We can simplify further ~~using~~ by defining

$$\left.\begin{aligned} E_x X &= -\frac{\hbar^2}{2m}\left(\frac{d^2X}{dx^2}\right) \\ E_y Y &= -\frac{\hbar^2}{2m}\left(\frac{d^2Y}{dy^2}\right) \\ E_z Z &= -\frac{\hbar^2}{2m}\left(\frac{d^2Z}{dz^2}\right) \end{aligned}\right] \; -\frac{\hbar^2}{2m}\left(\frac{\frac{d^2}{dx^2}X}{X} + \frac{\frac{d^2}{dy^2}Y}{Y} + \frac{\frac{d^2}{dz^2}Z}{Z}\right) \longrightarrow \frac{E_xX}{X} + \frac{E_yY}{Y} + \frac{E_zZ}{Z} = E = E_x + E_y + E_z$$

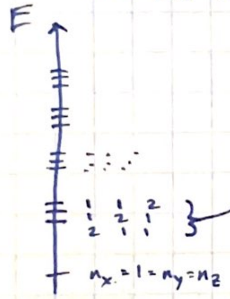
Compare this result to $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)$ in one dimension: We see that this expression is a combination of 1-D motions in 3-D.

Now, we have 3 quantum numbers describing the system, for each independent motion in the system. Note also that each X, Y, and Z as well as their corresponding energy values are quantized, similarly to the 1-D case:

$$X = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi n_x x}{a}\right) \qquad Y = \sqrt{\frac{2}{b}}\sin\left(\frac{\pi n_y \cancel{b} x}{b}\right) \qquad Z = \sqrt{\frac{2}{c}}\sin\left(\frac{\pi n_z x}{c}\right)$$

$$E_x = \frac{h^2}{8ma^2}n_x^2 \quad n_x = 1, 2, 3\ldots \qquad E_y = \frac{h^2}{8mb^2}n_y^2 \quad n_y = 1, 2, 3\ldots \qquad E_z = \frac{h^2}{8mc^2}n_z^2 \quad n_z = 1, 2, 3\ldots$$

Note that the normalization factor depends on the lengths of the box in that direction.



If there is more than one state corresponding to the same level of energy, that is, if a = b, or b = c, this is known as <u>degeneracy</u>.

Heisenberg's Uncertainty Principle:

Suppose $\Psi = \underbrace{b_1\phi_1}_{} + \underbrace{b_2\phi_2}_{}$, in superposition

Possible measurements: a_1 $\quad a_2$ → If we measure either of these eigenvalues, the wave function collapses and exists in a pure state $\Psi = \phi_1$, for example (if a_1 is measured)

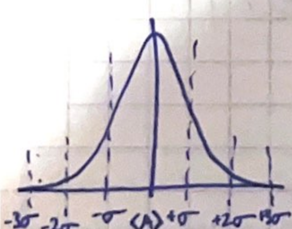
→ How can we accurately measure something?

Question of <u>precision</u>, NOT accuracy:

$$A_{measured} = \langle A \rangle \pm \delta A \qquad (\text{like } \bar{x} \pm \sigma_{\bar{x}})$$

We know from statistics that $P(\delta A)$ is normally or gaussian distributed:

Where the gaussian is $\frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{\delta A^2}{2\sigma^2}}$ in this case



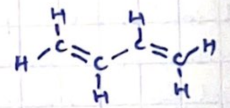
We know variance is

$$\sigma^2 = \frac{\Sigma(A - \langle A \rangle)^2}{N} = \frac{\Sigma \langle A^2 \rangle - \langle A \rangle^2}{N}$$

And standard deviation is

$$\sigma = \Delta A = \left|\sqrt{\langle A^2 \rangle - \langle A \rangle^2}\right|$$

Applications to chemistry: Conjugated Polyenes



Butadiene, C_4H_6

- The pi-electrons are delocalized in the structure, and are free to move along the molecule in a manner similar to e^- moving along in a 1-D box.
- The movement of electrons across the structure creates color: e^- transferring through the structure's energy can be described as:

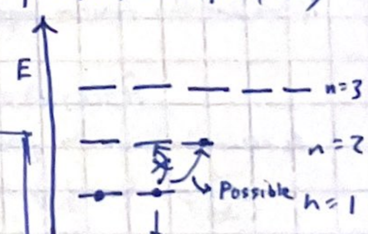
$$\Delta E = E_{n+1} - E_n = \frac{h^2}{8ma^2}(2n+1) = h\nu = h\frac{c}{\lambda}.$$

$\therefore \lambda \propto a^2$ – More conjugation (increase in a) results in increase of λ.

where n: # of $\frac{\pi\, e^-}{2}$

Applying pauli's exclusion principle, more specifically,

$$\lambda \propto \frac{a^2}{2n+1}.$$



Transition impossible as $\lambda \propto \frac{a^2}{2n+1}$

With this statistical background, we can apply this to quantum measurements, where

$$A = \hat{A}\Psi$$

– Must know $\hat{A}$ and Ψ.

