Quantum

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On the Roadmap

1 Introduction

1.1 Classical Failures

1.1.1 Photoelectric Effect

It is well-known that when monochromatic light is incident on a metal surface, *photoelectrons* are emitted. However, it was seen that:

- Below a certain threshold frequency for a given metal, no photoelectrons are emitted whatever the intensity
- The photoelectrons have a maximum kinetic energy, dependent on the wavelength and independent of the intensity
- The photocurrent *does* depend on the intensity

These observations, inconsistent with the Classical idea that energy is continuously being transferred to the metal, are reconciled by positing that light consists of discrete packets of electromagnetic energy (*photons*), which transfer their energy to a single electron each. The energy is proportional to the frequency of the light: $E = h\nu$, where h is Planck's constant.

A stopping voltage can be used to measure the maximum kinetic energy of the photoelectrons: $\mathrm{KE}_{\max} = eV_0$. The *work function* of a metal is the minimum energy needed to release an electron from a metal, so we should have:

$$h\nu = eV_0 + W \;\Rightarrow V_0 = \frac{h}{e}\nu - \frac{W}{e}$$

which is indeed what is observed.

1.1.2 Black-Body Radiation

It can be shown that the density of modes in the electromagnetic spectrum of a black body between ν and $\nu + \mathrm{d}\nu$ is:

$$\mathrm{d}n = \frac{8\pi\nu^2}{c^3}\mathrm{d}\nu$$

The energy per mode is $k_B T$, so the energy density is given by:

$$\rho(\nu, T)\mathrm{d}\nu = \frac{8\pi\nu^2}{c^3}k_B T\mathrm{d}\nu$$

— The Rayleigh-Jeans Law. But this predicts that for large ν, ρ increases massively, but in fact the spectra of black bodies (like the Sun) peak at a certain wavelength and decay in both directions. Planck reconciled this by suggesting that each mode must be an integer multiple of $h\nu$, rather than each mode having energy $k_B T$, it instead has average energy:

$$\bar{\epsilon} = \frac{\sum_0^\infty nh\nu e^{-nh\nu/k_B T}}{\sum_0^\infty e^{-nh\nu/kB_T}} = \frac{h\nu}{e^{h\nu/k_B T} - 1}$$

giving a new energy density profile:

$$\rho(\nu, T) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_B T} - 1}$$

which not only resolves the "ultraviolet catastrophe", but also reproduces the above result for small ν.

1.2 Wave-Particle Duality

In his PhD thesis, de Broglie suggested that individual particles can behave as waves, analogously to how light waves can behave as individual particles. These waves have a wavevector $\mathbf{k}$ satisfying $\mathbf{p} = \hbar\mathbf{k}$, where $\hbar = h/2\pi$.

1.2.1 Bohr Atoms

Bohr then suggested that electrons in atoms might exist in orbits around the nuclei, at specific radii such that the circumference of the orbit corresponds to a whole number of wavelengths:

$$2\pi r_n = n\lambda = 2\pi n/k \;\Rightarrow\; kr_n = n$$

and the angular momentum is therefore quantised as:

$$L = mvr_n = pr_n = p\frac{n}{k} = n\hbar$$

The total energy becomes:

$$\begin{aligned} E &= \frac{1}{2}V(r_n) = -T(r_n) \\ &= -\frac{e^2}{8\pi\epsilon_0 r_n} = -\frac{p^2}{2m} = -\frac{n^2\hbar^2}{2mr_n^2} \\ \Rightarrow r_n &= \frac{4\pi\epsilon_0 n^2\hbar^2}{me^2} \\ \Rightarrow E &= -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{me^4}{8\epsilon_0^2 h^2}\frac{1}{n^2} \\ &= -\frac{hcR}{n^2} \text{ where } R = \frac{me^4}{8\epsilon_0^2 h^3 c} \end{aligned}$$

Further, we can calculate the velocities:

$$\begin{aligned} v_n &= \frac{n\hbar}{mr_n} = \frac{n\hbar}{m}\frac{me^2}{4\pi\epsilon_0 n^2\hbar^2} \\ &= \underbrace{\frac{e^2}{4\pi\epsilon_0\hbar c}}_{\alpha}\frac{c}{n} = \frac{\alpha c}{n} \end{aligned}$$

where α is the *fine structure constant*, almost exactly equal to 1/137.

1.2.2 Davisson-Germer Diffraction

De Broglie wavelengths are often very small, and the easiest way to observe diffraction effects is to use a crystal with an appropriate interatomic distance. The scattering is analogous to Bragg reflection, for which the appropriate equation is:

$$n\lambda = d\sin\theta$$

where the maximum off-axis reflection occurs at θ. Davisson and Germer used the Ni [111] plane, with $d = 2.15$Å as known from X-ray diffraction, but by accelerating electrons through a known voltage, thus giving them a known energy, momentum, and wavelength, they independently found $d = 2.18$Å, in quite good agreement.

1.3 Wavefunctions

It is a postulate of quantum mechanics that all the information that exists about a system is encoded in its *wavefunction*, Ψ. For example, the probability that, when the particle is measured, it will be located in $x \in [a, b]$ is:

$$P(x \in [a, b]) = \int_a^b |\Psi(x, t)|^2 \, \mathrm{d}x$$

as such, the integral over all space is 1. For a plane wave, $\Psi(\mathbf{r}, t) = Ae^{i(\mathbf{p}\cdot\mathbf{r} - Et)/\hbar}$, we see that $P(\mathbf{r}, t) = |A|^2$ and the particle is equally likely to be found anywhere [for plane waves the fact that they cannot be normalised is often swept under the rug in various ways]. For more general superpositions of waves, the dispersion relation is found to be:

$$\omega = \frac{E}{\hbar} = \frac{p^2}{2m\hbar} = \frac{\hbar}{2m}k^2$$

... quadratic. Wavefunctions can be written in both position space (as above), or momentum space:

$$\Psi(\mathbf{r}, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}^3} \Psi(\mathbf{p}, t) e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \, \mathrm{d}^3\mathbf{p}$$
$$\Phi(\mathbf{p}, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}^3} \Psi(\mathbf{r}, t) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \, \mathrm{d}^3\mathbf{r}$$

Parseval's theorem ensures that both are normalised.

Wavefunctions can represent multiple particles a and b; they may be denoted $\Psi(\mathbf{r}_a, \mathbf{r}_b, t)$. In this case, $|\Psi(\mathbf{r}_a, \mathbf{r}_b, t)|^2$ is a *joint probability distribution* on $\mathbf{r}_a$ and $\mathbf{r}_b$. One can "marginalise" this into a single probability distribution by integrating over one of the variables:

$$P(\mathbf{r}_a, t) = \int |\Psi(\mathbf{r}_a, \mathbf{r}_b, t)|^2 \, \mathrm{d}^3\mathbf{r}_b$$

Some many-particle wavefunctions are *separable*, that is they can be expressed as $\Psi(\mathbf{r}_a, \mathbf{r}_b, t) = \psi_a(\mathbf{r}_a, t)\psi_b(\mathbf{r}_b, t)$. If not, the particles are said to be *entangled*, as the individual probability distributions depend on each other. If the position particle a is measured, the distribution of $\mathbf{r}_b$ depends on what the value of $\mathbf{r}_a$ was. Wavefunctions may be more generally expressed as *kets*, such as $|\psi\rangle$. This essentially provides a general way of denoting the state a particle is in, without reference to the variables it depends on.

1.4 Operators

Operators convert one state into another, in the same way as a matrix converts one vector to another:

$$\hat{A}\,|\psi\rangle = |\phi\rangle$$

An example of an operator operating on a function is $\frac{\mathrm{d}}{\mathrm{d}x}$, this converts one function into another. Parallels often emerge between the ways that vectors, functions (which are sort of infinite-dimensional vectors), and kets can be used. For example, there is often a set of *basis states*, of which all possible states can be expressed as a linear combination, in the same way as functions can be expressed as linear combinations of e^{ikx} or $\delta(x - x')$, and vectors can be expressed as LC of $\hat{\boldsymbol{e}}_i$. If the basis is $\{|a_i\rangle\}$, then we can write

$$|\psi\rangle = \sum_i a_i\,|a_i\rangle$$

An inner product can be defined for functions and states in the same way as it is defined for vectors: for functions, this is given by

$$\int f^*(x)g(x)\,\mathrm{d}x$$

where the integral is over all the relevant space, as the inner product of two 3D vectors is taken over each of the 3 components. For general states, this is written concisely as $\langle\psi|\phi\rangle$; we see that $\langle\psi|\phi\rangle = \langle\phi|\psi\rangle^*$. The inner product can also be used to find the generalised "length" — the *norm* — of a state:

$$\||\psi\rangle\| \equiv \sqrt{\langle\psi|\psi\rangle}$$

if you'll pardon all the lines.

With the inner product in mind, we can obtain expressions for the a_i in the linear combination above:

$$\begin{aligned}\langle a_j|\psi\rangle &= \sum_i a_i\,\langle a_j|a_i\rangle = \sum_i a_i\delta_{ij} = a_j\\ \Rightarrow a_i &= \langle a_i|\psi\rangle\end{aligned}$$

where the second equality follows in the case that the basis $\{|a_i\rangle\}$ is orthonormal. The basis is further said to be *complete* if the following holds:

$$\sum_i |a_i\rangle\langle a_i| = \hat{I}$$

since

$$\sum_i |a_i\rangle\langle a_i| \sum_j a_j\,|a_j\rangle = \sum_{i,j} |a_i\rangle\,a_j\delta_{ij} = \sum_i a_i\,|a_i\rangle$$

provided the indices that j runs over are a subset of those that i runs over.

A general operator can be expressed in vector form as:

$$\hat{A} \equiv \sum_{i,j} A_{ij} \, |a_i\rangle\langle a_j|$$

so $\hat{A}$ converts $|a_k\rangle$ to $\sum_i A_{ik} \, |a_i\rangle$. The A_{ij} are known as the *matrix elements* of $\hat{A}$. These elements can also be extracted from the operator using:

$$A_{ij} = \langle a_i|\hat{A}|a_j\rangle$$

The Hermition conjugate, or adjoint, of an operator is denoted $\hat{A}^\dagger$, and defined by:

$$\langle\phi|\hat{A}|\psi\rangle = \langle\psi|\hat{A}^\dagger|\phi\rangle^*$$

And so we have $A^\dagger_{ij} = A^*_{ji}$, so it is analogous to a conjugate transpose. Operators for which $\hat{A} = \hat{A}^\dagger$ are known as *Hermitian operators*, and are the tools QM is built with.

1.4.1 Quantum Operators

There are many operators used in QM. If they correspond to an "observable", that is, something that can be measured, it will correspond to an Hermitian operator. The following operators are common, along with their representation in position space:

$$\begin{aligned}
\hat{\mathbf{r}} &\equiv \mathbf{r}\cdot \\
\hat{\mathbf{p}} &\equiv -i\hbar\boldsymbol{\nabla} \\
\hat{T} &\equiv \frac{\hat{\mathbf{p}}\cdot\hat{\mathbf{p}}}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \\
\hat{V} &\equiv V(\mathbf{r}) \\
\hat{H} &\equiv \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \\
&= i\hbar\frac{\partial}{\partial t} \\
\hat{\mathbf{L}} &\equiv \hat{\mathbf{r}} \times \hat{\mathbf{p}} = -i\hbar\mathbf{r} \times \boldsymbol{\nabla}
\end{aligned}$$

There are also $\hat{\mathbf{S}}$ and $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ but they operate on spaces beyond 3D space so don't really have functional dependence I can write about. For all of these operators, it can be shown that $\hat{A} = \hat{A}^\dagger$, as was asserted above. Hermitian operators have the properties that their eigenvalues are all real, and different

eigenvalues correspond to orthogonal eigenvectors; degenerate eigenvectors may be constructed into an orthogonal set by the Gram-Schmidt procedure.

