Summer 2024 Research

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1 Useful Notes on Quantum Mechanics (QM)

1.1 Prerequisites

Here are some references about the Mathematics of QM, as the main postulates will not be comprehensively addressed.

- https://peverati.github.io/pchem2/Postulates.html
- https://www.youtube.com/playlist?list=PL8ER5-vAoiHAWm1UcZsiauUGPlJChgNXC

1.2 The Schrödinger Equation

The **Hamiltonian** is an idea from classical mechanics, it describes the total energy of the system, which is the sum of the kinetic and potential energy in a system.

$$H = \frac{1}{2}mv^2 + V$$

The time-independent **Schrödinger Equation** (S.E.) can be derived by leveraging the relation between momentum, p, and the kinetic energy:

$$p = mv \implies v = \frac{p}{m}$$

$$\implies \frac{1}{2}mv^2 = \frac{1}{2}m(\frac{p}{m})^2 = \frac{1}{2}\frac{p^2}{m} = \frac{p^2}{2m}$$

$$\therefore\ H = \frac{p^2}{2m} + V$$

In QM, it is appropriate to use operators on wavefunctions, so we must use the linear momentum operator $\hat{p}$ in place of p.

$$\hat{p}_x \equiv \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\implies \hat{H} = \frac{1}{2m}(\frac{\hbar}{i}\frac{\partial}{\partial x})^2 + V(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

Note that the Hamiltonian operator $\hat{H}$ is defined in relation to the energy of a system.

$$\hat{H}\psi = E\psi$$

$$\therefore\ -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V(x)\psi = E\psi$$

This is the time-independent S.E. in one dimension.

The S.E. is described in higher dimensions with the Laplacian operator ∇^2.

$$\nabla^2 \equiv \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} + \cdots + \frac{\partial^2}{\partial x_n^2}$$

This is a more general form of the S.E. :

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi}$$

Wavefunctions are solutions to the S.E. (solutions obey $\hat{H}\psi = E\psi$) that satisfy the boundary conditions of a given situation.

1.3 Operators

In QM, we work with a wavefunction ψ associated with some particle. This wavefunction describes the motion of the particle and is a function of spatial coordinates, **i.e.** $\psi(x)$, $\psi(x,y,z)$, $\psi(r,\theta)$.

We must 'operate' on the wavefunction to gain information about physical quantities in a system. Operators correspond to 'observables'.

$$\textbf{i.e. } \nabla^2\psi(x,y) = \frac{\partial^2}{\partial x^2}\psi(x,y) + \frac{\partial^2}{\partial y^2}\psi(x,y)$$

A wavefunction ψ is an eigenfunction of an operator $\hat{\Omega}$ if and only if:

$$\hat{\Omega}\psi = \omega\psi$$

We call ω the eigenvalue of the eigenfunction. Eigenvalues are the 'expectation values' of operators.

i.e. in $\hat{H}\psi = E\psi$, the total energy of the system, E, is an eigenvalue and therefore expectation value of the Hamiltonian operator, $\langle H\rangle$, is equal to E.

Note: Operators can 'commute'. The commutator is also an operator. Suppose we have two operators $\hat{\Omega}_1$ and $\hat{\Omega}_2$, the commutator of $\hat{\Omega}_1, \hat{\Omega}_2$ is:

$$[\hat{\Omega}_1, \hat{\Omega}_2] \equiv \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1$$

- Two operators commute if $[\hat{\Omega}_1, \hat{\Omega}_2] = 0$. This means that we can measure these observables with infinite precision simultaneously.
- If $[\hat{\Omega}_1, \hat{\Omega}_2] \neq 0$, these operators are incompatible and do not compute. We cannot measure these observables with infinite precision simultaneously. There is a significant degree of uncertainty in one of the observables when measuring the other.

Here is an example of how the commutator works using the position and momentum operators:

$$\hat{x}\psi \equiv x\psi, \quad \hat{p}_x\psi = \frac{\hbar}{i}\frac{\partial}{\partial x}\psi$$

$$[\hat{x}, \hat{p}_x]\psi = \hat{x}(\hat{p}_x\psi) - \hat{p}_x(\hat{x}\psi) = x(\frac{\hbar}{i}\frac{\partial}{\partial x}\psi) - \frac{\hbar}{i}\frac{\partial}{\partial x}(x\psi) = \frac{\hbar}{i}(x\frac{\partial}{\partial x}\psi - \frac{\partial}{\partial x}x\psi)$$