If a particle is in the pure state, then $A = \hat{A}\Psi$, and $\hat{A}\Psi = a\Psi$ – There is only one possible outcome from this measurement – a – similar to a classical situation.

If a particle is in the superposition state, then $\hat{A}\Psi \neq a\Psi$ and $\Psi = \underbrace{b_1}\phi_1 + \underbrace{b_2}\phi_2 + \ldots$ depending on probabilities.

Measurements: a_1 a_2

Probabilities of particle in respective state

If $\langle A \rangle = a_1 P_1 + a_2 P_2$, and $P_1 = P_2 = 1/2$,

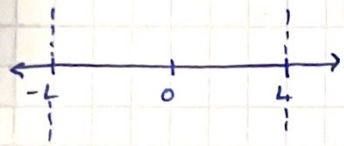
then $\langle A \rangle = \dfrac{a_1 + a_2}{2}$.

To calculate imprecision, we apply $\Delta A = \sigma = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$:

$$\langle \hat{A}^2 \rangle = \tfrac{1}{2}a_1^2 + \tfrac{1}{2}a_2^2 = \frac{a_1^2 + a_2^2}{2}$$
$$\langle A \rangle^2 = \frac{(a_1 + a_2)^2}{2^2} = \frac{(a_1 + a_2)^2}{4}$$
$$\Delta A = \sigma = \left| \sqrt{\frac{a_1^2 + a_2^2}{2} - \frac{(a_1 + a_2)^2}{4}} \right| = \frac{a_1 - a_2}{2} \quad \Delta A \neq 0.$$

If a_1 and a_2 are different, then ΔA cannot be 0: as long as there are 2 unique eigenvalues, $\Delta A \neq 0$.

We apply this to momentum and coordinate, in the case of a 1-D box:



Consider a free particle with $\Psi = \frac{1}{\sqrt{2L}} e^{ikx}$:

Momentum consideration:

$$\Psi = \frac{1}{\sqrt{2L}} e^{ikx}, \quad \langle p \rangle = \hbar k, \quad \langle p^2 \rangle = (\hbar k)^2 = \langle p \rangle^2$$
$$\therefore \Delta p = \sqrt{(\hbar k)^2 - (\hbar k)^2} = 0.$$

	Δx	Δp
1-D Free Particle	∞	0
Wave Packet	0	∞
Particle in Box	$\frac{a}{2}\sqrt{\frac{1}{3} - \frac{2}{\pi^2 n^2}}$	$\frac{\hbar\pi n}{a}$

Coordinate consideration:

This particle is **not** in a pure state – therefore, no one eigenvalue is possible for this particle ~~[illegible]~~

$$\langle x^2 \rangle = \frac{1}{2L}\int_{-L}^{L} x^2\,dx = \frac{L^2}{3}, \quad \therefore \Delta x = \sqrt{\frac{L^2}{3} - 0} = \sqrt{\frac{L^2}{3}}$$

$\langle x \rangle = 0$, $\therefore \langle x \rangle^2 = 0$ as equal probability of particle existing from $-L$ to L (waves are delocalized)

Consider the meaning of our results:

$\Delta p = 0$

$\Delta x = \sqrt{\frac{L^2}{3}}$: As $L \to \infty$, $\Delta x \to \infty$

By adding waves together, through <u>wave packing</u>, waves may be localized:

Increase k and $n \to \infty$:

$$A(x) = \sum_{k=1}^{k_{max}} \cos(kx) \rightarrow$$

Particle localizes to a point for a definitive measurement of position. However, as $n \to \infty$, $\Delta p \to \infty$ as proven below:

The larger the box in a P.I.B. case, the smaller the error in momentum, and the larger the error in ~~precision~~ position.

