e^{-\frac{ax^2}{2}}$

where

$H_0(\sqrt{a}\,x) = 1$

$H_1(\sqrt{a}\,x) = 2\sqrt{a}\,x$

$H_2(\sqrt{a}\,x) = 2(2ax^2-1)$

$H_3(\sqrt{a}\,x) = 4\sqrt{a}\,x(2ax^2-3)$

and

$A_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{a}{\pi}\right)^{1/4}$

and $a = \frac{\sqrt{k\mu}}{\hbar}$