All the models we have learned so far can be applied to a more unified model for energy:

$$E_{mol} = \underbrace{\frac{h^2}{8ma^2}(n_x)^2 + \frac{h^2}{8mb^2}(n_y)^2 + \frac{h^2}{8mc^2}(n_z)^2 + \ldots}_{\text{Translational}} \underbrace{\;}_{\text{(however many dimensions)}} + \underbrace{h\nu(n+\tfrac{1}{2})}_{\text{Vibrational}} + \underbrace{\frac{\hbar^2}{2I}(m_\ell)^2}_{\text{Rotational}}$$

Similarly for the wave function:

$$\Psi_{mol} = (\Psi_{trans})(\Psi_{vib})(\Psi_{rot}) = \left[\sqrt{\frac{2}{a}}\sin\left(\frac{\pi n_x x}{a}\right)\cdot\sqrt{\frac{2}{a}}\sin\left(\frac{\pi n_y x}{b}\right)\ldots\right]\left[A_n H_n(x\sqrt{a})e^{-\frac{ax^2}{2}}\right]\left[\frac{1}{\sqrt{2\pi}}e^{im_\ell\phi}\right]$$

Technically $\not\approx$, since $\Delta x$ for vibrational motion is different from the $x$ in translational motion.

Generally, however, these formulae are not used since the motions are considered independent of each other.

Application to Spectroscopy:

Typically $\lambda$ is measured, and $\Delta E$ is needed:

Translational motion: $n \to n+1$

$$\Delta E_{n\to n+1} = \frac{h^2}{8ma^2}\left[(n+1)^2 - n^2\right] = \frac{h^2}{8ma^2}(2n+1)$$

Vibrational motion: $n \to n+1$

$$\Delta E_{n\to n+1} = h\nu = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{when } \mu = \frac{m_1 m_2}{m_1+m_2}$$

Rotational motion: $m_\ell \to m_\ell + 1$

$$\Delta E_{m_\ell \to m_\ell+1} = \frac{h^2}{2I}(2m_\ell+1) = \frac{\hbar^2}{2\mu r^2}(2m_\ell+1)$$

For example, compare the rotational motion of $H_2$ to its kinetic energy at 300 K:

$$\Delta E_{n=0\to n=1} = \frac{\hbar^2}{2\mu r^2} \qquad \mu = \tfrac{1}{2}(m_H) = \tfrac{1}{2}(1.7\times10^{-27}\,kg)$$

$$r = 0.74\,\text{Å} \approx 0.74\times10^{-10}\,m$$

$$\Delta E_{n=0\to n=1} = \left(\frac{6.626\times10^{-34}}{2\pi}\right)^2\left(\frac{1}{2(\tfrac{1}{2})(1.7\times10^{-27}\,kg)(0.74\times10^{-10}\,m)^2}\right)$$

$$\approx \frac{10^{-68}\,J^2s^2}{(1.7\times10^{-27}\,kg)(0.5\times10^{-20}\,m^2)} \approx \frac{2}{1.7}10^{-21}\,J \to \approx 1.2\times10^{-21}\,J$$

Compare to 300 K:

$$\tfrac{1}{2}k_B T = \tfrac{1}{2}(1.4\times10^{-23}\,J/K)(300) \approx 2\times10^{-21}\,J$$

Generally, at room temperature QM needs to be considered.

Back to harmonic oscillators: We never showed how to normalize one.

→ How can we normalize the wave function of a harmonic oscillator?

Recall that $\Psi_n = A_n H_n(x\sqrt{a})e^{-\frac{ax^2}{2}}$. We can normalize this by regular method of $\int|\Psi|^2 dx = 1$. However, we soon run into a problem:

$$PDF = A_n^2 H_n(x\sqrt{a})e^{-ax^2}$$

$$\int_{-\infty}^{\infty} PDF = \underbrace{\int_{-\infty}^{\infty}(A_n)^2 H_n(x\sqrt{a})e^{-ax^2}dx}$$

This term is essentially

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2}dx \to \text{How is this integrated?}$$

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

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

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

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

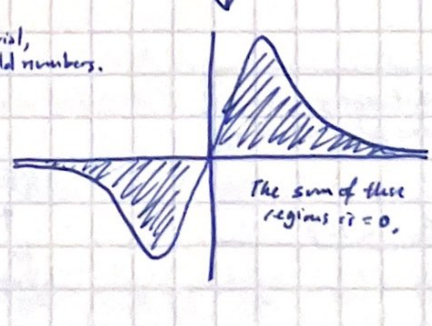
$H_3(\sqrt{a}x) = 4\sqrt{a}x(2ax^2-3)$

These integrals can take 1 of 2 different forms:

1) $\int_{-\infty}^{\infty} x^{2m+1}e^{-ax^2}dx$ (odd power)