$$\implies \frac{\hbar}{i}(x\frac{\partial}{\partial x}\psi - \frac{\partial}{\partial x}x\psi) = \frac{\hbar}{i}(x\frac{\partial}{\partial x}\psi - (\psi\frac{\partial}{\partial x}x + x\frac{\partial}{\partial x}\psi)) = \frac{\hbar}{i}(x\frac{\partial}{\partial x}\psi - \psi\frac{\partial}{\partial x}x - x\frac{\partial}{\partial x}\psi) = -\frac{\hbar}{i}\psi\frac{\partial}{\partial x}x$$

$$\implies [\hat{x}, \hat{p}_x]\psi = -\frac{\hbar}{i}\psi\frac{\partial}{\partial x}x = -\frac{i}{i}\frac{\hbar}{i}\psi = i\hbar$$

$$\boxed{[\hat{x}, \hat{p}_x]\psi = i\hbar\psi \iff [\hat{x}, \hat{p}_x] = i\hbar}$$

Since $[\hat{x}, \hat{p}_x] \neq 0$, the position and momentum operators are incompatible. We can't measure the exact position and momentum (and velocity by consequence) of a particle at the same time due to uncertainty. The **uncertainty principle** will be discussed in more detail later on, we have other important topics to cover first.

1.4 Born Interpretation of QM and Bra-Ket Notation

Max Born developed a system for understanding how the wavefunction can be used to create a **probability density function** for the location of a particle.

A wavefunction can contain complex numbers ($\psi \in \mathbb{C}$), meaning it can be written in the form $z = a + bi$. For every complex number z, there is a **complex conjugate** of z, $z^* = a - bi$. The squared magnitude of a complex number (which is a vector in the Complex plane) is equal to z^*z.

$$z \in \mathbb{C}, \ |z|^2 \equiv z^*z$$

- If $\psi \in \mathbb{C}, \ |\psi|^2 = \psi^*\psi$
- If $\psi \in \mathbb{R}, \ |\psi|^2 = \psi^*\psi = \psi\psi = \psi^2$

The **Born interpretation** is the idea that the probability of finding a particle in some position interval $[x,\ x+dx]$ (in the one-dimensional case) is proportional to the integral of the square of the wavefunction.

$$P(x \leq X \leq x+dx) \propto \int_{x}^{x+dx} \psi^* \psi dx$$

To make $|\psi|^2$ a proper probability density function, we must normalize the wavefunction so that the integral of its square over all space is equal to 1.

$$\int_{-\infty}^{\infty} \psi^* \psi d\tau = 1$$

To simplify how we represent these expressions, **Paul Dirac** developed **Bra-Ket** notation. This is by no means a complete description of the mathematical depth of this system, but here are some foundational rules to get started:

- Bra: $\langle \psi | = \psi^*$
- Ket: $| \psi \rangle = \psi$
- Bra-Ket: $\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} \psi^* \psi d\tau = 1$, $\langle \psi | \phi \rangle = \int_{-\infty}^{\infty} \psi^* \phi d\tau$
- Conjugate: $\langle \psi | \phi \rangle^* = \langle \phi | \psi \rangle$
- Factoring: $\langle c_1 \psi | c_2 \psi \rangle = c_2 \langle c_1 \psi | \psi \rangle = c_2 \langle \psi | c_1 \psi \rangle^* = c_2 c_1^* \langle \psi | \psi \rangle^*$
- $\langle \psi | \hat{\Omega} | \psi \rangle = \int_{-\infty}^{\infty} \psi^* \hat{\Omega} \psi d\tau = \hat{\Omega} \psi = \langle \Omega \rangle$ (Expectation value of an operator)
- $\langle \psi | \hat{\Omega}_1 + \hat{\Omega}_2 | \psi \rangle = \langle \psi | \hat{\Omega}_1 | \psi \rangle + \langle \psi | \hat{\Omega}_2 | \psi \rangle$ (Linear Combination of operators)
- Let $| \psi \rangle = c_1 | \psi_1 \rangle + c_2 | \psi_2 \rangle$ (Linear Combination of Basis States),
  Note: Think of basis states like basis vectors. In 3 dimensions,

$$\langle c_1\psi_1 + c_2\psi_2 | c_1\psi_1 + c_1\psi_2 \rangle = \langle c_1\psi_1 | c_1\psi_1 \rangle + \langle c_1\psi_1 | c_2\psi_2 \rangle + \langle c_1\psi_1 | c_2\psi_2 \rangle + \langle c_2\psi_2 | c_1\psi_1 \rangle$$

