Principles of Quantum Mechanics

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Weirdly there are no equations in the Formula Book for this course.

1 Harmonic Oscillator

Because I always forget the basics.

1.1 $D = 1$

The Hamiltonian is

$$\hat{H} = \frac{1}{2M}\hat{P}^2 + \frac{1}{2}M\omega^2\hat{X}^2$$

Consider the operators

$$\hat{A} \equiv \frac{1}{\sqrt{2M\hbar\omega}}\left(M\omega\hat{X} + i\hat{P}\right) \qquad \hat{A}^\dagger = \frac{1}{\sqrt{2M\hbar\omega}}\left(M\omega\hat{X} - i\hat{P}\right)$$

We find

$$\hat{A}^\dagger\hat{A} = \frac{M^2\omega^2\hat{X}^2 + iM\omega\left[\hat{X},\hat{P}\right] + \hat{P}^2}{2M\hbar\omega} = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2} \qquad \hat{A}\hat{A}^\dagger = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}$$

where we have used $\left[\hat{X},\hat{P}\right] = i\hbar$, derived later. We thus have:

$$\hat{H} = \hbar\omega\left(\hat{A}^\dagger\hat{A} + \frac{1}{2}\right) \equiv \hbar\omega\left(\hat{N} + \frac{1}{2}\right) \qquad \left[\hat{A},\hat{A}^\dagger\right] = 1$$

where $\hat{N} \equiv \hat{A}^\dagger\hat{A}$. Its commutation relations with $\hat{A}^{(\dagger)}$ are

$$\left[\hat{N},\hat{A}\right] = \left[\hat{A}^\dagger\hat{A},\hat{A}\right] = -\hat{A} \qquad \left[\hat{N},\hat{A}^\dagger\right] = \left[\hat{A}^\dagger\hat{A},\hat{A}^\dagger\right] = \hat{A}^\dagger$$

and thus if $\hat{N}\left|n\right\rangle = n\left|n\right\rangle$, then

$$\begin{aligned}\hat{N}\hat{A}\left|n\right\rangle &= \hat{A}\hat{N}\left|n\right\rangle - \hat{A}\left|n\right\rangle \\ &= (n-1)\hat{A}\left|n\right\rangle\end{aligned} \qquad \begin{aligned}\hat{N}\hat{A}^\dagger\left|n\right\rangle &= \hat{A}^\dagger\hat{N}\left|n\right\rangle + \hat{A}^\dagger\left|n\right\rangle \\ &= (n+1)\hat{A}^\dagger\left|n\right\rangle\end{aligned}$$

so $\hat{A}\,|n\rangle$ and $\hat{A}^\dagger\,|n\rangle$ are both also eigenstates of $\hat{N}$, with eigenvalues different by ± 1 respectively. The square norms of these new states are:

$$\langle n|\hat{A}^\dagger\hat{A}|n\rangle = n \qquad\qquad \langle n|\hat{A}\hat{A}^\dagger|n\rangle = n+1$$

But the norm of a state must be at least 0 (this is an axiom of a Hilbert Space), and so $n \geq 0$. The lowering process must therefore end at the state $|0\rangle$ with $n = 0$, as then $\left\|\hat{A}\,|0\rangle\right\|^2 = 0 \Rightarrow \hat{A}\,|0\rangle = 0$. Using the norms above, we can then write the new states as:

$$\boxed{\hat{A}\,|n\rangle = \sqrt{n}\,|n-1\rangle} \qquad\qquad \boxed{\hat{A}^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle}$$

(give or take a phase), so that all the states $|k\rangle$ are normalised. The prefactor is always the largest of the two numbers involved. Given that we are starting at $|0\rangle$, we can write:

$$|n\rangle = \frac{1}{\sqrt{n!}}\left(\hat{A}^\dagger\right)^n |0\rangle$$

where the prefactor compensates for all the scalar multiplication that $\hat{A}^\dagger$ does. As the states $|n\rangle$ are eigenstates of $\hat{N}$ eigenvalue n, they must also be eigenstates of $\hat{H} = \hbar\omega(\hat{N} + 1/2)$ with eigenvalue $\hbar\omega(n + 1/2)$, which is the spectrum of $\hat{H}$ in this case.

1.2 $D = 3$

$$\hat{H} = \frac{1}{2M}\hat{\mathbf{P}}^2 + \frac{1}{2}M\omega^2\hat{\mathbf{X}}^2$$

Enter the vector operators:

$$\hat{\mathbf{A}} \equiv \frac{1}{\sqrt{2M\hbar\omega}}\left(M\omega\hat{\mathbf{X}} + i\hat{\mathbf{P}}\right) \qquad\qquad \hat{\mathbf{A}}^\dagger = \frac{1}{\sqrt{2M\hbar\omega}}\left(M\omega\hat{\mathbf{X}} - i\hat{\mathbf{P}}\right)$$

We now find

$$\hat{\mathbf{A}}^\dagger \cdot \hat{\mathbf{A}} = \hat{A}_i^\dagger\hat{A}_i = \frac{M^2\omega^2\hat{X}_i\hat{X}_i + iM\omega\left[\hat{X}_i, \hat{P}_i\right] + \hat{P}_i\hat{P}_i}{2M\hbar\omega} = \frac{M^2\omega^2\hat{\mathbf{X}}^2 - 3\hbar M\omega + \hat{\mathbf{P}}^2}{2M\hbar\omega} = \frac{\hat{H}}{\hbar\omega} - \frac{3}{2}$$

$$\left[\hat{A}_i, \hat{A}_j\right] = 0 \qquad\qquad \left[\hat{A}_i^\dagger, \hat{A}_j^\dagger\right] = 0 \qquad\qquad \left[\hat{A}_i, \hat{A}_j^\dagger\right] = \delta_{ij}$$

It is now more convenient to think in terms of energy eigenstates $|E_n\rangle$, rather than eigenstates of what would be the diagonal tensor $\hat{\mathbf{N}}$. We require:

$$0 \leq \left\|\sum_{i=1}^{3}\hat{A}_i\,|E_n\rangle\right\|^2 = \langle E_n|\hat{\mathbf{A}}^\dagger \cdot \hat{\mathbf{A}}|E_n\rangle = \left\langle E_n\left|\frac{\hat{H}}{\hbar\omega} - \frac{3}{2}\right|E_n\right\rangle = \frac{E_n}{\hbar\omega} - \frac{3}{2}$$

and so the ground state energy $E_0 = 3\hbar\omega/2$. Applying any component of $\hat{\mathbf{A}}^\dagger$ to $|E_0\rangle$ will generate a new state, and we can eventually build up a series of states:

$$|\mathbf{n}\rangle = |n_x\rangle \otimes |n_y\rangle \otimes |n_z\rangle = \frac{1}{\sqrt{n_x!n_y!n_z!}}\left(\hat{A}_x^\dagger\right)^{n_x}\left(\hat{A}_y^\dagger\right)^{n_y}\left(\hat{A}_z^\dagger\right)^{n_z}|\mathbf{0}\rangle$$

with energy $E_\mathbf{n} = (N + 3/2)\hbar\omega$ where $N = n_x + n_y + n_z$. Note the high degeneracy here of $(N + 1)(N + 2)/2$, as there are many ways to obtain N quanta of energy from three different contributions.

2 Transformations

After a passive transformation (say, a shift or rotation of coordinates), the state of a particle will be described by a new state. This state must still be normalised, however: if the transformation is $\hat{U} : |\psi\rangle \to |\psi'\rangle = \hat{U}|\psi\rangle$, then we require $\langle\psi'|\psi'\rangle = 1$. By writing $|\psi\rangle = |\phi\rangle + \lambda|\chi\rangle$ for arbitrary $|\phi\rangle$, $|\chi\rangle$ and λ, and imposing $\langle\alpha|\alpha\rangle = \langle\alpha|\hat{U}^\dagger\hat{U}|\alpha\rangle$ for all states, one can show that $\hat{U}$ must represent a unitary operator, that is, $\hat{U}^\dagger\hat{U} = 1$.