2) $\int_{-\infty}^{\infty} x^{2m}e^{-ax^2}dx$ (even power)

$$1)\ \int_{-\infty}^{\infty} x^{2m+1}e^{-ax^2}dx = \int_{-\infty}^{\infty} x^{2m}(xe^{-ax^2})dx = \underbrace{\int_{-\infty}^{0} x^{2m}xe^{-ax^2}dx + \int_{0}^{\infty} x^{2m}xe^{-ax^2}dx}_{} = 0$$



The sum of these regions is = 0.

$$2)\ \int_{-\infty}^{\infty} x^{2m}e^{-ax^2}dx = 2\underbrace{\int_{0}^{\infty} x^2 e^{-ax^2}dx}_{\text{Table integral}}$$

$$= \sqrt{\frac{\pi}{a}}\left(\frac{1\cdot3\cdot5\cdot\ldots\cdot(2m-1)}{2^{m+1}a^m}\right) \text{ for } m \geq 1$$

Like factorial, but for odd numbers.

For example, if $m=0$, then

$$\int_{0}^{\infty} e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

Application - find the probability distribution function for the harmonic oscillator at $n=0$:

$$\psi(x) = A_n H_n(x\sqrt{a}) e^{-\frac{ax^2}{2}}$$

$$\int_{-\infty}^{\infty} |\psi|^2 dx = \int_{-\infty}^{\infty} A_n^2 H_n(x\sqrt{a}) e^{-ax^2} dx = 1, \quad n=0, \quad H_0 = 1$$

$$\int_{-\infty}^{\infty} A_0^2 e^{-ax^2} dx = A_0^2 \int_{-\infty}^{\infty} e^{-ax^2} dx = 2A_0^2 \int_{0}^{\infty} e^{-ax^2} dx$$

$$2A_0^2 \cdot \left(\sqrt{\tfrac{\pi}{a}}(\tfrac{1}{2})\right) = A_0^2 \sqrt{\tfrac{\pi}{a}}$$

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

$A_0 = (a/\pi)^{1/4}$

To normalize, $A_0^2 = \sqrt{\frac{a}{\pi}}$,

$\therefore A_0 = \left(\frac{a}{\pi}\right)^{1/4}$.

We can also apply this knowledge to determine the average value for the potential of a harmonic oscillator:

$$\langle U \rangle = \langle \tfrac{1}{2} k x^2 \rangle = \tfrac{1}{2} k \langle x^2 \rangle$$

Use expectation value equation $\dfrac{\int \psi^* \hat{A} \psi \, dx}{\int |\psi|^2 dx}$

In this case $\hat{A} = x^2$, and $\frac{1}{2}kx^2 = \psi_{n=0}$ is already normalized, so $\int |\psi|^2 dx = 1$ and we can solve for just $\int_{-\infty}^{\infty} \psi_{n=0}(x) \cdot x^2 \psi_{n=0}(x) dx$. Since $\psi_{n=0}(x) = A_0 \cancel{H_0(x\sqrt{a})} e^{-\frac{ax^2}{2}}$,

$$= \int_{-\infty}^{\infty} A_0 e^{-\frac{ax^2}{2}} \cdot x^2 \left(A_0^2 e^{-\frac{ax^2}{2}}\right) dx = A_0^2 \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx$$

Follows the pattern $\int_{-\infty}^{\infty} x^{2m} e^{-ax^2}$ where $m=1$.

$$A_0^2 \cdot 2 \int_{0}^{\infty} x^2 e^{-ax^2} dx$$

$$\sqrt{\frac{\pi}{a}}\left(\frac{1}{2^{(1+1)}a}\right) = \frac{1}{4a}\sqrt{\frac{\pi}{a}}$$

$$A_0^2 \cdot 2\left(\frac{1}{4a}\sqrt{\frac{\pi}{a}}\right)$$

$A_0 = \frac{1}{\sqrt{2^0 0!}}\left(\frac{a}{\pi}\right)^{1/4} = \left(\frac{a}{\pi}\right)^{1/4}$

$$\sqrt{\frac{a}{\pi}}\left(\sqrt{\frac{\pi}{a}} \cdot \frac{1}{2a}\right)$$

$$= \boxed{\frac{1}{2a} = \langle x^2 \rangle}$$

We can use this result in our original statement that $\langle U \rangle = \langle \frac{1}{2} k x^2 \rangle$:

$$\langle U \rangle = \tfrac{1}{2} k \left(\frac{1}{2a}\right), \quad a = \frac{\sqrt{k\mu}}{\hbar}, \quad \langle U \rangle = \tfrac{1}{2} k \frac{\hbar}{2\sqrt{k\mu}} = \tfrac{1}{4} \frac{\hbar k}{\sqrt{k\mu}} = \tfrac{1}{4} \hbar \underbrace{\sqrt{\frac{k}{\mu}}}_{\omega_{HO}}$$

$E_n = (n + \frac{1}{2}) h\nu$, in this case $n=0$

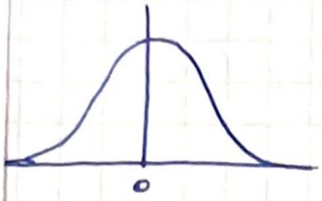
$$\tfrac{1}{2} E_0 = \tfrac{1}{2}\left(\frac{h\nu}{2}\right) = \tfrac{1}{2}\left(\frac{\hbar \omega_{HO}}{2}\right) = \tfrac{1}{4} \hbar \omega_{HO}$$

for a harmonic oscillator.