For a particle in a box:

$$\Psi = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi n x}{a}\right) = \sqrt{\frac{2}{a}}\frac{1}{2i}\Big(\underbrace{e^{\frac{i\pi n x}{a}}}_{\frac{\hbar\pi n}{a}} - \underbrace{e^{-\frac{i\pi n x}{a}}}_{-\frac{\hbar\pi n}{a}}\Big)$$

Momentum:

$\langle p \rangle^2 = 0$, previously proven

$\langle p^2 \rangle = \left(\frac{\hbar\pi n}{a}\right)^2$:

$$\boxed{\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \frac{\hbar\pi n}{a}}$$

note that as $n \to \infty$, $\Delta p \to \infty$.

For σ^2,

$$\sigma^2 = \frac{a^2}{12} - \frac{a^2}{4\pi^2 n^2} = \frac{a^2}{4}\left(\frac{1}{3} - \frac{2}{\pi^2 n^2}\right)$$

Then $\boxed{\Delta x = \sigma = \frac{a}{2}\sqrt{\frac{1}{3} - \frac{2}{\pi^2 n^2}}}$

Note that as $n \to \infty$, $\Delta x \to \frac{a}{2}\sqrt{\frac{1}{3}}$.

Position: (Previously proven)

$\langle x \rangle = a/2$, $\langle x \rangle^2 = 0$

~~Relating Δx and Δp,~~

$$\cancel{\Delta x \Delta p = \left(\frac{a}{2}\sqrt{\frac{1}{3} - \frac{2}{\pi^2 n^2}}\right)\left(\frac{\hbar\pi n}{a}\right) = \frac{\hbar}{2}\sqrt{\frac{\pi^2 n^2}{3} - 2}}$$

So now we know $\Delta x = \frac{a}{2}\sqrt{\frac{1}{3} - \frac{2}{\pi^2 n^2}}$, $\Delta p = \frac{\hbar \pi n}{a}$, we can relate the two:

$$\Delta x \Delta p = \left(\frac{a}{2}\sqrt{\frac{1}{3} - \frac{2}{\pi^2 n^2}}\right)\left(\frac{\hbar \pi n}{a}\right) = \frac{\hbar}{2}\sqrt{\frac{\pi^2 n^2}{3} - 2} = \Delta x \Delta p.$$

We can see that since $\sqrt{\frac{\pi^2 n^2}{3} - 2} \geq 0$, $\boxed{\Delta x \Delta p \geq \frac{\hbar}{2}}$

Thus, it is fundamentally impossible for both x and p of a particle to be measured with complete accuracy.

What is the mathematical explanation behind this?

Recall that two operators commute if $\hat{A}\hat{B}\psi = \hat{B}\hat{A}\psi$. This may be redefined as $\hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi = 0$: In a quantum system, if two variables are to be known with arbitrary precision, then this statement (that the operators commute) MUST be true.

Some notation & properties:

- The commutator of two operators is defined as $[\hat{A},\hat{B}] = (\hat{A}\hat{B} - \hat{B}\hat{A})$.
- When 2 operators commute,

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\psi = 0 = [\hat{A},\hat{B}]\psi.$$

↳ Therefore $[\hat{A},\hat{B}]\psi = -[\hat{B},\hat{A}]\psi$

- When 2 operators do not commute,

$$\Delta A \Delta B = \frac{1}{2}\left|\underbrace{\langle[\hat{A},\hat{B}]\rangle}_{\text{Expectation value of commutator}}\right|$$

$$[\hat{A},\hat{A}]\psi = 0$$
$$[\hat{A},c\hat{B}]\psi = c[\hat{A},\hat{B}]\psi$$
$$[\hat{A},\hat{B}+\hat{C}]\psi = [\hat{A},\hat{B}]\psi + [\hat{A},\hat{C}]\psi$$
$$[\hat{A},\hat{B}\hat{C}]\psi = [\hat{A},\hat{B}]\hat{C}\psi + \hat{B}[\hat{A},\hat{C}]\psi$$
$$[\hat{A},\hat{A}^2] = 0 = [\hat{A},\hat{A}^n]$$