Most operators only refer to the variables of a single particle. For example, when there are multiple particles and the wavefunction is something like $|\psi_a\rangle\,|\psi_b\rangle$, the operator $\hat{\mathbf{p}}_a = -i\hbar\boldsymbol{\nabla}_a$ would operate only on $|\psi_a\rangle$, leaving $|\psi_b\rangle$ untouched.

One of the most important and controversial concepts in QM is *wavefunction collapse*. When an observable of a system is measured (one measures a particle's momentum, for example), the system spontaneously and immediately collapses into an eigenstate of the operator corresponding to that observable, that is, a state where:

$$\hat{A}\,|a_k\rangle = A_k\,|a_k\rangle$$

for some A_k; the value obtained by this measurement is the eigenvalue A_k. The eigenstates form a very useful basis for the system. In terms of them, we may write an operator in *diagonal form*:

$$\hat{A} \equiv \sum_i A_i\,|a_i\rangle\langle a_i|$$

In between measurements, the state of the system will in general no longer be in an eigenstate of any particular operator, and will become a superposition of the eigenstates, that is $\Psi = \sum_i c_i\,|a_i\rangle$. A postulate of quantum mechanics is that the probability that a measurement of $\hat{A}$ will result in a value A_i (that is, that the state will collapse into $|a_i\rangle$) is $|c_i|^2 = |\langle a_i|\Psi\rangle|^2$. The *expectation value* for the outcome of the measurement is therefore:

$$\begin{aligned}
\langle A\rangle &= \sum_i |c_i|^2 A_i \\
&= \left\langle \sum_i c_i\,|a_i\rangle \middle| \sum_j A_j c_j\,|a_j\rangle \right\rangle \\
&= \left\langle \sum_i c_i\,|a_i\rangle \middle| \hat{A} \middle| \sum_j c_j\,|a_j\rangle \right\rangle \\
&= \langle\Psi|\hat{A}|\Psi\rangle
\end{aligned}$$

From this we see that:

$$\langle A\rangle^* = \langle\Psi|\hat{A}|\Psi\rangle^* = \langle\Psi|\hat{A}^\dagger|\Psi\rangle = \langle\Psi|\hat{A}|\Psi\rangle = \langle A\rangle$$

That is, the operators being Hermitian leads to the expectation value of a measurement being real, as we require — if we found that we expect a particle's momentum to be complex, that would not be ideal!

We can also define the uncertainty on a measurement, by analogy with a standard deviation, by:

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

If the system is in an eigenstate, we have $\langle A^2 \rangle = \langle A \rangle^2$, so $\Delta A = 0$; for a system which is a linear combination of states, then in general $\Delta A \neq 0$.

1.5 Commutators

Two operators $\hat{A}$ and $\hat{B}$ are said to commute if $\hat{A}\hat{B} = \hat{B}\hat{A}$. One defines the *commutator* of $\hat{A}$ and $\hat{B}$ as:

$$\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

The *anticommutator* of $\hat{A}$ and $\hat{B}$ is defined as:

$$\left\{\hat{A}, \hat{B}\right\} \equiv \hat{A}\hat{B} + \hat{B}\hat{A}$$

If $\hat{A}$ and $\hat{B}$ commute, then $\left[\hat{A}, \hat{B}\right] = 0$. Further, if the eigenstates of $\hat{A}$ are $|a_i\rangle$, then:

$$\hat{A}\hat{B}\,|a_i\rangle = \hat{B}\hat{A}\,|a_i\rangle = A_i\hat{B}\,|a_i\rangle$$

so $\hat{B}\,|a_i\rangle$ is also an eigenstate of $\hat{A}$, with the same eigenvalue A_i. This means that $\hat{B}\,|a_i\rangle$ must simply be a scalar multiple of $|a_i\rangle$, and so $|a_i\rangle$ is also an eigenstate of $\hat{B}$. Therefore *commuting operators have the same set of eigenstates.*

Useful commutators between the above operators (and their vector components) include:

$$\begin{aligned}
[\hat{x}, \hat{p}_x] &= i\hbar \\
[\hat{\mathbf{r}}_a, \hat{\mathbf{p}}_b] &= 0 \\
[\hat{x}, F(\hat{p}_x)] &= i\hbar\frac{\partial F}{\partial \hat{p}_x} \\
[\hat{p}_x, G(\hat{x})] &= -i\hbar\frac{\partial G}{\partial \hat{x}} \\
\left[\hat{\mathbf{p}}, \hat{T}\right] &= 0 \\
\left[\hat{L}_x, \hat{L}_y\right] &= i\hbar\hat{L}_z
\end{aligned}$$

Note that in two cases there are *functions of operators*. These are very well-defined things; we have for example:

$$\exp \hat{A} \equiv \hat{I} + \hat{A} + \frac{\hat{A}^2}{2} + ...$$

The operator $F(\hat{A})$ will clearly have the same eigenstates as $\hat{A}$, but the eigenvalues will instead be $F(a_i)$.

The product of the uncertainties of two observables $\Delta A \Delta B$ depends on the commutator of the two corresponding operators. Consider the operator $\hat{A}_d \equiv \hat{A} - \langle A \rangle$, with $\hat{A}_d^2 \equiv \hat{A}^2 - 2\langle A \rangle \hat{A} + \langle A \rangle^2$, and $\langle A_d^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2 = \Delta A^2$; consider a similar operator $\hat{B}_d$. It is clear that, provided $\hat{A}$ and $\hat{B}$ are Hermitian, each of the above operators is also Hermitian. Consider now, for real λ, the ket:

$$|\phi\rangle = \left(\hat{A}_d + i\lambda \hat{B}_d\right)|\psi\rangle$$

we require:

$$\begin{aligned}
\langle \phi | \phi \rangle = \langle \psi | \left(\hat{A}_d - i\lambda \hat{B}_d\right)\left(\hat{A}_d + i\lambda \hat{B}_d\right)|\psi\rangle \geq 0 \\
\langle \psi | \hat{A}_d^2 | \psi \rangle + \lambda^2 \langle \psi | \hat{B}_d^2 | \psi \rangle + \lambda \left\langle \psi \middle| i\left[\hat{A}_d, \hat{B}_d\right] \middle| \psi \right\rangle \geq 0 \\
\Delta A^2 + \lambda^2 \Delta B^2 + \lambda \left\langle i\left[\hat{A}_d, \hat{B}_d\right] \right\rangle \geq 0
\end{aligned}$$

where the operator in the final term can be shown to be Hermitian, so the final term is real. To be ≥ 0 for all λ (which was chosen arbitrarily), we require the determinant of the quadratic in λ to be negative; that is:

$$\begin{aligned}
\left\langle i\left[\hat{A}_d, \hat{B}_d\right] \right\rangle^2 - 4\Delta A^2 \Delta B^2 \leq 0 \\
\Delta A \Delta B \geq \frac{1}{2}\left| \left\langle i\left[\hat{A}_d, \hat{B}_d\right] \right\rangle \right|
\end{aligned}$$

Now the commutator in the final term can be written as:

$$\left[\hat{A}_d, \hat{B}_d\right] = \left[\hat{A} - \langle A \rangle, \hat{B} - \langle B \rangle\right] = \left[\hat{A}, \hat{B}\right]$$

so we have simply:

$$\Delta A \Delta B \geq \frac{1}{2}\left| \left\langle i\left[\hat{A}, \hat{B}\right] \right\rangle \right|$$

the *generalised uncertainty principle*. For $\hat{A} \equiv \hat{x}, \hat{B} \equiv \hat{p}_x$, this gives:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

as is well-known. There is equality if $|\psi\rangle$ corresponds to a *minimum uncertainty state* $|\psi_\mu\rangle$. Following all the inequalities back, we find that minimum uncertainty states satisfy $\langle\phi|\phi\rangle = 0$, and so:

$$\left(\hat{A}_d + i\lambda\hat{B}_d\right)|\psi_\mu\rangle = |0\rangle$$

for $\hat{x}$ and $\hat{p}_x$ in function space, this corresponds to:

$$[x - \langle x\rangle - i\lambda\langle p\rangle]\psi_\mu(x) + \lambda\hbar\frac{\mathrm{d}\psi_\mu(x)}{\mathrm{d}x} = 0$$

an ODE with the family of (normalised) solutions:

$$\psi_\mu(x) = \frac{1}{\sqrt{2\pi\lambda\hbar}}\exp\left(-\frac{(x-\langle x\rangle)^2}{2\lambda\hbar}\right)\exp\left(\frac{i\langle p\rangle x}{\hbar}\right)$$

Therefore the minimum uncertainty state between the operators $\hat{x}$ and $\hat{p}_x$ is the product of a Gaussian and a plane wave.

2 Schrödinger's Equation

From the two different expressions for $\hat{H}$ above, we have:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{r})\Psi$$

the *time-dependent Schrödinger Equation*. By separation of variables into $\Psi(\mathbf{r},t) = \psi(\mathbf{r})T(t)$, we can obtain

$$\frac{i\hbar}{T}\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{\psi}\left[-\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi\right]$$

being functions of different variables, we can set both equal to a constant, say, oh I don't know, E. Then we have, for T:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{E}{i\hbar}T \Rightarrow T(t) = Ae^{-iEt/\hbar}$$

and for ψ:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi = E\psi$$

the *time-independent Schrödinger Equation*. We see that both parts of these are eigenvalue equations $\hat{H}\psi = E\psi$, so the solutions of the SE are eigenstates of $\hat{H}$. The full solution is then:

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt/\hbar}$$

and we see that $|\Psi(\mathbf{r},t)| = |\psi(\mathbf{r})|$, so probability distributions of eigenstates of $\hat{H}$ do not vary in time — these eigenstates are therefore called *stationary states*.

Wavefunctions satisfying the TISE must satisfy certain boundary conditions. It is clear that ψ and $\boldsymbol{\nabla}\psi$ must be continuous, as otherwise $\nabla^2\psi$ would not exist. The exception is where $V(\mathbf{r})$ has an infinite discontinuity, as this leads in turn to $\nabla^2\psi$ having an infinite discontinuity, so $\boldsymbol{\nabla}\psi$ may be discontinuous.

2.1 Probability Current

As the integral of $|\Psi|^2$ over all space must always be 1, it can be considered as a conserved quantity, and so for any bounded region we can define a probability current $\mathbf{J}$, such that:

$$
\begin{aligned}
&\frac{\partial|\Psi|^2}{\partial t} + \boldsymbol{\nabla}\cdot\mathbf{J} = 0 \\
&\Rightarrow \int_{\partial V} \mathbf{J}\cdot\mathrm{d}\mathbf{S} = -\frac{\partial}{\partial t}\int_V \Psi^*\Psi\,\mathrm{d}V \\
&\qquad = -\int_V \left[\frac{\partial\Psi^*}{\partial t}\Psi + \Psi^*\frac{\partial\Psi}{\partial t}\right]\mathrm{d}V \\
&\qquad = -\int_V \left[\frac{1}{-i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\Psi^* + V(\mathbf{r})\Psi^*\right)\Psi + \Psi^*\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{r})\Psi\right)\right]\mathrm{d}V \\
&\qquad = -\int_V \left[\frac{\hbar}{2mi}\Psi\nabla^2\Psi^* - \frac{\hbar}{2mi}\Psi^*\nabla^2\Psi\right]\mathrm{d}V \\
&\qquad = \frac{\hbar}{2mi}\int_V \left[\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^* + \boldsymbol{\nabla}\Psi^*\cdot\boldsymbol{\nabla}\Psi - \boldsymbol{\nabla}\Psi\cdot\boldsymbol{\nabla}\Psi^*\right]\mathrm{d}V \\
&\qquad = \frac{\hbar}{2mi}\int_V \boldsymbol{\nabla}\cdot\left[\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*\right]\mathrm{d}V \\
&\qquad = \int_{\partial V} \Re\left[\frac{\hbar}{mi}\Psi^*\boldsymbol{\nabla}\Psi\right]\cdot\mathrm{d}\mathbf{S} = \int_{\partial V}\Re\left[\Psi^*\frac{\hat{\mathbf{p}}}{m}\boldsymbol{\nabla}\Psi\right]\cdot\mathrm{d}\mathbf{S} \\
&\quad \Rightarrow \mathbf{J} \equiv \Re\left[\Psi^*\frac{\hat{\mathbf{p}}}{m}\Psi\right]
\end{aligned}
$$

which sorta makes sense as $\hat{\mathbf{p}}/m$ can be thought of as the "velocity operator", in a sense.