Transformations form a group. There should exist a homomorphism between the unitary transformation operators $\hat{U}$ and the transformations themselves.

It is often known how transformations affect certain operators. Meanwhile, the transformation operators themselves must satisfy:

$$\langle\psi'|\hat{Q}|\psi'\rangle = \langle\psi|\hat{U}^\dagger\hat{Q}\hat{U}|\psi\rangle$$

and so an operator changes from $\hat{Q}$ to $\hat{U}^\dagger\hat{Q}\hat{U}$ after the transformation.

2.1 Generators

Many transformations depend on a continuous parameter θ (a counter-example would be a reflection). For those that do, infinitesimal transformations by $\delta\theta$ exist. We write

$$\hat{U}(\delta\theta) = 1 - i\delta\theta\hat{T} + \mathcal{O}(\delta\theta^2)$$

where $\hat{T}$ is independent of θ and called the *generator* of the transformation. In the limit,

$$\frac{\partial\hat{U}}{\partial\theta} = -i\hat{T} \qquad \Rightarrow \qquad \frac{\partial|\psi\rangle}{\partial\theta} = -i\hat{T}|\psi\rangle$$

Being unitary, we require

$$1 - i\delta\theta\hat{T} + i\delta\theta\hat{T}^\dagger = 1 \qquad \Rightarrow \qquad \hat{T} = \hat{T}^\dagger$$

thus $\hat{T}$ is Hermitian and so an observable. The transformation of operators then looks like:

$$\hat{U}^\dagger(\delta\theta)\hat{A}\hat{U}(\delta\theta) = \hat{A} + i\delta\theta\Big[\hat{T}, A\Big] \qquad \Rightarrow \qquad \frac{\partial A}{\partial\theta} = i\Big[\hat{T}, A\Big]$$

A finite transformation $\hat{U}(\theta)$ can be made by applying the $\hat{U}(\delta\theta)$ operator $N = \theta/\delta\theta$ times:

$$\hat{U}(\theta) = \hat{U}(\theta/N)^N = \left(1 - i\frac{\theta}{N}\hat{T}\right)^N \to \exp\left(-i\theta\hat{T}\right)$$

2.2 Translations

The translation operators will be represented by grey $\hat{U}(\mathbf{a})$ for a translation by a vector $\mathbf{a}$.

We know that on translation by a vector $\mathbf{a}$, the expectation of the operator $\hat{\mathbf{X}}$ will shift by $\mathbf{a}$. Thus we can write down

$$\hat{U}^\dagger(\mathbf{a})\hat{\mathbf{X}}\hat{U}(\mathbf{a}) = \hat{\mathbf{X}} + \mathbf{a}$$

on the grounds that the expectation value of either side is the new expectation value of a system's position after a translation by $\mathbf{a}$.

Operating through by $\hat{U}$, we find $\left[\hat{\mathbf{X}}, \hat{U}(\mathbf{a})\right] = \mathbf{a}\hat{U}(\mathbf{a})$.

For an eigenstate of $\hat{\mathbf{X}}$ so that $\hat{\mathbf{X}}\,|\mathbf{x}\rangle = \mathbf{x}\,|\mathbf{x}\rangle$, the translated state $\hat{U}(\mathbf{a})\,|\mathbf{x}\rangle$ has

$$\hat{\mathbf{X}}\hat{U}(\mathbf{a})\,|\mathbf{x}\rangle = \hat{U}(\mathbf{a})\hat{\mathbf{X}}\,|\mathbf{x}\rangle + \mathbf{a}\hat{U}(\mathbf{a})\,|\mathbf{x}\rangle = (\mathbf{x}+\mathbf{a})\hat{U}(\mathbf{a})\,|\mathbf{x}\rangle$$

and so $\hat{U}(\mathbf{a})\,|\mathbf{x}\rangle$ must be a multiple of $|\mathbf{x}+\mathbf{a}\rangle$. Taking its norm we find that this multiple must have unit modulus, and is taken to be 1: $\hat{U}(\mathbf{a})\,|\mathbf{x}\rangle = |\mathbf{x}+\mathbf{a}\rangle$.

The position space wavefunction of a given state $|\psi\rangle$ is given by $\psi(\mathbf{x}) = \langle\mathbf{x}|\psi\rangle$. Translating $|\psi\rangle$ into $|\psi'\rangle = \hat{U}\,|\psi\rangle$, we find that the new position space wavefunction is, as expected,

$$\psi'(\mathbf{x}) = \langle\mathbf{x}|\hat{U}(\mathbf{a})|\psi\rangle = \langle\mathbf{x}-\mathbf{a}|\psi\rangle = \psi(\mathbf{x}-\mathbf{a})$$

2.2.1 Translation Generator

The generator of the translation operator turns out experimentally to be $\hat{\mathbf{P}}/\hbar$; that is:

$$\hat{U}(\delta x) = 1 - i\hat{P}_x\delta x/\hbar \qquad \hat{U}(x) = \exp\left(-i\hat{P}_x x/\hbar\right)$$
$$\hat{U}(\delta\mathbf{a}) = 1 - i\hat{\mathbf{P}}\cdot\delta\mathbf{a}/\hbar \qquad \hat{U}(\mathbf{a}) = \exp\left(-i\hat{\mathbf{P}}\cdot\mathbf{a}/\hbar\right)$$

The infinitesimal translation therefore obeys:

$$\left(1 + i\delta\mathbf{a}\cdot\hat{\mathbf{P}}/\hbar\right)\hat{\mathbf{X}}\left(1 - i\delta\mathbf{a}\cdot\hat{\mathbf{P}}/\hbar\right) = \hat{\mathbf{X}} + \delta\mathbf{a} \qquad \Rightarrow \qquad \left[\hat{\mathbf{X}}, \delta\mathbf{a}\cdot\hat{\mathbf{P}}\right] = i\hbar\delta\mathbf{a}$$

but this is the case for any $\delta\mathbf{a}$. Take $\delta\mathbf{a} = \delta a\hat{\mathbf{e}}_x$:

$$\left[\hat{\mathbf{X}}, \delta a\hat{P}_x\right] = i\hbar\delta a\hat{\mathbf{e}}_x \qquad \Rightarrow \qquad \left[\hat{X}, \hat{P}_x\right] = i\hbar;\ \left[\hat{Y}, \hat{P}_x\right] = \left[\hat{Z}, \hat{P}_x\right] = 0$$

More generally, by choosing other $\delta\mathbf{a}$, we find $\left[\hat{X}_i, \hat{P}_j\right] = i\hbar\delta_{ij}$.