Applying this to momentum and coordinate, we have:

$$[\hat{x},\hat{p}]\psi = (\hat{x}\hat{p} - \hat{p}\hat{x})\psi = \hat{x}\hat{p}\psi - \hat{p}\hat{x}\psi.$$
$$\hat{x}\hat{p}\psi = \hat{x}\left(-i\hbar\frac{d}{dx}\psi\right) = -i\hbar x\frac{d}{dx}\psi$$
$$\hat{p}\hat{x}\psi = \hat{p}(x\psi) = -i\hbar\frac{d}{dx}(x\psi) = -i\hbar x\left(\frac{d}{dx}\psi\right) - i\hbar\psi\left(\overset{1}{\cancel{\frac{d}{dx}x}}\right)$$

$$[\hat{x},\hat{p}]\psi = \left(-i\hbar x\frac{d}{dx}\psi\right) - \left(-i\hbar x\frac{d}{dx}\psi - i\hbar\psi\right)$$
$$[\hat{x},\hat{p}]\psi = \underbrace{\cancel{-i\hbar x\frac{d}{dx}\psi} + \cancel{i\hbar x\frac{d}{dx}\psi}}_{0} + i\hbar\psi$$
$$[\hat{x},\hat{p}]\psi = i\hbar\psi \neq 0 \rightarrow$$ Therefore we cannot know both with arbitrary precision.

Can we also commute energy and momentum? Energy and position?

$$[\hat{E},\hat{p}]\psi = \hat{E}\hat{p}\psi - \hat{p}\hat{E}\psi = (\hat{E}\hat{p} - \hat{p}\hat{E})\psi.$$ However, recall that $\hat{E} = \frac{p^2}{2m} + U$.

For just kinetic energy, since $\frac{p^2}{2m} \rightarrow \frac{\hat{p}^2}{2m}$, using the properties of commutators we see:
(Assume $U=0$)

$$\left[\hat{p}, \frac{\hat{p}^2}{2m}\right] = \left[\frac{\hat{p}^2}{2m}, \hat{p}\right] = 0,$$ momentum commutes with kinetic energy, only if $U = 0$. However,

$$[\hat{p}, U] \neq 0$$

Note: If KE could equal 0 (which it can not), then $p=0$ and $\Delta x \Delta p \geq \frac{\hbar}{2}$ would be violated, since nothing multiplied by 0 results in $\hbar/2$.

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

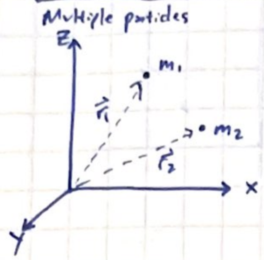
$$[\hat{x}, \hat{p}_y]\Psi = x(-i\hbar \tfrac{d}{dy}\Psi) - (-i\hbar(\underbrace{\tfrac{d}{dy} x y}_{\hookrightarrow\, x \frac{d}{dy} y}))$$

$\hookrightarrow x \frac{d}{dy} y$, since y ~~to~~ 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

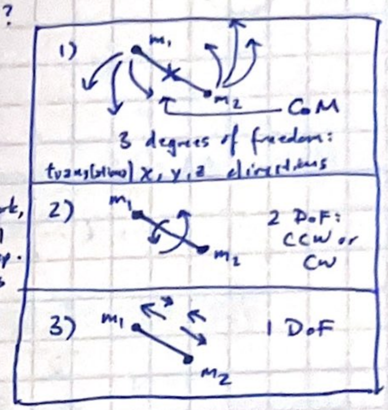


Particles 1 and 2 (m_1 and m_2) both have 3 degrees of freedom (movement in xyz directions) so total of 6 degrees of freedom when particles move independently of each other.

→ 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:

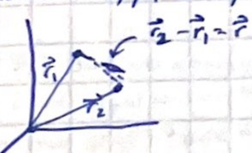
$$E = \underbrace{E_{tr}}_{\text{(Kinetic energy)}} + E_{vib} + E_{rot}$$

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



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

Each H atom is the same mass, and therefore $\mu = 1\left(\frac{1}{2}\right)$ a.m.u. = ½ a.m.u.

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

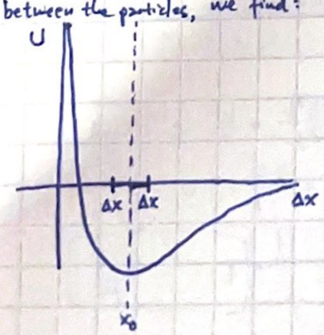
Consider H-Cl: What is the reduced mass?

$$\mu = 1\left(\frac{35}{36}\right)\text{a.m.u.} = \left(\frac{35}{36}\right)\text{a.m.u.} = \frac{35}{36}(1.7\times10^{-27}\text{ kg}).$$

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

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

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

Mass on a spring (Hooke's law)