2.2 Unbound Particles

By definition, an unbound particle has more energy than potential energy for some infinite region (which may be semi-infinite), that is $E > V(\mathbf{r})$. For the case where $V(\mathbf{r}) = V_0$ constant, the TISE gives:

$$\Psi(\mathbf{r}, t) = Ae^{i\mathbf{k}\cdot\mathbf{r}}e^{-iEt/\hbar}$$

where

$$|\mathbf{k}| = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

It is easily seen that the probability current for such wavefunctions is $|A|^2\hbar\mathbf{k}/m$. There may be regions encountered by this unbound particle for which $E < V(\mathbf{r})$. If $V_0 > E$ above, then the solution becomes:

$$\Psi(\mathbf{r}, t) = Ae^{\boldsymbol{\kappa}\cdot\mathbf{r}}e^{-iEt/\hbar}, |\boldsymbol{\kappa}| = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

for which it may be seen that in fact $\mathbf{J} = \mathbf{0}$. For problems containing several adjacent regions of constant $V(\mathbf{r})$, one constructs the solutions in each region depending on the V, and uses the boundary conditions mentioned above to fix the integration constants; in 1D there are often 1 or 2 per region. In particular, for a simple system of a potential step, we find that when a beam of particles is fired from one region to another, the ratios of the reflected amplitude to the incident amplitude (denoted r) and that of the transmitted to the incident (t) are given by:

$$r = \frac{k_1 - k_2}{k_1 + k_2} \qquad\qquad t = \frac{2k_1}{k_1 + k_2}$$

and the relevant probability flux ratios R and T as:

$$R \equiv \frac{|\mathbf{J}_r|}{|\mathbf{J}_i|} = \left|\frac{k_1 - k_2}{k_1 + k_2}\right|^2 \qquad\qquad T \equiv \frac{|\mathbf{J}_t|}{|\mathbf{J}_i|} = \frac{4|k_1||k_2|}{|k_1 + k_2|^2}$$

where we see that $R + T = 1$ as required (provided both are real). We also see that, if the second region has $V_0 > E$ and $\mathbf{k}_2$ is imaginary, we in fact have $R = 1$ and $T = 0$ as $\mathbf{J}_t = \mathbf{0}$.

For barriers (3-region systems), it is possible for particles to "tunnel through" a region where $V_0 > E$ and have a finite probability of ending up on the other side. This is seen in nature in field emission and radioactive decay; the former is exploited in *scanning tunnelling microscopy*.

2.3 Bound Particles

Bound particles only have $E > V$ over a finite region. In this case it turns out that the TISE gives a set of discrete ("quantised") states, whereas for the unbound case, any value of $\mathbf{k}$ was acceptable.

2.3.1 Infinite Square Well

The solutions for a square potential well, with:

$$V(x) = \begin{cases} V_0 < E & 0 \leq x \leq a \\ \infty & \text{otherwise} \end{cases}$$

are:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right),\ E_n = V_0 + \frac{\hbar^2 n^2 \pi^2}{2ma^2},\ n = 1, 2, 3, ...$$

Note that the lowest energy state has $n = 1$ and $T \neq 0$, suggesting that particles cannot be motionless when confined. This non-zero energy of the ground state is called the *zero-point energy*. Note also that there are an infinite number of these bound states, which are all orthogonal to each other.

2.3.2 Finite Square Well

A finite square potential well (note we shift the origin) has:

$$V(x) = \begin{cases} -V_0 < E = -E_n & |x| \leq a/2 \\ 0 & \text{otherwise} \end{cases}$$

with solutions:

$$\psi_n(x) = \begin{cases} C_n e^{\kappa_n x} & x < -a/2 \\ A_n \sin(k_n x) + B_n \cos(k_n x) & |x| \leq a/2 \\ D_n e^{-\kappa_n x} & x > a/2 \end{cases}$$

where

$$k_n = \sqrt{\frac{2m(V_0 - E_n)}{\hbar^2}} \qquad \kappa_n = \sqrt{\frac{2mE_n}{\hbar^2}}$$

Considerations of the boundary conditions give two possibilities for even and odd solutions: for even solutions, $k_n \tan(k_n a/2) = \kappa_n$; for odd solutions, $k_n \cot(k_n a/2) = -\kappa_n$; these must be solved numerically. Letting $X_n = k_n a/2, Y_n = \kappa_n a/2$, these become:

$$Y_n = \begin{cases} X_n \tan X_n & \psi \text{ even} \\ -X_n \cot X_n & \psi \text{ odd} \end{cases}$$

Also,

$$X_n^2 + Y_n^2 = \frac{ma^2 V_0}{2\hbar^2}$$

The solutions to this are discrete, and the number of solutions depends on V_0 and the number of trigonometric branches intersected by the circle described. The branches have intercepts at $X_q = q\pi/2$; there is thus always at least one solution; there are two solutions provided:

$$\frac{ma^2 V_0}{2\hbar^2} \geq \frac{\pi^2}{4}$$

and so on. The corresponding energies are given by:

$$E = -\frac{\hbar^2 \kappa_n^2}{2m} = -\frac{2\hbar^2 Y_n^2}{ma^2}$$

2.3.3 Harmonic Oscillator

The harmonic oscillator has $V(x) = \frac{1}{2}m\omega^2 x^2$, so the Hamiltonian is:

$$\hat{H} = \frac{1}{2m}\hat{p}_x^2 + \frac{m\omega^2}{2}\hat{x}^2$$

It is useful then to define the following operator and its conjugate:

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p}_x \qquad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p}_x$$

These operators have the following useful properties:

$$\begin{aligned}
\hat{a}\hat{a}^\dagger &= \frac{m\omega}{2\hbar}\hat{x}^2 + \frac{1}{2m\hbar\omega}\hat{p}_x^2 - \frac{i}{2\hbar}[\hat{x}, \hat{p}_x] \\
\hat{a}^\dagger\hat{a} &= \frac{m\omega}{2\hbar}\hat{x}^2 + \frac{1}{2m\hbar\omega}\hat{p}_x^2 + \frac{i}{2\hbar}[\hat{x}, \hat{p}_x] \\
\Rightarrow \left[\hat{a}, \hat{a}^\dagger\right] \equiv \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} &= -\frac{i}{\hbar}[\hat{x}, \hat{p}_x] = 1 \\
\left\{\hat{a}, \hat{a}^\dagger\right\} \equiv \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} &= \frac{2}{\hbar\omega}\hat{H} \Rightarrow \hat{H} = \frac{\hbar\omega}{2}\left(\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\right) \\
\Rightarrow \hat{H} &= \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) \\
&= \hbar\omega\left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right) \\
\Rightarrow \left[\hat{H}, \hat{a}\right] &= \hbar\omega\left[\hat{a}\hat{a}^\dagger, \hat{a}\right] = \hbar\omega\hat{a}\left[\hat{a}^\dagger, \hat{a}\right]
\end{aligned}$$

$$= -\hbar\omega\hat{a}$$

$$\Rightarrow \left[\hat{H}, \hat{a}^\dagger\right] = \hbar\omega\left[\hat{a}^\dagger\hat{a}, \hat{a}^\dagger\right] = \hbar\omega\hat{a}^\dagger\left[\hat{a}, \hat{a}^\dagger\right]$$

$$= +\hbar\omega\hat{a}^\dagger$$

Consider an energy eigenstate $|\phi_n\rangle$, where $\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle$. Then consider the eigenstate $\hat{a}|\phi_n\rangle$:

$$\hat{H}\hat{a}|\phi_n\rangle = \left(\hat{a}\hat{H} - \hbar\omega\hat{a}\right)|\phi_n\rangle = (E_n - \hbar\omega)\hat{a}|\phi_n\rangle$$

we see that $\hat{a}|\phi_n\rangle$ is another energy eigenstate, but with an energy eigenvalue of $\hbar\omega$ less than that of $|\phi_n\rangle$ (note that it is not necessarily normalised, yet). Similarly, considering $\hat{a}^\dagger|\phi_n\rangle$,

$$\hat{H}\hat{a}^\dagger|\phi_n\rangle = (\hat{a}^\dagger\hat{H} + \hbar\omega\hat{a}^\dagger)|\phi_n\rangle = (E_n + \hbar\omega)\hat{a}^\dagger|\phi_n\rangle$$

we see that it is another eigenstate with energy $\hbar\omega$ more than $|\phi_n\rangle$. Next, we consider the ground state $|\phi_0\rangle$, whatever that may be. Since there can be no state with a lower energy than the ground state, we require $\hat{a}|\phi_0\rangle = |0\rangle$, so $\hat{H}|\phi_0\rangle = \hbar\omega(\hat{a}^\dagger\hat{a} + 1/2)|\phi_0\rangle = \hbar\omega/2|\phi_0\rangle$. Thus the energy of the ground state is $\hbar\omega/2$, and the energies of the excited states are $3\hbar\omega/2, 5\hbar\omega/2, ... = (n+1/2)\hbar\omega$; this is the entire spectrum of the 1D QHO. With this spectrum known, and the knowledge that high-energy states are exponentially less likely to be occupied (depending on the temperature), one can model the vibrational specific heats of diatomic gases

Although $\hat{a}$ is not Hermitian or observable, $\hat{a}^\dagger\hat{a}$ must be; it is called $\hat{N}$; we see that $\hat{H} = \hbar\omega(\hat{N} + 1/2)$. Since $\hat{H}|\phi_n\rangle = (n + 1/2)\hbar\omega|\phi_n\rangle = \hbar\omega(\hat{N} + 1/2)|\phi_n\rangle$, we have that $\hat{N}|\phi_n\rangle = n|\phi_n\rangle$. That is, $\hat{H}$ and $\hat{N}$ share a set of eigenstates (they do indeed commute), and the eigenvalues of $\hat{N}$ are the "number of quanta in the system". $\hat{N}$ is called the *number operator* for this reason. The related operator $\hat{a}\hat{a}^\dagger = \hat{a}^\dagger\hat{a} + 1$, so has eigenvalues $n + 1$.