Therefore, we see that energy is equipartitioned between potential energy and kinetic energy:

$$\langle U \rangle = \tfrac{1}{2} E_0 = \langle K \rangle$$

We can also now consider $\langle x \rangle$:



$$\int_{-\infty}^{\infty} \underset{\uparrow \atop \psi^*}{e^{\frac{-ax^2}{2}}} \underset{\uparrow \atop \hat{A}}{x} \underset{\uparrow \atop \psi}{e^{\frac{-ax^2}{2}}} dx = 0 \rightarrow$$ This makes sense as the distribution of the particle across space is symmetric.

What about $\langle p \rangle$?

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A} \psi \, dx = A_0^2 \int_{-\infty}^{\infty} e^{\frac{-ax^2}{2}} \left(-i\hbar \frac{d}{dx} e^{\frac{-ax^2}{2}}\right) dx = -i\hbar A_0^2 \int_{-\infty}^{\infty} e^{\frac{-ax^2}{2}} \left(axe^{\frac{-ax^2}{2}}\right) dx = -i\hbar A_0^2 \int_{-\infty}^{\infty} axe^{-ax^2}$$
$$= 0.$$

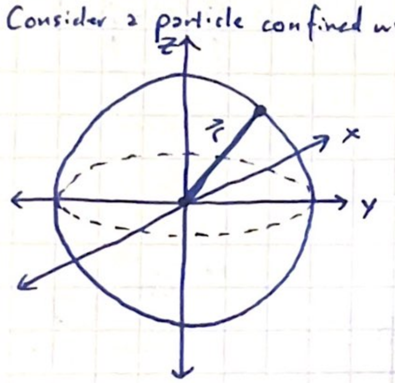
Be careful: Note that $\int_0^{\infty} x^{2m+1} e^{-\frac{ax^2}{2}} dx \neq \int_{-\infty}^{\infty} x^{2m+1} e^{-\frac{ax^2}{2}} dx$.

**From Particle in a Ring to Particle in a Sphere**

Recall that for a PIR, $\hat{\mathcal{H}} = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2}$. $\hat{\mathcal{H}}\psi = E\psi$, and $-\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2}\psi = \frac{\hbar^2}{2I} m_\ell^2 \psi$, $-\frac{d^2}{d\phi^2}\psi_{m_\ell} = m_\ell^2 \psi$

This will be useful to us later...

Consider a particle confined within a sphere with radius r:



"Particle in a sphere" - rigid rotor:

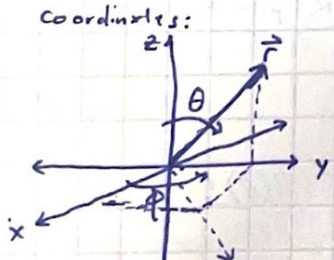
→ We can assume that $U = 0$ here since the particle independently rotates and is locked to the surface of the sphere (we assume $\frac{\partial}{\partial r} = 0$).

Recall that for 3D movement of a particle, we ~~did the conversion of~~ used the the x, y, and z compounds:

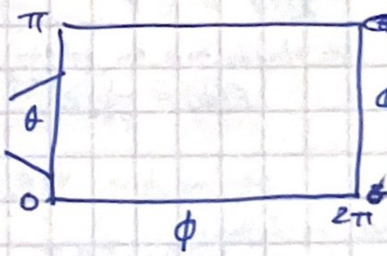
$$\hat{\mathcal{H}}\psi = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

Cartesian coordinates are a problem, since x, y, and z are not independent of each other.

Similar to $\{x, y\} \rightarrow \{r, \theta\}$ for polar coordinates, we now do $\{x, y, z\} \rightarrow \{r, \theta, \phi\}$ for spherical coordinates:



$$z = r\cos\theta$$
$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$



Realize that movement along the slice, with changing $\phi$ and constant $\theta$, is the same as the PIR problem

→ Movement along $\phi$ is similar to x movement, movement along $\theta$ is similar to y movement.

→ Movement of $\phi$ and $\theta$ are independent of each other → 2 independent quantization effects.

To convert $\hat{\mathcal{H}}\psi = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi = -\frac{\hbar^2}{2\mu}\nabla^2\psi$ to spherical coordinates, we use the Laplacian operator:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\left(\sin\theta \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{\partial^2}{\partial \phi^2}\right)$$

Which is very messy so let's clean it up accordingly for our scenario.