We can find the effect of the momentum operator in position space. Infinitesimally,

$$\begin{aligned}
\psi'(\mathbf{x}) - \psi(\mathbf{x}) &= \psi(\mathbf{x}-\delta\mathbf{a}) - \psi(\mathbf{x}) \\
\langle\mathbf{x}|\hat{U}(\delta\mathbf{a}) - 1|\psi\rangle &= -\delta\mathbf{a}\cdot\boldsymbol{\nabla}\psi = -\frac{i}{\hbar}\delta\mathbf{a}\cdot\,\langle\mathbf{x}|\hat{\mathbf{P}}|\psi\rangle \\
\Rightarrow\ \langle\mathbf{x}|\hat{\mathbf{P}}|\psi\rangle &= -i\hbar\boldsymbol{\nabla}\psi(\mathbf{x})
\end{aligned}$$

Consider eigenstates $|\mathbf{p}\rangle$ of $\hat{\mathbf{P}}$: $\hat{\mathbf{P}}\,|\mathbf{p}\rangle = \mathbf{p}\,|\mathbf{p}\rangle$, and their position space wavefunctions $\psi_{\mathbf{p}}(\mathbf{x}) \equiv \langle\mathbf{x}|\mathbf{p}\rangle$. The translated wavefunctions

$$\begin{aligned}
\psi_{\mathbf{p}}(\mathbf{x}-\mathbf{a}) \equiv \langle\mathbf{x}-\mathbf{a}|\mathbf{p}\rangle &= \langle\mathbf{x}|\hat{U}(\mathbf{a})|\mathbf{p}\rangle \\
&= \left\langle\mathbf{x}\middle|\exp\left(-i\hat{\mathbf{P}}\cdot\mathbf{a}/\hbar\right)\middle|\mathbf{p}\right\rangle = \exp\left(-i\mathbf{p}\cdot\mathbf{a}/\hbar\right)\langle\mathbf{x}|\mathbf{p}\rangle \\
&= \exp\left(-i\mathbf{p}\cdot\mathbf{a}/\hbar\right)\psi_{\mathbf{p}}(\mathbf{x}) \\
\Rightarrow \langle\mathbf{x}|\mathbf{p}\rangle &= \frac{1}{(2\pi\hbar)^{3/2}}e^{i\mathbf{x}\cdot\mathbf{p}/\hbar}
\end{aligned}$$

where the prefactor ensures that $\langle\mathbf{p}'|\mathbf{p}\rangle = \delta(\mathbf{p}-\mathbf{p}')$.

2.2.2 Homomorphism

We must have $\hat{U}(\mathbf{a})\hat{U}(\mathbf{b}) = \hat{U}(\mathbf{b})\hat{U}(\mathbf{a})$, because translations commute. Thus

$$(1 + \delta a_i \hat{P}_i/\hbar)(1 + \delta b_j \hat{P}_j/\hbar) = (1 + \delta b_j \hat{P}_j/\hbar)(1 + \delta a_i \hat{P}_i/\hbar) \qquad \Rightarrow \qquad a_i b_j \hat{P}_i \hat{P}_j = a_i b_j \hat{P}_j \hat{P}_i$$

Because this is true for any $\delta\mathbf{a}$ and $\delta\mathbf{b}$, we have $\left[\hat{P}_i, \hat{P}_j\right] = 0$.

2.3 Rotations

Rotation operators will be represented by BrickRed $\hat{U}(\boldsymbol{\alpha})$ for a rotation of $|\boldsymbol{\alpha}|$ about the axis $\hat{\boldsymbol{\alpha}}$ through the origin.

On rotation specified by a vector $\boldsymbol{\alpha}$, the expectation of $\hat{\mathbf{X}}$ will translate according to

$$\hat{U}^\dagger(\boldsymbol{\alpha})\hat{\mathbf{X}}\hat{U}(\boldsymbol{\alpha}) = \mathbf{R}(\boldsymbol{\alpha})\hat{\mathbf{X}}$$

where $\mathbf{R}(\boldsymbol{\alpha})$ is the rotation matrix. For an infinitesimal rotation, $\hat{\mathbf{R}}(\delta\boldsymbol{\alpha}) = 1 + \delta\boldsymbol{\alpha}\times$, that is:

$$\hat{U}^\dagger(\delta\boldsymbol{\alpha})\hat{\mathbf{X}}\hat{U}(\delta\boldsymbol{\alpha}) = \hat{\mathbf{X}} + \delta\boldsymbol{\alpha} \times \hat{\mathbf{X}} \qquad \Rightarrow \qquad \left[\hat{\mathbf{X}}, \hat{U}(\delta\boldsymbol{\alpha})\right] = \hat{U}(\delta\boldsymbol{\alpha})\delta\boldsymbol{\alpha} \times \hat{\mathbf{X}}$$

2.3.1 Rotation Generator

The generator of the rotation operator is $\hat{\mathbf{J}}/\hbar$:

$$\hat{U}(\delta\boldsymbol{\alpha}) = 1 - i\hat{\mathbf{J}} \cdot \delta\boldsymbol{\alpha}/\hbar \qquad\qquad \hat{U}(\boldsymbol{\alpha}) = \exp\left(-i\hat{\mathbf{J}} \cdot \boldsymbol{\alpha}/\hbar\right)$$

Substituting the former into the commutation relation above,

$$-\frac{i}{\hbar}\delta\alpha_j\left[\hat{X}_i, \hat{J}_j\right] = \epsilon_{ijk}\delta\alpha_j\hat{X}_k \qquad \Rightarrow \qquad \left[\hat{J}_i, \hat{X}_j\right] = i\hbar\epsilon_{ijk}\hat{X}_k$$

[note the relabelling of $i \leftrightarrow j$ if you're worried about the sign].

2.3.2 Homomorphism

Using $\hat{\mathbf{R}}(\delta\boldsymbol{\alpha}) = 1 + \delta\boldsymbol{\alpha}\times$ for two composed infinitesimal rotations $\delta\boldsymbol{\alpha}$ and $\delta\boldsymbol{\beta}$, we find that

$$\mathbf{R}(\delta\boldsymbol{\beta})\mathbf{R}(\delta\boldsymbol{\alpha}) - \mathbf{R}(\delta\boldsymbol{\alpha})\mathbf{R}(\delta\boldsymbol{\beta}) = \mathbf{R}(\delta\boldsymbol{\beta} \times \delta\boldsymbol{\alpha}) - I$$

and thus the homomorphism gives

$$\begin{aligned}
\left[\hat{U}(\delta\boldsymbol{\beta}), \hat{U}(\delta\boldsymbol{\alpha})\right] &= \hat{U}(\delta\boldsymbol{\beta} \times \delta\boldsymbol{\alpha}) - 1 \\
-\frac{1}{\hbar^2}\left[\delta\boldsymbol{\beta} \cdot \hat{\mathbf{J}}, \delta\boldsymbol{\alpha} \cdot \hat{\mathbf{J}}\right] &= 1 - \frac{i}{\hbar}(\delta\boldsymbol{\beta} \times \delta\boldsymbol{\alpha}) \cdot \hat{\mathbf{J}} - 1 \\
\delta\beta_i\delta\alpha_j\left[\hat{J}_i, \hat{J}_j\right] &= i\hbar\epsilon_{ijk}\delta\beta_i\delta\alpha_j\hat{J}_k \\
\left[\hat{J}_i, \hat{J}_j\right] &= i\hbar\epsilon_{ijk}\hat{J}_k
\end{aligned}$$

from which we can also find that $\left[\hat{J}_i, \hat{\mathbf{J}}^2\right] = 0$.

2.3.3 Relationship with Translation

Composing an infinitesimal rotation $\delta\boldsymbol{\alpha}$ with an infinitesimal translation $\delta\mathbf{a}$ gives

$$\begin{aligned}\mathbf{R}(\delta\boldsymbol{\alpha})(\mathbf{x}+\delta\mathbf{a})-(\mathbf{R}(\delta\boldsymbol{\alpha})\mathbf{x}+\delta\mathbf{a}) &= \delta\boldsymbol{\alpha}\times\delta\mathbf{a}=\mathbf{x}+\delta\boldsymbol{\alpha}\times\delta\mathbf{a}-\mathbf{x}\\ \left[\hat{U}(\delta\boldsymbol{\alpha}),\hat{U}(\delta\mathbf{a})\right] &= \hat{U}(\delta\boldsymbol{\alpha}\times\delta\mathbf{a})-1\\ -\frac{1}{\hbar^2}\delta\alpha_i\delta a_j\left[\hat{J}_i,\hat{P}_j\right] &= -\frac{i}{\hbar}\epsilon_{ijk}\delta\alpha_i\delta a_j\hat{P}_k \qquad \Rightarrow \qquad \left[\hat{J}_i,\hat{P}_j\right]=i\hbar\epsilon_{ijk}\hat{P}_k\end{aligned}$$

This is the same form of $\hat{\mathbf{J}}$'s commutations with $\hat{\mathbf{X}}$ and $\hat{\mathbf{J}}$ itself. Any operator with such a relation with $\hat{\mathbf{J}}$ is called a vector operator.