To complete this scheme, we must ensure that the generated states are normalised, that is $\langle\phi|\phi\rangle = 1$. Consider the state $\hat{a}|\phi_n\rangle = c_n|\phi_{n-1}\rangle$. This has a square mod of:

$$|c_n|^2 = \langle\phi_n|\hat{a}^\dagger\hat{a}|\phi_n\rangle = n$$

so, give or take a phase, $c_n = \sqrt{n}$. Similarly, $\hat{a}^\dagger|\phi_n\rangle = d_n|\phi_{n+1}\rangle$, so

$$|d_n|^2 = \langle\phi_n|\hat{a}\hat{a}^\dagger|\phi_n\rangle = n + 1$$

so $d_n = \sqrt{n+1}$. We thus have:

$$\hat{a}|\phi_n\rangle = \sqrt{n}|\phi_{n-1}\rangle \qquad \hat{a}^\dagger|\phi_n\rangle = \sqrt{n+1}|\phi_{n+1}\rangle$$

$$|\phi_n\rangle = \frac{\left(\hat{a}^\dagger\right)^n}{\sqrt{n!}}|\phi_0\rangle$$

We can now analyse the properties of the wavefunctions corresponding to these states. We know that $\hat{a}\phi_0(x) = 0$, so

$$\begin{aligned}\sqrt{\frac{m\omega}{2\hbar}}\hat{x}\phi_0 - i\sqrt{\frac{1}{2m\hbar\omega}}\hat{p}_x\phi_0 &= 0\\ m\omega x\phi_0 + \hbar\frac{\mathrm{d}\phi_0}{\mathrm{d}x} &= 0\\ \Rightarrow \phi_0(x) &= \left(\frac{\pi\hbar}{m\omega}\right)^{1/4} e^{-m\omega x^2/2\hbar}\end{aligned}$$

where the function has been normalised. The higher-energy wavefunctions can then be obtained simply by applying the $\hat{a}^\dagger$ operator (including the normalisation) repeatedly.

2.3.4 Two-Particle Interactions

$$\hat{H} = \frac{\hat{\mathbf{p}}_a^2}{2m_a} + \frac{\hat{\mathbf{p}}_b^2}{2m_b} + \hat{V}(\hat{\mathbf{r}}_a, \hat{\mathbf{r}}_b)$$

Often the potential depends only on $\mathbf{r} = \mathbf{r}_b - \mathbf{r}_a$ (or even $r = |\mathbf{r}_b - \mathbf{r}_a|$). We also define $\mathbf{R}$ as the centre of mass:

$$\mathbf{R} \equiv \frac{m_a\mathbf{r}_a + m_b\mathbf{r}_b}{M}, M \equiv m_a + m_b$$

and seek to reframe the problem in terms of $\mathbf{r}$ and $\mathbf{R}$, since $\hat{V}$ only depends on the former. The centre-of-mass momentum $\mathbf{P}$ and the relative momentum $\mathbf{p}$ are calculated using the following formulae for the gradients with respect to the new variables:

$$\begin{aligned}\boldsymbol{\nabla}_a \equiv \frac{\partial\mathbf{R}}{\partial\mathbf{r}_a}\boldsymbol{\nabla}_\mathbf{R} + \frac{\partial\mathbf{r}}{\partial\mathbf{r}_a}\boldsymbol{\nabla}_\mathbf{r} &= \frac{m_a}{M}\boldsymbol{\nabla}_\mathbf{R} - \boldsymbol{\nabla}_\mathbf{r}\\ \Rightarrow \hat{\mathbf{p}}_a &= \frac{m_a}{M}\hat{\mathbf{P}} - \hat{\mathbf{p}}\\ \boldsymbol{\nabla}_b \equiv \frac{\partial\mathbf{R}}{\partial\mathbf{r}_b}\boldsymbol{\nabla}_\mathbf{R} + \frac{\partial\mathbf{r}}{\partial\mathbf{r}_b}\boldsymbol{\nabla}_\mathbf{r} &= \frac{m_b}{M}\boldsymbol{\nabla}_\mathbf{R} + \boldsymbol{\nabla}_\mathbf{r}\\ \Rightarrow \hat{\mathbf{p}}_b &= \frac{m_b}{M}\hat{\mathbf{P}} + \hat{\mathbf{p}}\\ \Rightarrow \frac{\hat{\mathbf{p}}_a^2}{2m_a} + \frac{\hat{\mathbf{p}}_b^2}{2m_b} &= \frac{m_a + m_b}{2M^2}\hat{\mathbf{P}}^2 + \left(\frac{1}{2m_a} + \frac{1}{2m_b}\right)\hat{\mathbf{p}}^2\\ &= \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu}, \text{ where } \mu \equiv \left(m_a^{-1} + m_b^{-1}\right)^{-1}\end{aligned}$$

$$\Rightarrow \hat{H} = \underbrace{\frac{\hat{\mathbf{P}}^2}{2M}}_{\hat{H}_R} + \underbrace{\frac{\hat{\mathbf{p}}^2}{2\mu} + \hat{V}(r)}_{\hat{H}_r}$$

as one might have expected. Selecting a separable solution $\psi(\mathbf{R}, \mathbf{r}) = \psi_R(\mathbf{R})\psi_r(\mathbf{r})$, we have:

$$\psi_r \hat{H}_R \psi_R + \psi_R \hat{H}_r \psi_r = E\psi_R\psi_r \Rightarrow \underbrace{\frac{1}{\psi_R}\hat{H}_R\psi_R}_{E_R} + \underbrace{\frac{1}{\psi_r}\hat{H}_r\psi_r}_{E_r} = E$$

where $E_R + E_r = E$. This gives by separation the two equations:

$$\hat{H}_R\psi_R = E_R\psi_R \qquad \hat{H}_r\psi_r = E_r\psi_r$$
$$\frac{\hat{\mathbf{P}}^2}{2M}\psi_R = E_R\psi \qquad \frac{\hat{\mathbf{p}}^2}{2\mu}\psi_r + \hat{V}(r)\psi_r = E_r\psi_r$$

The first equation has plane wave solutions; the second is a radial problem (see Section 3), but effectively for only one particle; the overall solution is the product of these two.

2.4 Time Dependence

At a given point in time, a general state is in a superposition of energy eigenstates:

$$|\psi(\mathbf{r}, t)\rangle = \sum_n c_n(t)\,|\phi_n(\mathbf{r})\rangle$$

The c_n can in fact be deduced to some extent. According to the TDSE:

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}|\psi(\mathbf{r},t)\rangle &= \hat{H}\,|\psi(\mathbf{r},t)\rangle \\
\Rightarrow \sum_n i\hbar\frac{\mathrm{d}c_n}{\mathrm{d}t}|\phi_n(\mathbf{r})\rangle &= \sum_n c_n(t)E_n\,|\phi_n(\mathbf{r})\rangle \\
\Rightarrow \frac{\mathrm{d}c_n}{\mathrm{d}t} &= -\frac{iE_n}{\hbar}c_n \\
\Rightarrow c_n(t) &= c_n(0)e^{-iE_nt/\hbar} \\
\Rightarrow |\psi(\mathbf{r},t)\rangle &= \sum_n c_n(0)e^{-iE_nt/\hbar}\,|\phi_n(\mathbf{r})\rangle \quad = \sum_n c_n(0)e^{-i\hat{H}t/\hbar}\,|\phi_n(\mathbf{r})\rangle \\
&= e^{-i\hat{H}t/\hbar}\sum_n c_n(0)\,|\phi_n(\mathbf{r})\rangle \\
&= e^{-i\hat{H}t/\hbar}\,|\psi(\mathbf{r},0)\rangle
\end{aligned}$$

We can thus define a *time evolution operator* $\hat{U}(t;t_0) = \exp\Big(-i\hat{H}(t-t_0)/\hbar\Big)$, the effect of which is to evolve a wavefunction forwards (or indeed backwards) in time. We see that if the state of the system is an energy eigenstate (that is, only one of the c_n is non-zero), then the state simply cycles round in phase, so the expectation values of any observable is independent of time. Going back to the TDSE, we obtain:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\Big(\hat{U}\left|\psi(\mathbf{r},0)\right\rangle\Big) &= \hat{H}\hat{U}\left|\psi(\mathbf{r},0)\right\rangle \\ \Rightarrow i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{U} &= \hat{H}\hat{U} \end{aligned}$$

which could also be arrived at by abuse of notation in the definition of $\hat{U}$.

2.4.1 Ehrenfest's Theorem

Ehrenfest's Theorem gives the time variation of the expectation values of operators:

$$\begin{aligned} \frac{\mathrm{d}\left\langle A\right\rangle}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\left\langle\psi|\hat{A}|\psi\right\rangle \\ &= \frac{\mathrm{d}\left\langle\psi\right|}{\mathrm{d}t}\hat{A}\left|\psi\right\rangle + \left\langle\psi\left|\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}\right|\psi\right\rangle + \left\langle\psi\right|\hat{A}\frac{\mathrm{d}\left|\psi\right\rangle}{\mathrm{d}t} \\ &= -\frac{1}{i\hbar}\left\langle\psi|\hat{H}\hat{A}|\psi\right\rangle + \frac{1}{i\hbar}\left\langle\psi|\hat{H}\hat{A}|\psi\right\rangle + \left\langle\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}\right\rangle \\ \Rightarrow \frac{\mathrm{d}\left\langle A\right\rangle}{\mathrm{d}t} &= \frac{i}{\hbar}\left\langle\left[\hat{H},\hat{A}\right]\right\rangle + \left\langle\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}\right\rangle \end{aligned}$$

Usually the second term is zero as operators are usually time-independent. Setting $\hat{A} = \hat{H}$, we see that $\mathrm{d}\left\langle\hat{H}\right\rangle/\mathrm{d}t = 0$, that is, the expectation value of the energy never changes with time, regardless of what state the system is (but provided $\langle\mathrm{d}\hat{H}/\mathrm{d}t\rangle = 0$). However, operators which do *not* commute with $\hat{H}$ have an expectation value which varies in time; if a system is in an eigenstate of $\hat{A}$, then at a later time a measurement of $\hat{A}$ will give a different result. Let $\hat{A} = \hat{x}$; we have:

$$\frac{\mathrm{d}\left\langle\hat{x}\right\rangle}{\mathrm{d}t} = \frac{i}{\hbar}\left\langle\left[\frac{\hat{p}_x^2}{2m} + \hat{V}(x), \hat{x}\right]\right\rangle = \frac{i}{\hbar}\left\langle\frac{-2i\hbar\hat{p}_x}{2m}\right\rangle = \frac{\left\langle\hat{p}_x\right\rangle}{m}$$

in an interesting analogy with Classical Mechanics. We also have:

$$\frac{\mathrm{d}\left\langle\hat{p}_x\right\rangle}{\mathrm{d}t} = \frac{i}{\hbar}\left\langle\left[\frac{\hat{p}_x^2}{2m} + \hat{V}(x), \hat{p}_x\right]\right\rangle = \frac{i}{\hbar}\left\langle i\hbar\frac{\mathrm{d}\hat{V}}{\mathrm{d}\hat{x}}\right\rangle = -\left\langle\frac{\mathrm{d}\hat{V}(\hat{x})}{\mathrm{d}\hat{x}}\right\rangle$$

which also looks familiar, however this is not quite the Classical analogy it might seem, as this would in fact be $-\mathrm{d}\hat{V}(\langle\hat{x}\rangle)/\mathrm{d}\hat{x}$.

It is also possible to derive an uncertainty relation involving time – though it must be interpreted correctly. We have:

$$\begin{aligned}\Delta E\Delta A &\geq \frac{1}{2}\left|\left\langle i\left[\hat{H},\hat{A}\right]\right\rangle\right| \\ &= \frac{\hbar}{2}\left|\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t}\right| \\ \Rightarrow \Delta E\Delta t &\geq \frac{\hbar}{2}, \text{ where} \\ \Delta t &\equiv \Delta A/\left|\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t}\right|\end{aligned}$$

that is, Δt should be interpreted as the likely time for $\langle A\rangle$ to change by ΔA. If ΔE is small, then the coefficients of most energy eigenstates are small, so it takes a long time to deviate significantly from the initial energy eigenstate. Indeed, when $\Delta E = 0$, the state *is* an energy eigenstate and $\Delta t \to \infty$.