$$\implies c_1 c_1^* \langle \psi_1 | \psi_1 \rangle + c_2 c_1^* \langle \psi_2 | \psi_1 \rangle + c_2 c_2^* \langle \psi_2 | \psi_2 \rangle + c_1 c_2^* \langle \psi_1 | \psi_2 \rangle$$

$$\implies c_1 c_1^*(1) + c_2 c_1^* \langle \psi_2 | \psi_1 \rangle + c_2 c_2^*(1) + c_1 c_2^* \langle \psi_1 | \psi_2 \rangle = c_1 c_1^* + c_2 c_1^* \langle \psi_2 | \psi_1 \rangle + c_2 c_2^* + c_1 c_2^* \langle \psi_1 | \psi_2 \rangle$$

$$\therefore \langle c_1\psi_1 + c_2\psi_2 | c_1\psi_1 + c_1\psi_2 \rangle = c_1 c_1^* + c_2 c_1^* \langle \psi_2 | \psi_1 \rangle + c_2 c_2^* + c_1 c_2^* \langle \psi_1 | \psi_2 \rangle$$

A way to determine the similarity between two functions is to take their L^2 inner product in Hilbert Space ($\mathcal{H}$). Much like vectors, if two functions have no overlap their inner product is equal to zero. The inner product is a generalized form of the dot product that can be applied to functions. Suppose we have $f, g \in \mathbb{C}$ over a region R:

$$\langle f, g \rangle = \int_R f g^* d\tau.$$

This looks remarkably similar to Bra-Ket notation, in fact, it is equivalent to an operation defined above.

$$\langle f, g\rangle = \langle g|f\rangle$$

. Suppose I have an unnormalized wavefunction $\psi = f(\tau)$ and I want to normalize it, its normalized version can be written as $\psi = Nf(\tau)$ (where $N \in \mathbb{R}$).

$$\psi^*\psi = (Nf(\tau))^* Nf(\tau) = N^2 f(\tau)^* f(\tau)$$

$$\implies \int_{-\infty}^{\infty} \psi^*\psi d\tau = \int_{-\infty}^{\infty} N^2 f(\tau)^* f(\tau) d\tau = N^2 \int_{-\infty}^{\infty} f(\tau)^* f(\tau) d\tau = 1$$

$$\implies N^2 = (\int_{-\infty}^{\infty} f(\tau)^* f(\tau) d\tau)^{-1} \implies N = (\int_{-\infty}^{\infty} f(\tau)^* f(\tau) d\tau)^{-1/2} = \langle\psi|\psi\rangle^{-1/2}$$

$$\therefore\ N = \frac{1}{\sqrt{\langle\psi|\psi\rangle}},\ \psi = \frac{1}{\sqrt{\langle\psi|\psi\rangle}} f(\tau)$$

Let's look at an example of this. Imagine a scenario where the motion of a particle is fixed to a ring on a sphere. We can represent the unit circle in the complex plane as $f(\theta) = e^{im\theta}$ where $m = 1$, for this to be a wavefunction, it must be finite and single-valued. That is, on a ring, the condition $f(\theta) = f(\theta + 2\pi)$ should be satisfied and $\forall\theta,\ f(\theta) \neq \infty$:

$$e^{i\pi} = -1$$

$$e^{im(\theta+2\pi)} = e^{im\theta}e^{im2\pi} = e^{im\theta}e^{i\pi(2m)} = e^{im\theta}(-1)^{2m} = e^{im\theta} \quad (\text{if } m \in \mathbb{Z},\ (-1)^{2m} = 1)$$

$$\implies e^{im(\theta+2\pi)} = e^{im\theta}$$

So we can now say that our wavefunction is $\psi(\theta) = Nf(\theta) = Ne^{im\theta}$. Note that the entire space of motion for a ring would be from $\phi = 0$ to 2π.

Let's find N:

$$\langle\psi|\psi\rangle = \int_0^{2\pi} e^{-im\theta}e^{im\theta} d\theta = \int_0^{2\pi} e^{(im-im)\theta} d\theta = \int_0^{2\pi} e^{(0)\theta} d\theta = \int_0^{2\pi} d\theta = \theta\Big|_0^{2\pi} = 2\pi$$

$$\therefore N = \frac{1}{\sqrt{2\pi}}, \psi(\theta) = \frac{1}{\sqrt{2\pi}} e^{im\theta}$$