2.3.4 Composite Systems

For a composite system, a rotation can be considered in two parts: a translation of the system's centre of mass[1] around an arc of a circle (keeping the body's orientation fixed), and a rotation about the centre of mass[1]; both use the same angle.

Circular Translation $\hat{U}(\delta\boldsymbol{\alpha})$. If the system is initially at $\mathbf{x}$, and we translate around about the origin by an angle $\delta\boldsymbol{\alpha}$, we have translated the system by $\delta\boldsymbol{\alpha}\times\mathbf{x}$. The transformation operator for circular translations thus obeys

$$\hat{U}^\dagger(\delta\boldsymbol{\alpha})\hat{\mathbf{X}}\hat{U}(\delta\boldsymbol{\alpha})=\hat{\mathbf{X}}+\delta\boldsymbol{\alpha}\times\hat{\mathbf{X}}$$

which is satisfied by

$$\hat{U}(\delta\boldsymbol{\alpha})=1-\frac{i}{\hbar}(\delta\boldsymbol{\alpha}\times\hat{\mathbf{X}})\cdot\hat{\mathbf{P}}=1-\frac{i}{\hbar}\delta\boldsymbol{\alpha}\cdot\hat{\mathbf{L}}$$

where $\hat{\mathbf{L}}=\hat{\mathbf{X}}\times\hat{\mathbf{P}}$, from which we can find

$$\left[\hat{L}_i,\hat{X}_j\right]=i\hbar\epsilon_{ijk}X_k \qquad \left[\hat{L}_i,\hat{P}_j\right]=i\hbar\epsilon_{ijk}P_k \qquad \left[\hat{L}_i,\hat{L}_j\right]=i\hbar\epsilon_{ijk}L_k \qquad \left[\hat{J}_i,\hat{L}_j\right]=i\hbar\epsilon_{ijk}\hat{L}_k$$

which all follow from the commutation relations of $\hat{\mathbf{X}}$ and $\hat{\mathbf{P}}$.

System Rotation. This is more complicated, as in general we don't know the internal structure of our system; it may not have one. Defining the spin operator $\hat{\mathbf{S}}\equiv\hat{\mathbf{J}}-\hat{\mathbf{L}}$ and using the commutators of $\hat{\mathbf{J}}$ and $\hat{\mathbf{L}}$, it is simple to derive

$$\begin{aligned}&\left[\hat{S}_i,\hat{S}_j\right]=i\hbar\epsilon_{ijk}\hat{S}_k && \left[\hat{S}_i,\hat{\mathbf{S}}^2\right]=0 &&\\ &\left[\hat{S}_i,\hat{X}_j\right]=0 && \left[\hat{S}_i,\hat{P}_j\right]=0 && \left[\hat{S}_i,\hat{L}_j\right]=0\end{aligned}$$

2.4 Time Translation

Time translation operators will be represented by green $\hat{U}(t)$ for a time translation through t. Time translation means that we can write $|\psi(t)\rangle=\hat{U}(t)\,|\psi(0)\rangle$.

The generator for time translations turns out to be $\hat{H}/\hbar$, that is $\hat{U}(t)=\exp\left(-i\hat{H}t/\hbar\right)$ for a time-independent $\hat{H}$; importantly, $[\hat{H},\hat{U}]=0$. The difference

$$|\psi(t+\delta t)\rangle-|\psi(t)\rangle=-\frac{i}{\hbar}\hat{H}\delta t\,|\psi(t)\rangle \qquad \Rightarrow \qquad \boxed{i\hbar\frac{\partial\,|\psi\rangle}{\partial t}=\hat{H}\,|\psi\rangle} \qquad \text{(TDSE)}$$

[1] Or other point of interest of the system

2.4.1 Heisenberg Picture

Consider the matrix element $\langle\chi(t)|\hat{Q}|\psi(t)\rangle$, where in general $\hat{Q}$ may depend on time. This may be written $\langle\chi(0)|\hat{U}^\dagger\hat{Q}\hat{U}|\psi(0)\rangle = \langle\chi(0)|\hat{Q}_H|\psi(0)\rangle$, where

$$\hat{Q}_H(t) = \hat{U}^\dagger(t)\hat{Q}(t)\hat{U}(t)$$

is the operator $\hat{Q}$ *in the Heisenberg Picture*. This is just an alternate way of looking at matrix elements and expectation values: what we call the "state" of a particle is no longer $|\psi(t)\rangle$, but $|\psi(0)\rangle$; the time evolution is now the operators' job.

Differentiating the above, we find[2]

$$\frac{\mathrm{d}\hat{Q}_H}{\mathrm{d}t} = \frac{i}{\hbar}\Big[\hat{H}, \hat{Q}_H\Big] + \hat{U}^\dagger\frac{\mathrm{d}\hat{Q}}{\mathrm{d}t}\hat{U} \qquad \text{(Heisenberg)}$$

For example, if $\hat{H} = \hat{\mathbf{P}}^2/2M + V(\hat{\mathbf{X}})$, we obtain

$$\frac{\mathrm{d}\hat{\mathbf{X}}_H}{\mathrm{d}t} = \frac{i}{2M\hbar}\Big[\hat{\mathbf{P}}^2, \hat{\mathbf{X}}\Big] = \frac{\hat{\mathbf{P}}}{M}$$
$$\frac{\mathrm{d}\hat{\mathbf{P}}_H}{\mathrm{d}t} = \frac{i}{\hbar}\Big[V(\hat{\mathbf{X}}), \hat{\mathbf{P}}\Big] = -\boldsymbol{\nabla}_{\hat{\mathbf{X}}}V$$

2.4.2 Conservation

If $\hat{Q}$ commutes with $\hat{H}$ (and thus $\hat{U}$), it is equal to $\hat{Q}_H$. Such operators are said to be conserved, as their operation does not change in time.

This often occurs as a result of $\hat{H}$ being invariant under a transformation. If a transformation represented by $\hat{U}(\theta) = e^{-i\theta\hat{T}}$ leaves $\hat{H}$ unchanged, we have $\hat{U}^\dagger\hat{H}\hat{U} = \hat{H}$ and so $\Big[\hat{H}, \hat{T}\Big] = 0$. The observable $\hat{T}$ therefore does not change with time. For instance, if $\hat{H}$ is invariant under translations, then the translation generator $\hat{\mathbf{P}}/\hbar$, will not change with time (as expected if there is no potential energy).