2.4.2 Heisenberg Picture

It is possible to reassign the time dependence in QM from the wavefunctions (in the afore-used Schrödinger picture) to the operators; this requires a redefinition of the operators. We have:

$$\begin{aligned}\langle A(t)\rangle &= \langle\psi(t)|\hat{A}|\psi(t)\rangle \\ &= \langle\psi(0)|e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}|\psi(0)\rangle = \langle\psi(0)|\hat{U}^\dagger\hat{A}\hat{U}|\psi(0)\rangle \\ &= \langle\psi(0)|\hat{A}^H(t)|\psi(0)\rangle \text{ , where} \\ \hat{A}^H(t) &\equiv e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar} = \hat{U}^\dagger\hat{A}\hat{U}\end{aligned}$$

This new, time-dependent, operator is $\hat{A}$ in the Heisenberg picture. It is clear that $\hat{H}^H(t) = \hat{H}$, that is, the Hamiltonian is independent of time. Heisenberg picture operators might be thought of as "diagonalised" Schrödinger picture operators, and as such all operative properties such as commutation relations are identical in both pictures. The time derivative of $\hat{A}^H$ can be seen to be:

$$\begin{aligned}\frac{\mathrm{d}\hat{A}^H}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\hat{U}^\dagger\hat{A}\hat{U} \\ &= \frac{\mathrm{d}\hat{U}^\dagger}{\mathrm{d}t}\hat{A}\hat{U} + \hat{U}^\dagger\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}\hat{U} + \hat{U}^\dagger\hat{A}\frac{\mathrm{d}\hat{U}}{\mathrm{d}t} \\ &= \frac{i}{\hbar}\hat{U}^\dagger\hat{H}\hat{A}\hat{U} + 0 - \frac{i}{\hbar}\hat{U}^\dagger\hat{A}\hat{H}\hat{U} = \frac{i}{\hbar}\left(\hat{U}^\dagger\hat{H}\hat{U}\hat{U}^\dagger\hat{A}\hat{U} - \hat{U}^\dagger\hat{A}\hat{U}\hat{U}^\dagger\hat{H}\hat{U}\right)\end{aligned}$$

$$= \frac{i}{\hbar}\left[\hat{H}^H, \hat{A}^H\right]$$
$$\Rightarrow i\hbar\frac{\mathrm{d}\hat{A}^H}{\mathrm{d}t} = \left[\hat{A}^H, \hat{H}\right]$$

Heisenberg's Equation, equivalent to Schrödinger's.

3 Angular Momentum

This turns out to be a pretty big thing in QM. First, we consider point particles; then consider that the particles may be spinning on their axes.

3.1 Orbital Angular Momentum, $\hat{\mathbf{L}}$

The quantum operators for the angular momentum components are:

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$$

and cyclic permutations. There would have been potential difficulties with deciding which way round $\hat{y}$ and $\hat{p}_z$ should go, but they commute so it doesn't matter. Further, we see that $\hat{\mathbf{L}} = \hat{\mathbf{L}}^\dagger$. The operators of the angular momentum components have an interesting commutation relation:

$$\begin{aligned}\left[\hat{L}_x, \hat{L}_y\right] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\ &= \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x - \hat{p}_y[\hat{z}, \hat{z}]\hat{p}_x - \hat{y}[\hat{p}_z, \hat{p}_z]\hat{x} + \hat{p}_y[\hat{z}, \hat{p}_z]\hat{x} \\ &= i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) \\ &= i\hbar\hat{L}_z\end{aligned}$$

and cyclic permutations thereof. Therefore only one component of $\hat{\mathbf{L}}$ can be known at once, usually taken to be $\hat{L}_z$. A further interesting commutation relation is:

$$\begin{aligned}\left[\hat{L}_\alpha^2, \hat{L}_z\right] &= \hat{L}_\alpha\hat{L}_\alpha\hat{L}_z - \hat{L}_z\hat{L}_\alpha\hat{L}_\alpha + \hat{L}_\alpha\hat{L}_z\hat{L}_\alpha - \hat{L}_\alpha\hat{L}_z\hat{L}_\alpha \\ &= \hat{L}_\alpha\left[\hat{L}_\alpha, \hat{L}_z\right] + \left[\hat{L}_\alpha, \hat{L}_z\right]\hat{L}_\alpha = \left\{\hat{L}_\alpha, \left[\hat{L}_\alpha, \hat{L}_z\right]\right\}\end{aligned}$$

This is useful just because it enables one to calculate a more important one:

$$\begin{aligned}\left[\hat{L}^2, \hat{L}_z\right] &= \left[\hat{L}_x^2, \hat{L}_z\right] + \left[\hat{L}_y^2, \hat{L}_z\right] + \left[\hat{L}_z^2, \hat{L}_z\right] \\ &= \left\{\hat{L}_x, \left[\hat{L}_x, \hat{L}_z\right]\right\} + \left\{\hat{L}_y, \left[\hat{L}_y, \hat{L}_z\right]\right\} + 0\end{aligned}$$

$$= i\hbar\Big(-\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x + \hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y\Big) = 0$$

so it is possible to simultaneously know the *total* angular momentum and no more than one of the components.

We now derive the eigenstates of $\hat{L}^2$ and $\hat{L}_z$, using ladder operators. Consider:

$$\hat{L}_+ \equiv \hat{L}_x + i\hat{L}_y \qquad\qquad \hat{L}_- \equiv \hat{L}_x - i\hat{L}_y = \hat{L}_+^\dagger$$

these ladder operators are not observables, similar to $\hat{a}$ and $\hat{a}^\dagger$. We have:

$$\Big[\hat{L}_z, \hat{L}_+\Big] = \Big[\hat{L}_z, \hat{L}_x\Big] + i\Big[\hat{L}_z, \hat{L}_y\Big] = \hbar\Big(\hat{L}_x + i\hat{L}_y\Big) = \hbar\hat{L}_+$$
$$\Big[\hat{L}_z, \hat{L}_-\Big] = \Big[\hat{L}_z, \hat{L}_x\Big] - i\Big[\hat{L}_z, \hat{L}_y\Big] = -\hbar\Big(\hat{L}_x - i\hat{L}_y\Big) = -\hbar\hat{L}_-$$

So consider an eigenstate of $\hat{L}_z$, that is $\hat{L}_z\,|\phi_n\rangle = L_n\,|\phi_n\rangle$, and the related ket $\hat{L}_+\,|\phi_n\rangle$. The L_z of *this* state is found...

$$\hat{L}_z\hat{L}_+\,|\phi_n\rangle = \hat{L}_+\hat{L}_z\,|\phi_n\rangle + \hbar\hat{L}_+\,|\phi_n\rangle = (L_n + \hbar)\hat{L}_+\,|\phi_n\rangle$$

...to be $L_n + \hbar$. Similarly for $\hat{L}_-$:

$$\hat{L}_z\hat{L}_-\,|\phi_n\rangle = \hat{L}_-\hat{L}_z\,|\phi_n\rangle - \hbar\hat{L}_-\,|\phi_n\rangle = (L_n - \hbar)\hat{L}_-\,|\phi_n\rangle$$

So in the same way as $\hat{a}^\dagger$ and $\hat{a}$ generate new eigenstates of $\hat{H}$, $\hat{L}_+$ and $\hat{L}_-$ generate new eigenstates of $\hat{L}_z$.

Since $\hat{L}_z$ commutes with $\hat{L}^2$, these eigenstates must all be eigenstates of $\hat{L}^2$, too. And since $\hat{L}^2$ clearly commutes with $\hat{L}_x$ and $\hat{L}_y$ too, $\hat{L}^2$ must commute with $\hat{L}_+$ and $\hat{L}_-$. Say $\hat{L}^2\,|\phi_n\rangle = L^2\,|\phi_n\rangle$. Then:

$$\hat{L}^2\hat{L}_+\,|\phi_n\rangle = \hat{L}_+\hat{L}^2\,|\phi_n\rangle = L^2\hat{L}_+\,|\phi_n\rangle$$

so the new states generated by the ladder operators have the same L^2. However, the laddering cannot go on forever in either direction, because it must be that $L_z^2 \leq L^2$, so we require there to be some maximum value of L_z, denoted $\ell\hbar$, such that $\ell^2\hbar^2 \leq L^2$ The possible values of L_z are denoted $m_\ell\hbar$, and we see that m_ℓ can take the values: $\ell, \ell-1, \ldots -\ell+1, -\ell$, where the negative values are implied by symmetry. The states are then denoted $|\ell, m_\ell\rangle$.

The value of L^2 can be calculated in terms of ℓ. Consider:

$$\hat{L}_-\hat{L}_+ = \Big(\hat{L}_x - i\hat{L}_y\Big)\Big(\hat{L}_x + i\hat{L}_y\Big) = \hat{L}^2 - \hat{L}_z^2 + i\Big[\hat{L}_x, \hat{L}_y\Big] = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$$

Operating this on the highest state $|\ell, \ell\rangle$ gives $|0\rangle$, since $\hat{L}_+\,|\ell, \ell\rangle = |0\rangle$. Thus:

$$|0\rangle = \left(L^2 - \ell^2\hbar^2 - \ell\hbar^2\right)|\ell, \ell\rangle \Rightarrow L^2 = \ell(\ell+1)\hbar^2$$

So the magnitude of the orbital angular momentum vector $\hat{\mathbf{L}}$ is $\sqrt{\ell(\ell+1)}\hbar$, and the component in the z- (or indeed any) direction is quantised as $m_\ell\hbar$, where $m_\ell \in \{-\ell, -\ell+1, ..., \ell-1, \ell\}$. ℓ is known as the *orbital angular momentum* quantum number, and m_ℓ the *magnetic angular momentum* quantum number. Summarising, we then have:

$$\hat{L}^2 |\ell, m_\ell\rangle = \ell(\ell+1)\hbar^2 |\ell, m_\ell\rangle \qquad \hat{L}_z |\ell, m_\ell\rangle = m_\ell\hbar |\ell, m_\ell\rangle$$

Note that for the $\ell = 0$ state (there is only one, $|0, 0\rangle$), all of the components are simultaneously known to be 0. This does not conflict with the uncertainty principle, which says that, for example $\Delta L_x \Delta L_y \geq \frac{\hbar}{2}\left|\left\langle \hat{L}_z \right\rangle\right|$, which is still technically true if all the components are exactly 0.

All that remains is to normalise the ladder operators. First, note the sibling of the above identity:

$$\hat{L}_+\hat{L}_- = \left(\hat{L}_x + i\hat{L}_y\right)\left(\hat{L}_x - i\hat{L}_y\right) = \hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z$$

And the two possibilities, taking the coefficients to be real and positive:

$$\begin{aligned}
\hat{L}_+ |\ell, m_\ell\rangle &= C_{\ell,m_\ell} |\ell, m_\ell + 1\rangle & \hat{L}_- |\ell, m_\ell\rangle &= D_{\ell,m_\ell} |\ell, m_\ell - 1\rangle \\
C^2_{\ell,m_\ell} &= \langle \ell, m_\ell | \hat{L}_-\hat{L}_+ | \ell, m_\ell\rangle & D^2_{\ell,m_\ell} &= \langle \ell, m_\ell | \hat{L}_+\hat{L}_- | \ell, m_\ell\rangle \\
&= \hbar^2\left[\ell(\ell+1) - m_\ell^2 - m_\ell\right] & &= \hbar^2\left[\ell(\ell+1) - m_\ell^2 + m_\ell\right] \\
\Rightarrow C_{\ell,m_\ell} &= \hbar\sqrt{\ell(\ell+1) - m_\ell(m_\ell+1)} & \Rightarrow D_{\ell,m_\ell} &= \hbar\sqrt{\ell(\ell+1) - m_\ell(m_\ell-1)}
\end{aligned}$$

These also have the required property that, for instance $\hat{L}_+ |\ell, \ell\rangle = |0\rangle$. So to sum up the ladder operators we have:

$$\hat{L}_\pm |\ell, m_\ell\rangle = \hbar\sqrt{\ell(\ell+1) - m_\ell(m_\ell \pm 1)} \, |\ell, m_\ell \pm 1\rangle$$

3.1.1 Spherical Harmonics

By converting the ladder operators to spherical polar coordinates, it is possible to obtain expressions for the wavefunctions corresponding to the $|\ell, m_\ell\rangle$. Firstly, it can be derived that:

$$\begin{aligned}
\hat{L}_x &\equiv i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\
\hat{L}_y &\equiv i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\
\hat{L}_z &\equiv -i\hbar\frac{\partial}{\partial\phi}
\end{aligned}$$

$$\Rightarrow \hat{L}_{\pm} \equiv \hbar e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$$

Note that all of these operators depend only on θ and ϕ, so their eigenfunctions of (denoted $Y_{\ell,m_\ell}(\theta,\phi)$ for $|\ell, m_\ell\rangle$) only depend on these two. Consider the eigenvalue equation for $\hat{L}_z$:

$$-i\hbar\frac{\partial Y_{\ell,m_\ell}}{\partial\phi} = m_\ell\hbar Y_{\ell,m_\ell} \Rightarrow Y_{\ell,m_\ell}(\theta,\phi) = F_{\ell,m_\ell}(\theta)e^{im_\ell\phi}$$

At this point, we see that not only does m_ℓ take values from $-\ell$ to ℓ in integer steps, but also that m_ℓ itself must be an integer (and thus so must ℓ), to ensure that the wavefunction is single-valued. This was not known before – there was the possibility that ℓ (and thus m_ℓ) was half-integer, and the scheme would still work – but it is now known that in fact $m_\ell \in \{-\ell, -\ell+1, ...-1, 0, 1, ..., \ell-1, \ell\}$; there are an odd number $(2\ell+1)$ different values of m_ℓ.

