

Vocabulary of mechanics in chemistry

Angular momentum

$L = \mathbf{p} \times \mathbf{r}$, or if p and r are perpendicular to one another (motion in a circle), $L = pr = mvr$. This is a convenient quantity for discussing rotations by an angle ϕ , just like $p = mv$ is convenient for discussing translational motion by a distance x .

Delta function

An "infinitely sharp" spike that still has an integral of 1. Think of it as a Gaussian whose Δx has gotten infinitely narrow, while its peak height has increased to stay normalized at 1. The function is important as the classical limit for a position wavefunction whose position is precisely known – but note in QM, the price to pay is that Δp of the corresponding momentum wavefunction (Fourier transform of $\Psi(x)$) becomes infinitely wide!

Dirac's notation

A shorthand notation that Dirac came up with to unify quantum mechanics as formulated by Heisenberg and later Schrödinger. The table below shows the meaning of some notations:

Position representation (conventional)	Dirac notation equivalent
$\Psi(x, t)$ called the wave function	$ t\rangle$ called the 'ket'
$\int dx \Psi^*(x, t) \text{ ___}$ (' ___ ' means you insert an expression there.)	$\langle t $ called the 'bra'
$A(x, \partial/\partial x)$ called an operator; operators turn one function into another.	A Called an operator; operators turn a ket (or bra) into another ket (or bra)
$\int dx \Psi^*(x, t) A \Psi(x, t)$ called a matrix element	$\langle t A t\rangle$ called a bra-ket = bracket Get it?
$\int dx \Psi^*(x, t) \Psi(x, t) = 1$ called normalization of the wavefunction	$\langle t t\rangle = 1$ called normalization
$\phi_n(x)$ called an eigenfunction	$ n\rangle$ called an eigenket
$\Psi(x, t) \int dx \Psi^*(x, t) \text{ ___}$ also an operator: it turns the function inserted at ' ___ ' into the function $\Psi(x, t)$ times a number	$ t\rangle\langle t $ also an operator

Eigenfunction

Linear operators \hat{A} in particular have the property that for some functions y , $\hat{A}y$ is proportional to y , or $\hat{A}y = ay$, where a is the proportionality constant. a is called an “**eigenvalue**” of operator \hat{A} . Some operators have only one eigenvalue, some infinitely many, and some have none. For example, take the operator $\partial/\partial x$. Are there functions that taking the derivative turns them into a multiple of themselves? There are, for example $\partial/\partial x (e^x) = (+1) e^x$. So e^x is an eigenfunction of the derivative operator, and its eigenvalue is $+1$. $Y=e^{-x}$ is also an eigenfunction, with eigenvalue -1 . Can you give an example of another eigenfunction of $\partial/\partial x$?

Eigenvalue (see **eigenfunction**)

Fourier principle and Fourier transform

The Fourier principle (of which the Heisenberg principle is a specific example) states that certain variable pairs are intrinsically Fourier conjugate. It means that a function of one of these variables is related to the analogous function of the other variable by Fourier transform. If t and ω for example are Fourier conjugate variables, $\Psi(\omega) = \int dt \exp[-i\omega t] \Psi(t)$. $\Psi(\omega)$ is called the “Fourier transform” of $\Psi(t)$. The functions $\Psi(\omega)$ and $\Psi(t)$ have the property that if one gets ‘fat,’ the other one gets ‘thin’. The widths Δt and $\Delta \omega$ of the functions is related by $\Delta t \Delta \omega = a/4\pi$, where the constant a equals 1 in this example. The functions intrinsically can never both be ‘thin’ simultaneously, since this contradicts the whole meaning of the variables t and ω . For example, if t is time and ω is frequency, a sound cannot be short in time (like a drum hit) and narrow in frequency (like a flute tone) at the same time. If $\Delta t \Delta \omega > a/4\pi$, then there is real uncertainty involved. For example, making a noise ‘pshhhht’ with your lips is both long in time and wide in frequency spectrum.

Heisenberg principle

In quantum mechanics $\Delta x \Delta p \neq 0$ because a quantum particle is not at a precise position and precise momentum simultaneously, just like in music a sound does not have precise pitch and precise location in time simultaneously. This is an inherent property of quantum particles, not an ‘uncertainty’ or ‘measurement error.’ According to Heisenberg, $\Delta x \Delta p = \hbar/2$, where $\hbar \approx 1.05 \cdot 10^{-34}$ J·s. This is small, and why it looks to observe as though big particles (like a ball) have a precise position and momentum simultaneously. For something as small as an electron, that’s not the case any longer. Rigorously, Δx and Δp are related to the width of the wavefunction as a function of position $\Psi(x)$, OR the wavefunction as a function of momentum $\Psi(p)$. The wavefunction is never a function of position and momentum simultaneously, rather, the two are related by the **Fourier principle and Fourier transform**.