2.5 Summary of Useful Commutators

$$\Big[\hat{X}_i, \hat{P}_j\Big] = i\hbar\delta_{ij} \qquad \Big[\hat{P}_i, \hat{P}_j\Big] = 0 \qquad \Big[\hat{X}_i, \hat{X}_j\Big] = 0$$
$$\Big[\hat{J}_i, \hat{X}_j\Big] = i\hbar\epsilon_{ijk}\hat{X}_k \qquad \Big[\hat{J}_i, \hat{P}_j\Big] = i\hbar\epsilon_{ijk}\hat{P}_k \qquad \Big[\hat{J}_i, \hat{J}_j\Big] = i\hbar\epsilon_{ijk}\hat{J}_k$$
$$\Big[\hat{L}_i, \hat{X}_j\Big] = i\hbar\epsilon_{ijk}\hat{X}_k \qquad \Big[\hat{L}_i, \hat{P}_j\Big] = i\hbar\epsilon_{ijk}\hat{P}_k \qquad \Big[\hat{L}_i, \hat{L}_j\Big] = i\hbar\epsilon_{ijk}\hat{L}_k$$
$$\Big[\hat{S}_i, \hat{X}_j\Big] = 0 \qquad \Big[\hat{S}_i, \hat{P}_j\Big] = 0 \qquad \Big[\hat{S}_i, \hat{S}_j\Big] = i\hbar\epsilon_{ijk}\hat{S}_k$$
$$\Big[\hat{J}_i, \hat{L}_j\Big] = i\hbar\epsilon_{ijk}\hat{L}_k \qquad \Big[\hat{J}_i, \hat{S}_j\Big] = i\hbar\epsilon_{ijk}\hat{S}_k \qquad \Big[\hat{L}_i, \hat{S}_j\Big] = 0$$
$$\Big[\hat{J}_i, \hat{\mathbf{J}}^2\Big] = 0 \qquad \Big[\hat{L}_i, \hat{\mathbf{L}}^2\Big] = 0 \qquad \Big[\hat{S}_i, \hat{\mathbf{S}}^2\Big] = 0$$

[2] Technically, $\hat{H}$ in the Heisenberg equation should be $\hat{H}_H$, but if $\hat{H}$ is time-independent (as we have assumed) then $\hat{H}$ commutes with $\hat{U}$ and there is no difference.

3 Angular Momentum

3.1 Eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$

$$\left[\hat{J}_i, \hat{J}_j\right] = i\hbar\epsilon_{ijk}\hat{J}_k \qquad \Rightarrow \qquad \left[\hat{J}_i, \hat{\mathbf{J}}^2\right] = 0$$

so although $\nexists$ simultaneous eigenstates of all the components of $\hat{\mathbf{J}}$ (and hence $\nexists$ eigenstates of $\hat{\mathbf{J}}$), $\exists$ simultaneous orthonormal eigenstates of $\hat{J}_z$ and $\hat{\mathbf{J}}^2$, which we provisionally denote $|\beta, m\rangle$:

$$\hat{\mathbf{J}}^2 |\beta, m\rangle = \beta\hbar^2 |\beta, m\rangle \qquad\qquad \hat{J}_z |\beta, m\rangle = m\hbar |\beta, m\rangle$$

Define:

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

$$\Rightarrow \left[\hat{J}_z, \hat{J}_\pm\right] = i\hbar\Big(\hat{J}_y \mp i\hat{J}_x\Big) = \pm\hbar\hat{J}_\pm \qquad\qquad \left[\hat{\mathbf{J}}^2, \hat{J}_\pm\right] = 0$$

Consider the state $\hat{J}_\pm |\beta, m\rangle$. We find

$$\begin{aligned}\hat{J}_z\hat{J}_\pm |\beta, m\rangle &= \hat{J}_\pm\Big(\hat{J}_z \pm \hbar\Big) |\beta, m\rangle \\ &= (m \pm 1)\hbar\hat{J}_\pm |\beta, m\rangle\end{aligned} \qquad\qquad \begin{aligned}\hat{\mathbf{J}}^2\hat{J}_\pm |\beta, m\rangle &= \hat{J}_\pm\hat{\mathbf{J}}^2 |\beta, m\rangle \\ &= \beta\hbar^2\hat{J}_\pm |\beta, m\rangle\end{aligned}$$

$\hat{J}_\pm |\beta, m\rangle$ thus has the same magnitude of $\hat{\mathbf{J}}$, but more/less is in the z-direction: $\hat{J}_\pm$ thus reorients the system. The norm of the new state is given by:

$$\begin{aligned}0 \leq \left\|\hat{J}_\pm |\beta, m\rangle\right\|^2 &= \langle\beta, m|\hat{J}_\mp\hat{J}_\pm|\beta, m\rangle = \left\langle\beta, m\middle|\left(\hat{J}_x^2 + \hat{J}_y^2 \pm i\left[\hat{J}_x, \hat{J}_y\right]\right)\middle|\beta, m\right\rangle \\ &= \left\langle\beta, m\middle|\left(\hat{\mathbf{J}}^2 - \hat{J}_z^2 \mp \hbar\hat{J}_z\right)\middle|\beta, m\right\rangle \\ &= (\beta - m(m \pm 1))\hbar^2\end{aligned}$$

Thus we cannot apply $\hat{J}_\pm$ to a starting state as many times as we want to; there is a floor and a ceiling, that is, maximum and minimum values of m so that

$$\beta = m_{\max}(m_{\max} + 1) \qquad\qquad \beta = m_{\min}(m_{\min} - 1)$$

which is solved by $m_{\min} = -m_{\max}$. Calling $j = m_{\max}$, and relabelling the eigenstates as $|j, m\rangle$,:

$$\hat{\mathbf{J}}^2 |j, m\rangle = j(j+1)\hbar^2 |j, m\rangle \qquad\qquad \hat{J}_z |j, m\rangle = m\hbar |j, m\rangle$$

$$\hat{J}_+ |j, m\rangle = \sqrt{j(j+1) - m(m+1)}\hbar |j, m+1\rangle = \sqrt{(j+m+1)(j-m)}\hbar |j, m+1\rangle$$

$$\hat{J}_- |j, m\rangle = \sqrt{j(j+1) - m(m-1)}\hbar |j, m-1\rangle = \sqrt{(j-m+1)(j+m)}\hbar |j, m-1\rangle$$

Getting from $|j, j\rangle$ to $|j, -j\rangle$ requires applying $\hat{J}_-$ $2j$ times, so $2j \in \mathbb{N}$.

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

All the above relations have been derived using the commutation relations obeyed by $\hat{\mathbf{J}}$, but $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ obey identical relations, and so have eigenstates of the same forms $|\ell, m\rangle$ and $|s, \sigma\rangle$.

The potential energy for an atom in a $\mathbf{B}$ field is $-\boldsymbol{\mu} \cdot \mathbf{B}$, where $\boldsymbol{\mu}$ (the magnetic dipole moment) is $\boldsymbol{\mu} = \gamma\hat{\mathbf{S}}$ and γ is a constant. Taking $\mathbf{B} = B\hat{\mathbf{e}}_z$ wlog, the Heisenberg picture gives:

$$\frac{\mathrm{d}\left\langle \hat{\mathbf{P}} \right\rangle}{\mathrm{d}t} = \gamma \left\langle \hat{S}_z \boldsymbol{\nabla} B \right\rangle$$

so the force on a particle in an inhomogeneous magnetic field depends on σ, which can have any value between $-s$ and s in integer steps. In the Stern-Gerlach experiment, a beam of neutral silver atoms was split into two, therefore they have $s = 1/2$, the smallest possible non-zero s.

3.2.1 $s = \frac{1}{2}$

Systems with $s = 1/2$ inhabit a space with a basis

$$\{|1/2, 1/2\rangle, |1/2, -1/2\rangle\}$$

more commonly denoted $\{|\uparrow\rangle, |\downarrow\rangle\}$, so that any state $|\psi\rangle = a|\uparrow\rangle + b|\downarrow\rangle$ for some $a, b, |a|^2 + |b|^2 = 1$. Denoting this state by the vector $(a, b)^\intercal$ and knowing $\hat{S}_x = (\hat{S}_+ + \hat{S}_-)/2$ and $\hat{S}_y = (\hat{S}_+ - \hat{S}_-)/2i$, we find the following matrices representing the action of the $\hat{S}_i$ operators.

$$\hat{S}_i = \begin{pmatrix} \langle\uparrow|\hat{S}_i|\uparrow\rangle & \langle\uparrow|\hat{S}_i|\downarrow\rangle \\ \langle\downarrow|\hat{S}_i|\uparrow\rangle & \langle\downarrow|\hat{S}_i|\downarrow\rangle \end{pmatrix}$$

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

We often write $\hat{\mathbf{S}} = (\hbar/2)\hat{\boldsymbol{\sigma}}$, where $\hat{\boldsymbol{\sigma}}$ is the Pauli vector whose entries are the matrices (without the prefactors) above. These matrices are Hermitian (so you only need to calculate one triangle), traceless (so you don't need to calculate the final term on the diagonal), and obey the relevant commutation relations.