Next, we derive the wavefunction $|\ell, \ell\rangle$. We know that $\hat{L}_+ |\ell, \ell\rangle = |0\rangle$, so

$$\frac{\partial F_{\ell,\ell}}{\partial\theta}e^{i\ell\phi} - \ell\cot\theta F_{\ell,\ell}e^{i\ell\phi} = 0 \Rightarrow F_{\ell,\ell}(\theta) = \sin^\ell\theta$$

as can be seen by inspection. Therefore, the wavefunctions for the states $|\ell, \ell\rangle$ are:

$$Y_{\ell,\ell}(\theta,\phi) \equiv N\sin^\ell\theta e^{i\ell\phi}$$

where N should be found by normalising the wavefunction according to:

$$\int |Y_{\ell,\ell}|^2 d\Omega = \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta\, |Y_{\ell,\ell}|^2 \sin\theta = 1$$

The rest of the wavefunctions may be found according to $\hat{L}_- Y_{\ell,m_\ell} \propto Y_{\ell,m_\ell-1}$, using the spherical polar form for $\hat{L}_-$. These wavefunctions are known as *spherical harmonics*.

For a rigid diatomic molecule, the energy of rotation can be written as:

$$E_{\mathrm{rot}} = \frac{\hat{\mathbf{L}}^2}{2I} = \frac{\ell(\ell+1)\hbar^2}{2I}$$

We see that E_{rot} depends only on ℓ, not on m_ℓ. As such, there is some degeneracy: for each value of E_{rot}, there is a single value of ℓ and hence $2\ell + 1$ possible values of m_ℓ, that is a degeneracy of $2\ell + 1$. This enables an analysis of the thermodynamics of rotational heat capacities, though the degeneracy makes it rather more complicated than that of the vibrational heat capacities mentioned earlier.

3.1.2 Central potentials

Particles experiencing central forces have the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r)$$

It turns out that this can also be written:

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2} + V(r)$$

Now consider a separable solution into radial and angular parts $\psi(r,\theta,\phi) = R(r)Y_{\ell,m_\ell}$. The TISE becomes, on division by Y:

$$-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}R + V(r)R = ER$$

— a second order ODE, whose difficulty depends on V. First, however, it is convenient to define $U(r) = rR(r)$, giving:

$$-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{U'}{r} - U\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^3}U + V(r)\frac{U}{r} = E\frac{U}{r}$$

$$-\frac{\hbar^2}{2m}U'' + \frac{\ell(\ell+1)\hbar^2}{2mr^2}U + V(r)U = EU$$

which is just the TISE but with an extra "centrifugal term". The most immediate use of this is to evaluate the hydrogen-like atom, with $V(r) = -Ze^2/4\pi\epsilon_0 r$, giving:

$$-\frac{\hbar^2}{2m}U'' + \frac{\ell(\ell+1)\hbar^2}{2mr^2}U - \frac{Ze^2}{4\pi\epsilon_0 r}U = EU$$

We then make the following substitutions:

$$A = \frac{2m}{\hbar^2}\frac{Ze^2}{4\pi\epsilon_0} \qquad\qquad \kappa^2 = -\frac{2mE}{\hbar^2}$$

which convert the above equation into:

$$U'' + \left[\frac{A}{r} + \kappa^2 - \frac{\ell(\ell+1)}{r^2}\right]U = 0$$

For large r, we have $U'' + \kappa^2 U = 0$, suggesting an asymptotic form of $U \propto e^{-\kappa r}$. By contrast, for *small* r, we have $U'' = \ell(\ell+1)U/r^2$, suggesting another

asymptotic form of $U \propto r^{\ell+1}$. We then posit the solution $U = G(r)r^{\ell+1}e^{-\kappa r}$, which on substitution gives:

$$G''r^{\ell+1}e^{-\kappa r} + 2(\ell+1)G'r^{\ell}e^{-\kappa r} - 2\kappa G'r^{\ell+1}e^{-\kappa r} - 2\kappa(\ell+1)Gr^{\ell}e^{-\kappa r} + AGr^{\ell}e^{-\kappa r} = 0$$
$$\Rightarrow rG'' + 2(\ell+1-\kappa r)G' + [A - 2\kappa(\ell+1)]G = 0$$

This is the associated Laguerre equation; its solutions are the associated Laguerre polynomials. Positing a series solution for G, we obtain the recurrence relation:

$$a_{q+1} = a_q \frac{2\kappa(q+\ell+1-A/2\kappa)}{(q+1)[q+2(l+1)]}$$

Apparently we require the series to converge, so there must be some value of $q \geq 0$ such that $q + \ell + 1 - A/2\kappa = 0$; we see immediately that $A/2\kappa$ must be an integer, $n \geq \ell + 1$, known as the *principal quantum number*. We then have:

$$\begin{aligned} n &= \frac{2m}{\hbar^2}\frac{Ze^2}{8\pi\epsilon_0}\sqrt{-\frac{\hbar^2}{2mE_n}} \\ \Rightarrow E_n &= -\frac{Z^2me^4}{32\pi^2\epsilon_0^2\hbar^2n^2} \\ &= -\frac{\hbar^2}{2m}\frac{Z^2}{a_0^2}\frac{1}{n^2}, \text{ where} \\ a_0 &= \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 53\text{pm} \end{aligned}$$

and furthermore, since $\ell \geq 0$, we have $n \geq 1$. So the $n = 1$ state has the possibility of $\ell = 0$; the $n = 2$ state has the possibilities of $\ell = 0, 1$ (which means that there can be states with $m_\ell \neq 0$); etc. The full solution is then:

$$\psi(r, \theta, \phi) = R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta, \phi)$$

with $R_{n,\ell}(r) = \sum_{q=0}^{n-\ell-1} a_q r^{\ell+q}e^{-\kappa r}$, and $Y_{\ell,m_\ell}(\theta, \phi)$ being spherical harmonics.

All that remains is the normalisation. This should be done according to $\int_0^\infty |R|^2r^2\,\mathrm{d}r = 1$, since the spherical harmonics have already been normalised in their solid angle.

3.2 Spin Angular Momentum, $\hat{\mathbf{S}}$

Classically, an electron moving around in a circle creates a loop current, which corresponds to a magnetic moment, given by:

$$\mu_z = \pi r^2 I = -\pi r^2 \frac{ev}{2\pi r} = -\frac{e}{2m_e}L_z = -\frac{e\hbar}{2m_e}m_\ell \equiv -\mu_B m_\ell$$

where we define the *Bohr Magneton* $\mu_B = e\hbar/2m_e$. The magnetic moment μ_z is therefore quantised in units of Bohr Magnetons. The potential energy of (and force on) a magnetic dipole in a magnetic field $\mathbf{B}$ is:

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} \Rightarrow F = \mu_z \frac{\partial B_z}{\partial z}$$

It was mentioned in the previous section that there are an odd number of possible values for m_ℓ, and hence μ_z, so when a beam of neutral atoms is passed through an inhomogeneous magnetic field, one would expect it to split into an odd number of beams – one for each value of m_ℓ. However, in the Stern-Gerlach experiment, where neutral Ag atoms (with $\sum m_\ell = 0$) were shot through such a field, the beam was split into *two*, where only one was expected. The conclusion is that there is some component of the angular momentum which does not arise from the motion of the electrons around the nucleus, as we imagine $\hat{L}$ represents. This extra angular momentum is known as *spin*, its operator is denoted $\hat{\mathbf{S}}$, and it is reluctantly attributed to the rotation of the electron about its axis.

Being a vector operator, we can write $\hat{\mathbf{S}} \equiv \hat{S}_x\hat{\mathbf{i}} + \hat{S}_y\hat{\mathbf{j}} + \hat{S}_z\hat{\mathbf{k}}$, and we further *assume* that the components of $\hat{\mathbf{S}}$ obey the same commutation relations as the components of $\hat{\mathbf{L}}$, that is, $\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z$, and cyclic permutations thereof. This is in fact all that was needed to describe all of the properties of $\hat{\mathbf{L}}$ above, so we can say that for $\hat{\mathbf{S}}$, assuming the components have the same commutation relations:

- $\left[\hat{S}^2, \hat{S}_z\right] = 0$
- The eigenvalues of $\hat{S}^2$ are $s(s+1)\hbar^2$ and those of $\hat{S}_z$ are $m_s\hbar$
- m_s, the *spin magnetic quantum number*, $\in \{-s, -s+1, ..., s-1, s\}$
- $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$ and $\hat{S}_\pm |s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}\,|s, m_s \pm 1\rangle$

However, it has not been specified what variables $\hat{\mathbf{S}}$ operates on, and in fact it operates on degrees of freedom other than 3D space. It turns out that there is no restriction that m_s must be an integer, and it may be half-integer. Indeed, for an electron, $s = 1/2$, so the magnitude of an electron's spin vector is $\hbar\sqrt{3}/2$, and m_s can be either $\pm 1/2$ (or "spin-up or spin-down"); these states are denoted $|\uparrow\rangle$ and $|\downarrow\rangle$ and have $S_z = \pm\hbar/2$. The total angular wavefunction might be written $|\psi\rangle = |\ell, m_\ell\rangle\,|\updownarrow\rangle = Y_{\ell,m_\ell}\,|\updownarrow\rangle$ as the direct product of the space/time dependent state and the spin dependent state; $\hat{\mathbf{L}}$ will only act on the former; $\hat{\mathbf{S}}$ only on the latter.