Matrix (see also **Operator**)

A Matrix M turns one vector into another. For example, $\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$ is a matrix that turns a 2-D vector $\vec{v} = \begin{pmatrix} x \\ y \end{pmatrix}$ into another. In this example,

$M\vec{v} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -y \\ x \end{pmatrix}$. Think about what this matrix does: it rotates the vector by 90° so its x-value is now the negative of its old y-value, and the new y-value is the old x value: $M \rightarrow = \hat{\uparrow}$, if we draw the vector as an arrow ($x=1, y=0$ in this example).

Molecular dynamics simulation

A solution of Newton's equation using classical mechanics: given initial conditions $x_n(t=0)$ and $p_n(t=0)$ for all the positions and velocities, use $F=ma$, discretized into the **Verlet algorithm** derived in lecture, to calculate $x_n(t)$ and $p_n(t)$ at all future times t . Note that in this notation, x_1 is x for the first particle, x_2 is y for the first particle, x_3 is z for the first particle, x_4 is x for the second particle, and so forth, when dealing with 3-D space.

Node

A place where the wavefunction (or any oscillatory function) goes through 0. Usually called "a root" by mathematicians.

Normalization

Since $P(x)=|Y(x)|^2$ is the probability per unit distance of finding a quantum particle at x , it must be normalized so the probability of finding the particle anywhere (between $x=-\infty$ and ∞) must add up to 1. Thus $\int dx P(x) = 1$ for integration from $-\infty$ to ∞ .

Operator (see also **Matrix**), designated by a 'hat' or '^'

An operator \hat{A} turns one function into another function. For example, "c", "x", " $\partial/\partial x$ " and " $()^2$ " are operators. Let the function be $y=x^2$. Then

-if $\hat{A}=c$, $\hat{A}y=cx^2$.

-if $\hat{A}=x$, $\hat{A}y=x^3$.

-if $\hat{A}=\partial/\partial x$, $\hat{A}y=2x$

-if $\hat{A}=()^2$, $\hat{A}y=(x^2)^2 = x^4$

The first three are linear operators, i.e. if a is a number, $\hat{A}(ay)=a\hat{A}y$. The last one is not, for example $\hat{A}(3y)=9\hat{A}y \neq 3\hat{A}y$

Force

There are four fundamental forces in nature: strong, weak, electromagnetic, and gravity. The first three have already been unified, but for now gravity resists mathematical attempts. The forces originate from properties of quantum particles, called 'charge,' 'mass'. For examples, a particle with more 'charge' exerts a stronger electrical force. A particle with more 'mass' exerts a stronger gravitational force. The force between two fundamental matter particles, which are always **fermions**, is mediated by other quantum particles, always **bosons**. For example, protons and electrons, which are charged, interact via photons. Protons and electrons also have mass, and interact via gravitons (but the electrical attraction is much stronger).

When the bosons have no mass (such as a photon), the force between two particles is proportional to $b_1 b_2 / r^2$, where r is the distance between the particles, and b_i is the property related to the force (mass or charge).

Potential energy

For sufficiently slowly moving particles, the attraction or repulsion can be described by a potential energy $V(x)$ related to the force by $F(x) = -\partial V(x) / \partial x$. If a particle is slowly moved from one place x_0 to another x_1 , since $dE = -F dx$, integrating this equation yields $\Delta E = -\int dx F(x) = V(x_1) - V(x_0)$, the energy difference between the two locations.

Probability

The probability \mathcal{P} of a particle being found somewhere moving at any velocity must be 1, so $\int dx dp \mathcal{P}(x, p) = 1$. In classical mechanics, the probability is an 'infinitely spiked' function because the particle is at a precise position x and momentum p . In quantum mechanics, x and p are Fourier conjugate and the probability is given by the magnitude-squared of the wavefunction, or $\mathcal{P}(x) = |\Psi(x)|^2$ and $\mathcal{P}(p) = |\Psi(p)|^2$. The wavefunction has some width to it (see **Heisenberg principle**), so the quantum probability is not infinitely spiked, but a quantum particle can be found at a variety of positions and momenta. (Just like a musical tone is found at a variety of times and pitches, you can never find a tone of perfect pitch at a perfect instant in time!)

Symplectic

An equation of motion such as $p = m \partial x / \partial t$, $F(x) = \partial p / \partial t = ma$ (classical mechanics) or $H\Psi = i \hbar \partial \Psi / \partial t$ (quantum mechanics) is symplectic if it preserves an area constructed from its fundamental variables. For example, in classical mechanics, if you start a bunch of trajectories near one another in phase space in a little patch, as they move along in time, the area of the patch remains the same. In quantum mechanics, if you start a wavefunction at time $t=0$ and let it move along in time, the area $\Delta x \Delta p$ of the quantum particle is preserved, and the area under $\mathcal{P}(x) = |\Psi(x)|^2$ is preserved.

Trajectory

In classical mechanics, x and p as a function of time are the trajectory of a particle. (In 1 dimension, there's only one x and p ; in more dimensions, there are more. For example, two 3-D particles require 6 x, y, z positions and 6 momenta).

Verlet algorithm

A discrete version of Newton's equations, derived in class, which can be used to propagate a **trajectory** from $x(t)$ and $p(t)$ (or $v(t)$) to $x(t+\Delta t)$ and $p(t+\Delta t)$ by one time step Δt .