A similar set of matrices can be calculated for $s = 1$.

3.3 Orbital Angular Momentum $\hat{\mathbf{L}}$

Unlike with body rotations, circular translations are contractible to a loop of 0 size, which turns out to preclude half-integer values of ℓ, and thus m. It can be shown that in spherical polars,

$$\langle \mathbf{x}|\hat{L}_z|\psi\rangle = -i\hbar\frac{\partial\psi(r,\theta,\phi)}{\partial\phi}$$

so position-space eigenfunctions of $\hat{L}_z$, $\psi_{\ell m} = \langle \mathbf{x}|\ell, m\rangle$, satisfy the differential equation

$$m\hbar\psi_{\ell m} = -i\hbar\frac{\partial\psi_{\ell m}}{\partial\phi} \qquad \Rightarrow \qquad \psi_{\ell m}(r,\theta,\phi) = K_{\ell m}(r,\theta)e^{im\phi}$$

for some function $K_{\ell m}$. This gives another reason that $\ell \in \mathbb{N}$: if it were not, half-integer values of m would be possible and the wavefunction would be multivalued. Calculating $\hat{L}_+$ in spherical polars and setting $\hat{L}_+ |\ell, \ell\rangle = 0$ gives:

$$\psi_{\ell\ell}(r, \theta, \phi) = R(r) \sin^\ell(\theta) e^{i\ell\phi}$$

Calculating $\hat{L}_-$ in spherical polars and repeatedly applying it to $\psi_{\ell\ell}$, one finds that $\psi_{\ell m} = R(r) Y_\ell^m(\theta, \phi)$, where Y_ℓ^m are the spherical harmonics. Importantly, these satisfy

$$Y_\ell^m(-\mathbf{x}) = (-1)^\ell Y_\ell^m(\mathbf{x})$$

3.3.1 Spherical Potentials

It can be shown that

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{X}}^2 \left(\hat{\mathbf{P}}^2 - \hat{P}_r^2 \right) \qquad \hat{P}_r = \frac{1}{2} \left(\frac{\hat{\mathbf{X}}}{\left|\hat{\mathbf{X}}\right|} \cdot \hat{\mathbf{P}} + \hat{\mathbf{P}} \cdot \frac{\hat{\mathbf{X}}}{\left|\hat{\mathbf{X}}\right|} \right)$$

where $\hat{P}_r$ is the radial momentum operator. As such, for a spherical potential

$$\hat{H} = \frac{\hat{P}_r^2}{2M} + \frac{\hat{\mathbf{L}}^2}{2M\hat{\mathbf{X}}^2} + V\left(\left|\hat{\mathbf{X}}\right|\right)$$

$[\hat{L}_i, \hat{X}_j] = i\hbar\epsilon_{ijk}\hat{X}_k$, so $[\hat{L}_i, \hat{\mathbf{X}}^2] = 0$, so the middle term can be written like that. Identical commutations apply between $\hat{\mathbf{L}}$ and $\hat{\mathbf{P}}$, which gives the relations

$$[\hat{H}, \hat{\mathbf{L}}] = \mathbf{0} \qquad [\hat{H}, \hat{\mathbf{L}}^2] = 0$$

and thus $\exists$ simultaneous eigenstates of $\hat{H}$, $\hat{\mathbf{L}}^2$, and $\hat{L}_z$, denoted $|n, \ell, m\rangle$ after the respective corresponding eigenvalues:

$$\hat{H} |n, \ell, m\rangle = E_{n\ell} |n, \ell, m\rangle \qquad \hat{\mathbf{L}}^2 |n, \ell, m\rangle = \ell(\ell+1)\hbar^2 |n, \ell, m\rangle \qquad \hat{L}_z |n, \ell, m\rangle = m\hbar |n, \ell, m\rangle$$

where we note that $E_{n\ell}$ cannot depend on m because $[\hat{H}, \hat{L}_\pm] = 0$, though it will generally depend on ℓ as $\hat{\mathbf{L}}^2$ is in the Hamiltonian.

As the energy eigenstates of this problem will also be eigenstates of $\hat{\mathbf{L}}^2$, we can rewrite

$$\hat{H} |n, \ell, m\rangle = \underbrace{\left(\frac{\hat{P}_r^2}{2M} + \frac{\ell(\ell+1)\hbar^2}{2M\hat{R}^2} + V\left(\hat{R}\right) \right)}_{\hat{H}_\ell} |n, \ell, m\rangle$$

where $\hat{R} = \left|\hat{\mathbf{X}}\right|$. There will be (at least) $(2\ell+1)$-fold degeneracy to each value of $E_{n\ell}$, as each of the $2\ell+1$ states with the same ℓ but different m will have the same energy.

$D = 3$ **Harmonic Oscillator Revisited.** In the first section, we used Cartesian coordinates to derive the following results, which should be coordinate-independent:

$$E_{\mathbf{n}} = (N + 3/2)\hbar\omega \qquad g_N = \frac{(N+1)(N+2)}{2}$$

We now reapproach this problem in spherical coordinates:

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{1}{2}M\omega^2\hat{\mathbf{X}}^2 \qquad \Rightarrow \qquad \hat{H}_\ell = \frac{\hat{P}_r^2}{2M} + \frac{\ell(\ell+1)\hbar^2}{2M\hat{R}^2} + \frac{1}{2}M\omega^2\hat{R}^2$$

which is essentially one-dimensional. We then introduce ladder operators

$$\hat{A}_\ell = \frac{1}{\sqrt{2M\hbar\omega}}\left(M\omega R + i\hat{P}_r - \frac{(\ell+1)\hbar}{R}\right)$$

with the final term noting the dependence on ℓ. Using the intuitive commutator $[\hat{R}, \hat{P}_r] = i\hbar$

$$\hat{H}_\ell = \hbar\omega\left(\hat{A}_\ell^\dagger\hat{A}_\ell + \ell + \frac{3}{2}\right) \qquad \left[\hat{A}_\ell, \hat{A}_\ell^\dagger\right] = 1 + \frac{(\ell+1)\hbar}{M\omega\hat{R}^2} = 1 + \frac{\hat{H}_{\ell+1} - \hat{H}_\ell}{\hbar\omega}$$

$$\begin{aligned}\left[\hat{A}_\ell, \hat{H}_\ell\right] \equiv \hat{A}_\ell\hat{H}_\ell - \hat{H}_\ell\hat{A}_\ell &= \hbar\omega\left[\hat{A}_\ell, \hat{A}_\ell^\dagger\hat{A}_\ell\right] = \hbar\omega\left[\hat{A}_\ell, \hat{A}_\ell^\dagger\right]\hat{A}_\ell \\ &= \hbar\omega\hat{A}_\ell + \left(\hat{H}_{\ell+1} - \hat{H}_\ell\right)\hat{A}_\ell \\ \Rightarrow \hat{H}_{\ell+1}\hat{A}_\ell &= \hat{A}_\ell\hat{H}_\ell - \hbar\omega\hat{A}_\ell\end{aligned}$$