For an electron we have:

$$\hat{S}_+ |\uparrow\rangle = |0\rangle \qquad \hat{S}_+ |\downarrow\rangle = \hbar |\uparrow\rangle \qquad \hat{S}_- |\uparrow\rangle = \hbar |\downarrow\rangle \qquad \hat{S}_- |\downarrow\rangle = |0\rangle$$

From the definitions of $\hat{S}_\pm$, we also have:

$$\hat{S}_x = \frac{\hat{S}_+ + \hat{S}_-}{2} \qquad \hat{S}_y = \frac{\hat{S}_+ - \hat{S}_-}{2i}$$

Their effect on the spin eigenstates is therefore:

$$\hat{S}_x |\downarrow\rangle = \frac{\hbar}{2} |\uparrow\rangle \qquad \hat{S}_x |\uparrow\rangle = \frac{\hbar}{2} |\downarrow\rangle \qquad \hat{S}_y |\downarrow\rangle = \frac{\hbar}{2i} |\uparrow\rangle \qquad \hat{S}_y |\uparrow\rangle = -\frac{\hbar}{2i} |\downarrow\rangle$$

And the eigenstates of $\hat{S}_x$ and $\hat{S}_y$ are therefore seen to be:

$$\hat{S}_x : \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle) \qquad \hat{S}_y : \frac{1}{\sqrt{2}}(|\uparrow\rangle + i|\downarrow\rangle)$$
$$\frac{1}{\sqrt{2}}(|\uparrow\rangle - |\downarrow\rangle) \qquad \frac{1}{\sqrt{2}}(|\uparrow\rangle - i|\downarrow\rangle)$$

with eigenvalues $\pm\hbar/2$ as with $\hat{S}_z$.

In the $|\uparrow\rangle$ eigenstate, $\Delta S_z = 0$, almost by definition of eigenstate, but one can also verify that $\langle S_z \rangle = \hbar/2$ and $\langle S_z^2 \rangle = \hbar^2/4$. However, $\Delta S_x \neq 0$. We have:

$$\hat{S}_x |\uparrow\rangle = \frac{\hbar}{2} |\downarrow\rangle \Rightarrow \langle S_x \rangle = \frac{\hbar}{2} \langle\uparrow|\downarrow\rangle = 0 \qquad \hat{S}_x^2 |\uparrow\rangle = \frac{\hbar^2}{4} |\uparrow\rangle \Rightarrow \langle S_x^2 \rangle = \frac{\hbar^2}{4}$$

giving ΔS_x (and by symmetry ΔS_y, which can be evaluated directly) $= \hbar/2$.

3.3 Total Angular Momentum, $\hat{\mathbf{J}}$

We can combine these two contributions to the total angular momentum of a system to give a *total angular momentum* operator $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. Remembering that $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ act on different variables, the commutation relations between the components of $\hat{\mathbf{J}}$ are:

$$\left[\hat{J}_x, \hat{J}_y\right] = \left[\hat{L}_x, \hat{L}_y\right] + \left[\hat{S}_x, \hat{S}_y\right] = i\hbar\left(\hat{L}_z + \hat{S}_z\right) = i\hbar\hat{J}_z$$

... the same as for $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$. As such, we have again that:

- $\left[\hat{J}^2, \hat{J}_z\right] = 0$

- The eigenvalues of $\hat{J}^2$ are $j(j+1)\hbar^2$ and those of $\hat{J}_z$ are $m_j\hbar$
- m_j, the *total angular momentum projection quantum number*, runs between $-j, -j+1, ..., j-1, j$
- $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$ and $\hat{J}_\pm |j, m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j \pm 1)}\, |j, m_j \pm 1\rangle$

The quantum number m_j is given by $m_j = m_\ell + m_s$, which seems reasonable as $\hat{J}_z = \hat{L}_z + \hat{S}_z$. j is related to the magnitude of the vector $\mathbf{J} = \mathbf{L} + \mathbf{S}$, which will depend not only on the magnitudes of $\mathbf{L}$ and $\mathbf{S}$, but also on their relative orientation. Clearly the maximum magnitude of $\mathbf{J}$ is achieved when the other two vectors are as parallel as possible, in a direction which we might as well take as the z-direction. Thus the maximum value of j is $\ell + s$. Conversely, the *minimum* magnitude of $\mathbf{J}$ is achieved when the $\mathbf{L}$ and $\mathbf{S}$ are as *antiparallel* as possible, meaning that the minimum value of j is $|\ell - s|$ (in general either can be the larger of the two, hence the absolute sign). Intermediate values of j are separated by an integer; the possible values of m_j can be found using a simple grid.

3.3.1 Clebsch-Gordon Coefficients

The total state describing the angular momentum is of the form $|j, m_j\rangle = \sum C_{\ell,m_\ell,s,m_s} |\ell, m_\ell\rangle |s, m_s\rangle$. The $|\ell, m_\ell\rangle$ can be replaced by Y_{ℓ,m_ℓ} if desired, but the others have no ordinary functional form so are stuck as kets. The coefficients C_{ℓ,m_ℓ,s,m_s} are known as the *Clebsch-Gordon coefficients* of $|j, m_j\rangle$. For a given system, with set values of ℓ and s (such as an electron with $\ell = 1$), we begin with the state which has the highest j and m_j, which can only be $|\ell + s, \ell + s\rangle = Y_{\ell,\ell} |s, s\rangle$; the rest of the states are found by considering ladder operators and orthogonality. For definiteness consider a system with $\ell = 1, s = 1/2$; the highest state is then $|3/2, 3/2\rangle = Y_{1,1} |\uparrow\rangle$ and so $C_{1,1,\frac{1}{2},\frac{1}{2}} = 1$ and all other Cs are 0.

To find $|3/2, 1/2\rangle$, we simply operate on $|3/2, 3/2\rangle$ with $\hat{J}_-$:

$$\begin{aligned}
\hat{J}_- \left|\frac{3}{2}, \frac{3}{2}\right\rangle &= \hat{L}_- Y_{1,1} |\uparrow\rangle + \hat{S}_- Y_{1,1} |\uparrow\rangle \\
\hbar\sqrt{\frac{3}{2}\frac{5}{2} - \frac{3}{2}\frac{1}{2}} \left|\frac{3}{2}, \frac{1}{2}\right\rangle &= \hbar\sqrt{1(2) - (1)(0)} Y_{1,0} |\uparrow\rangle + \hbar\sqrt{\frac{1}{2}\frac{3}{2} - \frac{1}{2}\frac{-1}{2}} Y_{1,1} |\downarrow\rangle \\
\left|\frac{3}{2}, \frac{1}{2}\right\rangle &= \sqrt{\frac{2}{3}} Y_{1,0} |\uparrow\rangle + \sqrt{\frac{1}{3}} Y_{1,1} |\downarrow\rangle
\end{aligned}$$

The states $|3/2, -1/2\rangle$ and $|3/2, -3/2\rangle$ can be similarly derived in this way. To find, say, $|1/2, 1/2\rangle$, it is known that the state must have $m_j = 1/2$, like

$|3/2, 1/2\rangle$, but as they are both eigenfunctions of $\hat{J}^2$ with different eigenvalues (owing to their different values of j), $|1/2, 1/2\rangle$ must be orthogonal to $|3/2, 1/2\rangle$. The only possible orthogonal state with $m_j = 1/2$ is:

$$\left|\frac{1}{2}, \frac{1}{2}\right\rangle = \sqrt{\frac{1}{3}} Y_{1,0} \left|\uparrow\right\rangle - \sqrt{\frac{2}{3}} Y_{1,1} \left|\downarrow\right\rangle$$

Then the only remaining state in this system, $|1/2, -1/2\rangle$ can also be derived by applying $\hat{J}_-$ as above.

3.3.2 Multiple Spins

When two particles are present, the analysis of the spins becomes slightly more complicated, but it turns out it can be analysed in a similar way to the $|j, m_j\rangle$ states above. If there are two particles with spins s_1, s_2, we can define *two* spin operators $\hat{\mathbf{S}}_1, \hat{\mathbf{S}}_2$, and a *total spin operator* $\hat{\mathbf{S}} \equiv \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$. For definiteness, consider two particles both with $s = 1/2$, each of which can have $m_s = \pm 1/2$. There are therefore 4 combined spin states denoted $|X_{s,m_s}\rangle$ where s is related to the magnitude of the total spin vector $\mathbf{S} = \mathbf{S_1} + \mathbf{S_2}$, and $m_s = m_{s1} + m_{s2}$.

As above, we realise that the largest possible magnitude of $\mathbf{S}$ is when the two spins are aligned and $s = s_1 + s_2$, and the largest possible m_s is $s_1 + s_2$. For the two-spin-1/2 system, we have the highest state as $|X_{1,1}\rangle = |\uparrow\rangle_1 |\uparrow\rangle_2$. We then use operators like $\hat{S}_- = \hat{S}_{1-} + \hat{S}_{2-}$, and recognise that, for, instance $\hat{S}_{1-}$ operates on the variables of particle 2, and so does not affect it:

$$\begin{aligned}
\hat{S}_- |X_{1,1}\rangle &= \hat{S}_{1-} |\uparrow\rangle_1 |\uparrow\rangle_2 + \hat{S}_{2-} |\uparrow\rangle_1 |\uparrow\rangle_2 \\
\hbar\sqrt{2} |X_{1,0}\rangle &= \hbar\sqrt{\frac{1}{2}\frac{3}{2} - \frac{1}{2}\frac{-1}{2}} |\downarrow\rangle_1 |\uparrow\rangle_2 + \hbar\sqrt{\frac{1}{2}\frac{3}{2} - \frac{1}{2}\frac{-1}{2}} |\uparrow\rangle_1 |\downarrow\rangle_2 \\
\Rightarrow |X_{1,0}\rangle &= \sqrt{\frac{1}{2}} |\downarrow\rangle_1 |\uparrow\rangle_2 + \sqrt{\frac{1}{2}} |\uparrow\rangle_1 |\downarrow\rangle_2 \\
\Rightarrow |X_{1,-1}\rangle &= |\downarrow\rangle_1 |\downarrow\rangle_2 \\
\Rightarrow |X_{0,0}\rangle &= \sqrt{\frac{1}{2}} |\downarrow\rangle_1 |\uparrow\rangle_2 - \sqrt{\frac{1}{2}} |\uparrow\rangle_1 |\downarrow\rangle_2
\end{aligned}$$

to be orthogonal to $|X_{1,0}\rangle$. The set of states with $s = 1$ is described as a *triplet state*; that with $s = 0$ a *singlet state*. Note that the triplet states are symmetric under particle exchange; the singlet state is antisymmetric.

3.4 Distinguishability

When there are multiple identical particles described by a wavefunction, exchanging the two particles would not change the state of the system in any way. In other words, we must have:

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1, t)|^2 \qquad \Rightarrow \Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \pm\Psi(\mathbf{r}_2, \mathbf{r}_1, t)$$

Ok that was a little shaky, as there could be any phase factor at the front rather than just $\pm$, but in fact these are the two exchange symmetries possible according to the *symmetrisation postulate*, which is not proven here. The *spin statistics theorem* states that the wavefunction of a set of particles with *half-integer* spin (known as *fermions*) is exchange antisymmetric, and that that of a set of *integer* spin particles (*bosons*) is exchange symmetric; there are no alternatives. Consider the case where there are two possible particles, each with the two possible energy states $|\alpha\rangle$ and $|\beta\rangle$. The possible two-particle states are therefore:

$$|\alpha\rangle\,|\alpha\rangle \qquad |\alpha\rangle\,|\beta\rangle \qquad |\beta\rangle\,|\alpha\rangle \qquad |\beta\rangle\,|\beta\rangle$$

However, because the two particles are identical, $|\alpha\rangle\,|\beta\rangle$ and $|\beta\rangle\,|\alpha\rangle$ are *the same thing!* As such, it would the above basis would not be a very good one to use. A better one would be:

$$|\alpha\rangle\,|\alpha\rangle \qquad \frac{1}{\sqrt{2}}(|\alpha\rangle\,|\beta\rangle + |\beta\rangle\,|\alpha\rangle) \qquad \frac{1}{\sqrt{2}}(|\alpha\rangle\,|\beta\rangle - |\beta\rangle\,|\alpha\rangle) \qquad |\beta\rangle\,|\beta\rangle$$

Here, the 2nd state (also written $|s\rangle$) is exchange-symmetric, and the 3rd state ($|a\rangle$) is exchange-antisymmetric. As such, these 4 states represent 3 bosonic states and 1 fermionic state.