Consider $|n,\ell,m\rangle$, an eigenstate of $\hat{H}_\ell$. $\hat{A}_\ell|n,\ell,m\rangle$, however, is an eigenstate of $\hat{H}_{\ell+1}$:

$$\hat{H}_{\ell+1}\hat{A}_\ell|n,\ell,m\rangle = \hat{A}_\ell\hat{H}_\ell|n,\ell,m\rangle - \hbar\omega\hat{A}_\ell|n,\ell,m\rangle = (E_{n\ell} - \hbar\omega)\hat{A}_\ell|n,\ell,m\rangle$$

So the new state $\hat{A}_\ell|n,\ell,m\rangle$ must be a state with lower energy, but higher ℓ, than $|n,\ell,m\rangle$. The square norm of the new state is

$$0 \leq \langle n,\ell,m|\hat{A}_\ell^\dagger\hat{A}_\ell|n,\ell,m\rangle = \frac{E_{n\ell}}{\hbar\omega} - \ell - \frac{3}{2}$$

and so one cannot continually apply $\hat{A}_\ell$, taking the state to lower energies and higher ℓ, forever. Each value of ℓ has a state $|0,\ell,m\rangle$ for which $\hat{A}_\ell|0,\ell,m\rangle = 0$. This state has energy

$$E_{0\ell} = \left(\ell + \frac{3}{2}\right)\hbar\omega$$

and therefore the ground state, with $\ell = 0$, is $E_{00} = 3\hbar\omega/2$ as before.

Similarly, taking the adjoint of an above result,

$$\hat{A}_\ell^\dagger\hat{H}_{\ell+1} = \hat{H}_\ell\hat{A}_\ell^\dagger - \hbar\omega\hat{A}_\ell^\dagger$$

So the state $\hat{A}_\ell^\dagger|n,\ell+1,m\rangle$ is an eigenstate not of $\hat{H}_{\ell+1}$, but $\hat{H}_\ell$:

$$\hat{H}_\ell\hat{A}_\ell^\dagger|n,\ell+1,m\rangle = \hat{A}_\ell^\dagger\hat{H}_{\ell+1}|n,\ell+1,m\rangle + \hbar\omega\hat{A}_\ell^\dagger|n,\ell+1,m\rangle = (E_{n,\ell+1} + \hbar\omega)\hat{A}_\ell^\dagger|n,\ell+1,m\rangle$$

So $\hat{A}_\ell^\dagger|n,\ell+1,m\rangle$ is a state of greater energy, but lower ℓ, than $|n,\ell+1,m\rangle$. One can therefore take the state $|0,\ell,m\rangle$ and generate new states with higher energies and lower ℓ until reaching a state with $\ell = 0$.

The situation is summarised in Figure 1. For each value of ℓ, $\exists$ a minimum energy state with energy $E_{0\ell} = (\ell + 3/2)\hbar\omega$, and one can generate new states of higher energy and lower ℓ using $\hat{A}_\ell^\dagger$, until reaching an $\ell = 0$ state.

By summing the annotated numbers along each row, the degeneracy of each energy level is found to be $(N+1)(N+2)/2$, the same as when we analysed it in Cartesian coordinates.

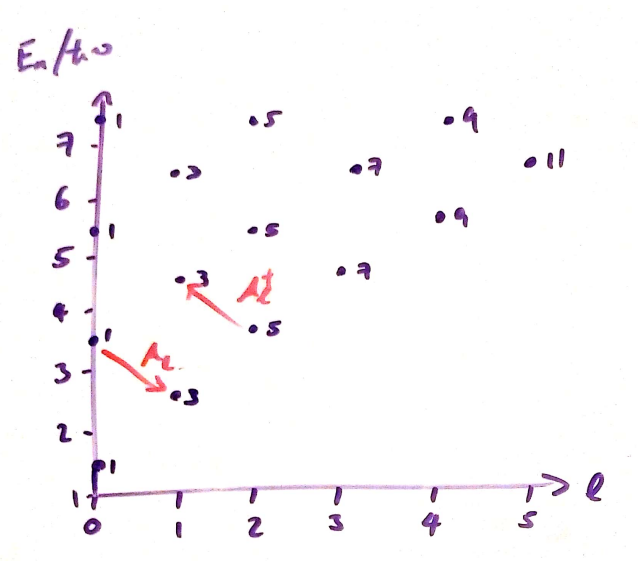

Figure 1 | Angular Momentum Eigenstates of the 3D Quantum Harmonic Oscillator. Example operations of $\hat{A}_\ell$ and $\hat{A}_\ell^\dagger$ are shown in red. Each point is annotated with the number of states of different m at that point $(2\ell + 1)$.

3.4 Two Particles

If we have two particles, the dimension of the space of combined angular momentum states is the product of the dimensions of the two: $(2j_1 + 1)(2j_2 + 1)$. Although this is spanned by the basis $\{|j_1, m_1\rangle |j_2, m_2\rangle\}$, it can be useful to use a basis of total angular momentum states $\{|j, m\rangle\}$; we are switching from an eigenbasis of $\hat{\mathbf{J}}_1^2$, $\hat{J}_{1z}$, $\hat{\mathbf{J}}_2^2$ and $\hat{J}_{2z}$ (the angular momentum operators of the individual systems) to an eigenbasis of $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ and $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$.

We first find how these joint operators act on the joint systems, i.e. getting $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ in terms of $\hat{\mathbf{J}}_1^2$, $\hat{J}_{1z}$, $\hat{\mathbf{J}}_2^2$ and $\hat{J}_{2z}$. We write $\hat{\mathbf{J}}^2 = \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + 2\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2$. The cross term can be written in terms of the $\hat{J}_{i\pm}$ and $\hat{J}_{iz}$, giving:

$$\hat{\mathbf{J}}^2 = \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + \hat{J}_{1-}\hat{J}_{2+} + \hat{J}_{1+}\hat{J}_{2-} + 2\hat{J}_{1z}\hat{J}_{2z}$$

Also, $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$.

We now look for the eigenstates of these new joint operators. We suspect that the maximally aligned state $|j_1, j_1\rangle |j_2, j_2\rangle$, where both particles are maximally along the z-axis, will be a joint eigenstate. We see that $\hat{J}_z |j_1, j_1\rangle |j_2, j_2\rangle = (j_1 + j_2)\hbar |j_1, j_1\rangle |j_2, j_2\rangle$, and

$$\begin{aligned}\hat{J}^2 |j_1, j_1\rangle |j_2, j_2\rangle &= (j_1(j_1+1) + j_2(j_2+1) + 2j_1j_2)\hbar^2 |j_1, j_1\rangle |j_2, j_2\rangle \\ &= (j_1 + j_2)(j_1 + j_2 + 1)\hbar^2 |j_1, j_1\rangle |j_2, j_2\rangle\end{aligned}$$

Not only is $|j_1, j_1\rangle |j_2, j_2\rangle$ therefore an eigenstate of the joint operators, the eigenvalues are consistent with a state $|j, j\rangle$ with $j = j_1 + j_2$; we can therefore write

$$|j, j\rangle = |j_1, j_1\rangle |j_2, j_2\rangle$$

By acting on the LHS with $\hat{J}_-$, and on the RHS with $\hat{J}_{1-} + \hat{J}_{2-}$ (which of course do the same thing), one obtains all the other states $|j, m\rangle$, with $m \in \{j, j-1, \ldots, -j+1, -j\}$, as a linear combination of the joint states $|j_1, m_1\rangle |j_2, m_2\rangle$ for which $m = m_1 + m_2$. These can be the only states involved if the state is to be an eigenstate of $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$. Also, $\left[\hat{\mathbf{J}}^2, \hat{J}_z\right] = 0$, so these states all have the same value of j; this is interpreted as the two states still being aligned with each other, but at different angles to the z-axis and hence different m.