There can be no fermionic states with two particles in the same state, according to the *Pauli exclusion principle*. If we suppose that the state $|\gamma\rangle\,|\gamma\rangle$ state is such a state and is non-zero, then by exchanging the two, we must gain the negative of the state, so we have $|\gamma\rangle\,|\gamma\rangle = -\,|\gamma\rangle\,|\gamma\rangle \Rightarrow |\gamma\rangle\,|\gamma\rangle = \mathbf{0}$. We thus arrive at a contradiction and such states cannot exist. Indeed, the average number of fermions in a quantum state j is given by $\left\langle n_j^{fd} \right\rangle = [\exp((E_j - \mu)/kT) + 1]^{-1}$, which is always ≤ 1. The PEP underlies the shape of the periodic table, the properties of a wide range of materials, and prevents white dwarfs from collapsing.

For larger numbers of particles, the analysis becomes progressively more complex; we now look at 3 particles. The lowest order state is denoted $|1, 1, 1\rangle$, and is clearly exchange symmetric, corresponding to three bosons all in the lowest state. By contrast, the state $|1, 1, 2\rangle$ has no exchange symmetry (it

is by no means equal to $|1,2,1\rangle$ for instance). Instead, we should use the symmetric state:

$$|1,1,2\rangle^s = \frac{1}{\sqrt{3}}(|1,1,2\rangle + |1,2,1\rangle + |2,1,1\rangle)$$

We see that each possible arrangement is equally likely (1/3), and that $|1,2,1\rangle^s = |1,1,2\rangle$; the same thing happens with $|1,2,2\rangle^s$.

Fermionic states must have all the particles in different states, and must be antisymmetric under exchange. These properties are all satisfied by the *Slater determinant*:

$$|N\rangle^a = \frac{1}{\sqrt{N!}} \begin{vmatrix} |1\rangle & |1\rangle & \cdots & |1\rangle \\ |2\rangle & |2\rangle & \cdots & |2\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |N\rangle & |N\rangle & \cdots & |N\rangle \end{vmatrix}$$

4 Extra Topics

4.1 Matrix Mechanics

If a system has a finite number of discrete states, there is an equivalent representation of these states as vectors, and of operators as matrices that change one state into another. The matrix formulation of QM can also be used to approximate an infinite number of states by truncation, but is generally only useful in the case of a few states.

Consider two potential wells V_1 and V_2. In isolation, they are associated with Hamiltonians $\hat{H}_i = \hat{T} + \hat{V}_i$, which are associated with eigenstates $\left\{\left|\phi_i^j\right\rangle\right\}$ with (negative) eigenvalues $\left\{E_i^j\right\}$. When the two wells weakly interact, we might use as a basis to describe the resulting states the two ground states $\{|\phi_1\rangle, |\phi_2\rangle\} \equiv \{|\phi_1^0\rangle, |\phi_2^0\rangle\}$; this process is known as hybridisation. We know that:

$$\hat{H}_1 |\phi_1\rangle = E_1 |\phi_1\rangle \qquad\qquad \hat{H}_2 |\phi_2\rangle = E_2 |\phi_2\rangle$$

but for this new combined Hamiltonian $\hat{H} = \hat{T} + \hat{V}_1 + \hat{V}_2 = \hat{H}_1 + \hat{V}_2 = \hat{H}_2 + \hat{V}_1$, all we know is that the solution to $\hat{H} |\psi\rangle = E |\psi\rangle$ is that $|\psi\rangle$ is a linear combination $c_1 |\phi_1\rangle + c_2 |\phi_2\rangle$ of the basis states. We therefore write:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

where the matrix elements $H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle$; we now evaluate these elements. We see that

$$H_{11} = \langle\phi_1|\hat{H}|\phi_1\rangle = \langle\phi_1|\hat{H}_1 + \hat{V}_2|\phi_1\rangle = E_1 + \langle\phi_1|\hat{V}_2|\phi_1\rangle \approx E_1$$

where we justify the approximation with the fact that the approximation is only weak, and so there is very little overlap between V_2 and $|\phi_1\rangle$ – or at least this second term would be very small compared to E_1. We can then see that $H_{22} \approx E_2$. Also, we set the off-diagonal term $H_{12} = \langle\phi_1|\hat{H}|\phi_2\rangle \equiv t \Rightarrow H_{21} = t^*$; these are known as "overlap integrals", and will probably be negative along with E_i. We then have the full matrix and can find the eigenvalues and eigenvectors:

$$\begin{vmatrix} E_1 - E & t \\ t^* & E_2 - E \end{vmatrix} = 0$$

$$\Rightarrow E^2 - (E_1 + E_2)E + E_1E_2 - |t|^2 = 0$$

$$\Rightarrow E = \frac{1}{2}\left(E_1 + E_2 \pm \sqrt{(E_2 - E_1)^2 + 4|t|^2}\right)$$

at which point we reassuringly see that in the limit $t \to 0$, $E = E_1, E_2$.

In the case where the two potential wells are identical, we have $E_1 = E_2 \equiv E_0$, which then gives $E = E_0 \pm |t|$. As for the coefficients, this gives (assuming t is negative and real):

$$\begin{pmatrix} \mp|t| & -|t| \\ -|t| & \mp|t| \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \mathbf{0} \Rightarrow c_2 = \pm c_1 = \frac{1}{\sqrt{2}}$$

So we have:

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle + |\phi_2\rangle) \qquad E_1 = E_0 - |t|$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}(|\phi_2\rangle - |\phi_2\rangle) \qquad E_2 = E_0 + |t|$$

The $|\psi_1\rangle$, with a lower energy, is referred to as the "bonding orbital"; $|\psi_2\rangle$ as the "antibonding orbital". If each original $|\phi_i\rangle$ was occupied by one electron, they can both go into the bonding orbital and thus lower the energy of the arrangement by $2|t|$.

If the two potential wells are different, then wlog we have $E_1 < E_2$. We also posit that $|t|/(E_2 - E_1) = \delta$ and assume that $\delta \ll 1$ for a considerable energy gap. We then have:

$$E = \frac{1}{2}\Big(E_1 + E_2 \pm (E_2 - E_1)\sqrt{1 + 4\delta^2}\Big) \approx \frac{1}{2}\big(E_1 + E_2 \pm (E_2 - E_1)(1 + 2\delta^2)\big)$$

which gives the two possibilities:

$$\begin{aligned} E_- &= E_1 - (E_2 - E_1)\delta^2 \\ &\equiv E_1 - \delta|t| \end{aligned} \qquad \begin{aligned} E_+ &= E_2 + (E_2 - E_1)\delta^2 \\ &\equiv E_2 + \delta|t| \end{aligned}$$

We see that the higher energy state is increased by roughly the same amount as the lower energy state is decreased. Calculating the coefficients gives:

$$\begin{pmatrix} \delta|t| & -|t| \\ -|t| & |t|/\delta + \delta|t| \end{pmatrix}\begin{pmatrix} c_1^1 \\ c_2^1 \end{pmatrix} \approx \begin{pmatrix} \delta|t| & -|t| \\ -|t| & |t|/\delta \end{pmatrix}\begin{pmatrix} c_1^1 \\ c_2^1 \end{pmatrix} = \mathbf{0} \qquad \Rightarrow c_2^1 = \delta c_1^1$$

$$\begin{pmatrix} -|t|/\delta - \delta|t| & -|t| \\ -|t| & -\delta|t| \end{pmatrix}\begin{pmatrix} c_1^2 \\ c_2^2 \end{pmatrix} \approx \begin{pmatrix} -|t|/\delta & -|t| \\ -|t| & -\delta|t| \end{pmatrix}\begin{pmatrix} c_1^2 \\ c_2^2 \end{pmatrix} = \mathbf{0} \quad \Rightarrow c_1^2 = -\delta c_2^2$$

So we have the wavefunctions:

$$|\psi_-\rangle = \frac{1}{\sqrt{1+\delta^2}}(|\phi_1\rangle + \delta\,|\phi_1\rangle) \qquad E_- = E_1 - \delta|t|$$

$$|\psi_-\rangle = \frac{1}{\sqrt{1+\delta^2}}(|\phi_2\rangle - \delta\,|\phi_1\rangle) \qquad E_+ = E_2 + \delta|t|$$

We see that, as with the equal potential case, the lower energy case has constructive interference; the higher, destructive. This is the sort of thing that is seen with ionic bonding, and the lowest energy wavefunction has a higher coefficient from the lower-energy basis function — hence the more electronegative atom has more of the charge density.

4.2 Density Operators

Density operators describe the state of a system of *individually* quantum parts, but which are combined *classically*. An example is a large number of diatomic molecules with exponentially decaying probabilities of being in a certain vibrational state. Suppose a system can be in a number of different states $|\psi_i\rangle$, and the probability of the system being in each state is P_i, and consider an ensemble of such systems. Then it is a simple probabilistic law that:

$$\langle A\rangle = \sum_i P_i \langle\psi_i|\hat{A}|\psi_i\rangle$$

Now we can in fact write this as:

$$\langle A\rangle = \mathrm{Tr}\left[\sum_i P_i\,|\psi_i\rangle\langle\psi_i|\,\hat{A}\right]$$

as can be appreciated by noting that, as with a matrix, the trace of a linear operator is equal to the sum of its eigenvalues. Then, defining the *density operator* for the overall system $\hat{O}$ as:

$$\hat{O} \equiv \sum_i P_i \left|\psi_i\right\rangle\!\left\langle\psi_i\right| \Rightarrow \langle A \rangle = \mathrm{Tr}\left[\hat{O}\hat{A}\right]$$

It is easily seen that $\mathrm{Tr}\,\hat{O} = 1$ (equivalent to all probabilities summing to 1) and that $\hat{O}^\dagger = \hat{O}$. We may also distinguish between *pure* and *mixed* states. Pure states have only one term in their density operator: $\hat{O} = \left|\psi_k\right\rangle\!\left\langle\psi_k\right|$; mixed states have at least two.

Finally, we can deduce the time dependence of the density operator as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{O}(t) = \frac{\mathrm{d}}{\mathrm{d}t}\sum_i P_i \left|\psi_i(t)\right\rangle\!\left\langle\psi_i(t)\right| = \frac{\mathrm{d}}{\mathrm{d}t}\left[\sum_i P_i \hat{U}\left|\psi_i(0)\right\rangle\!\left\langle\psi_i(0)\right|\hat{U}^\dagger\right] = \frac{\mathrm{d}}{\mathrm{d}t}\left[\hat{U}\hat{O}(0)\hat{U}^\dagger\right]$$

Then, using $\frac{\mathrm{d}}{\mathrm{d}t}\hat{U} = -\frac{i}{\hbar}\hat{H}\hat{U}$,

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\hat{O}(t) &= -\frac{i}{\hbar}\left[\hat{H}\hat{U}\hat{O}(0)\hat{U}^\dagger - \hat{U}\hat{O}(0)\hat{U}^\dagger\hat{H}^\dagger\right] \\
&= -\frac{i}{\hbar}\left[\hat{H}\hat{O}(t) - \hat{O}(t)\hat{H}\right] \\
\Rightarrow i\hbar\frac{\mathrm{d}\hat{O}}{\mathrm{d}t} &= \left[\hat{H}, \hat{O}\right]
\end{aligned}$$

This is *von Neumann's Equation*, a differential equation for a density operator. Compare:

$$\begin{aligned}
\Delta A \Delta B &\geq \frac{1}{2}\left|\left\langle\left[\hat{A}, \hat{B}\right]\right\rangle\right| \\
i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle &= \hat{H}\left|\psi(t)\right\rangle \\
i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{A}^H &= \left[\hat{A}^H, \hat{H}\right] \\
i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle &= \left\langle\left[\hat{A}, \hat{H}\right]\right\rangle
\end{aligned}$$