If the angular momenta of the two systems are not aligned, states will be generated with smaller values of j. The state $|j-1, j-1\rangle$ represents a state where the two systems are not perfectly aligned, but the same amount of angular momentum is oriented along the z-direction as of the state $|j, j-1\rangle$; this is represented in Figure 2.

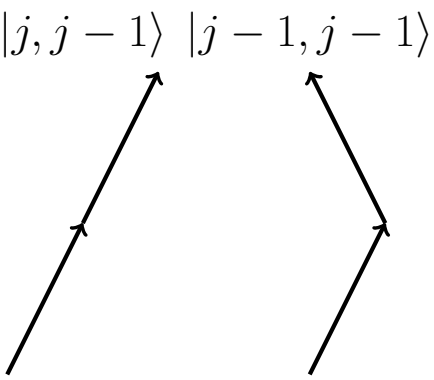

Figure 2 | Different Alignments of Joint Angular Momentum States. I'm so good at TikZ.

To construct $|j-1, j-1\rangle$, note that it must be a linear combination of $\{|j_1, j_1\rangle\,|j_2, j_2-1\rangle\,,$ $|j_1, j_1-1\rangle\,|j_2, j_2\rangle\}$ to have the right value of $m = j-1$. We can then use the fact that $|j-1, j-1\rangle$ is orthogonal[3] to $|j, j-1\rangle$ (constructed earlier) as the two states have different eigenvalues of $\hat{\mathbf{J}}^2$ which is Hermitian. Alternatively, we could use $\hat{J}_+\,|j-1, j-1\rangle = 0$; either way there remains only one possibility for the linear combination. Once $|j-1, j-1\rangle$ has been found, repeatedly apply $\hat{J}_- = \hat{J}_{1-} + \hat{J}_{2-}$ to give all the states $|j-1, m\rangle$, where m runs from $j-1$ to $1-j$.

The final picture is shown in Figure 3 below, for the combinations of $(j_1, j_2) = (1, 1)$ and $(1, 1/2)$. The number of states in each diagram is $(2j_1+1)(2j_2+1)$ – we have simply changed basis so the dimension of the space cannot change.

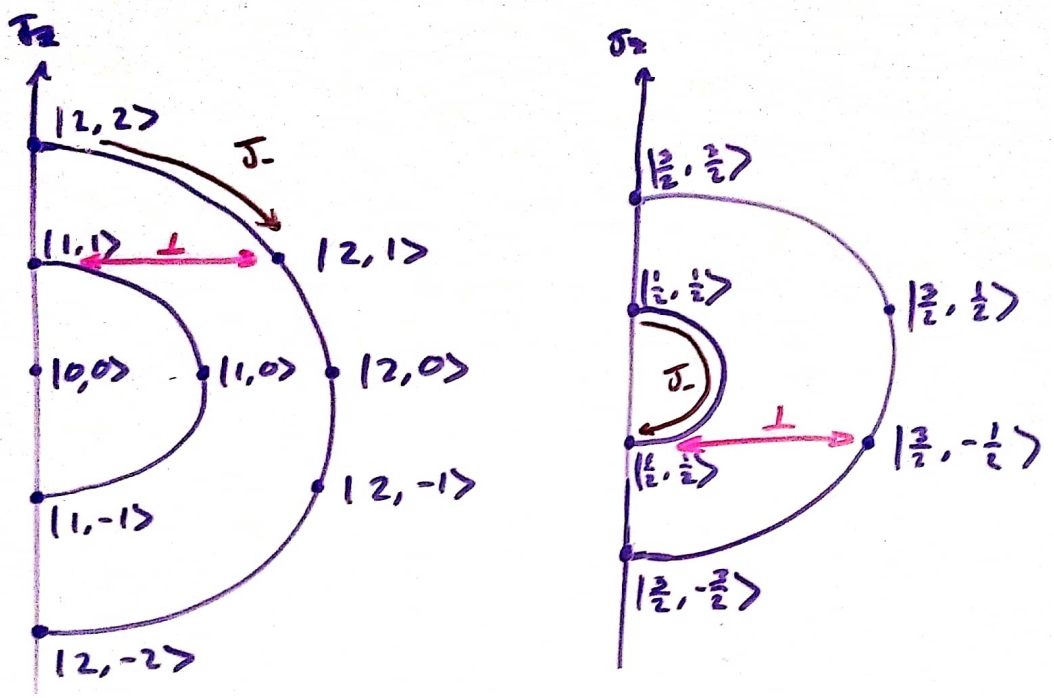

Figure 3 | Angular Momentum Eigenstates of Joint Systems. (a) shows the combined angular momentum eigenstates on combining a system with $(j_1, j_2) = (1, 1)$; (b) has $(j_1, j_2) = (1, 1/2)$. Example operations of $\hat{J}_- = \hat{J}_{1-} + \hat{J}_{2-}$ are shown in brown. All states in a given diagram are orthogonal to each other, but examples of states that must be constructed using this orthogonality are shown in pink.

[3] Don't be confused by the arrows drawn – orthogonality is meant in the Hilbert space sense!

4 Identical Particles

If two particles are indistinguishable, then the states $|\alpha_1;\alpha_2\rangle = |\alpha_1\rangle \otimes |\alpha_2\rangle$ (where α_i stands for *all* the quantum numbers of particle i) and $|\alpha_2;\alpha_1\rangle$ must be physically indistinguishable. That is to say that they are the same state of the projective Hilbert space, and thus may only differ by a phase $e^{i\phi}$. Exchanging twice gets back to the same state, so $e^{2i\phi} = 1$ and $\phi = 0$ or π. According to QFT, states representing a pair of indistinguishable particles with half-integer spin obtain a negative sign on exchange; integer spin has an unchanged state. Half-integer-spin particles are called fermions; integer-spin particles bosons. Two bosonic particles must be in the state $|\psi_b\rangle = \frac{1}{\sqrt{2}}(|\alpha_1;\alpha_2\rangle + |\alpha_2;\alpha_1\rangle)$. Two fermionic particles must be in the state $|\psi_f\rangle = \frac{1}{\sqrt{2}}(|\alpha_1;\alpha_2\rangle - |\alpha_2;\alpha_1\rangle)$. If $\alpha_1 = \alpha_2$, that is, the particles are in the exact same quantum state, $|\psi_f\rangle = 0$: two fermions cannot exist in the same quantum state (Pauli).

The above means that composite particles obey the statistics of their total spin: nucleons, consisting of three fermions, are themselves fermions and have half-integer spin; mesons consist of two fermions, and are bosons with integer spin.

4.1 Inelastic Collisions

Particle physics often involves particles colliding together to make some new ones. If two identical particles are created, their joint state will have a spatial part[4] and a spin part:

$$|\Psi\rangle = |\ell, m\rangle\,|s, \sigma\rangle$$

The former corresponds to the mutual rotation of the two particles about their centre of mass (orbital angular momentum); the latter corresponds to the orientation of their spins. Both $|\ell, m\rangle$ and $|s, \sigma\rangle$ may introduce a sign under exchange:

- For $|\ell, m\rangle$, as their position-space wavefunctions are the spherical harmonics $Y_\ell^m(\mathbf{X}_2 - \mathbf{X}_1)$, exchanging will introduce a sign $(-1)^\ell$
- For $|s, \sigma\rangle$, the exchange symmetry depends on its decomposition in $|s_1, \sigma_1\rangle$ and $|s_2, \sigma_2\rangle$.

If the two particles are fermions, then the *overall* sign change under exchange, the product of those from $|\ell, m\rangle$ *and* $|s, \sigma\rangle$, must be -1; for bosons the overall sign change must be $+1$. In other words, the exchange symmetry of the spatial and spin parts of the wavefunction must be opposite for fermions and equal for bosons. This provides constraints on the possible spatial states (i.e. values of ℓ) and spin states that two particles can be created in.

4.1.1 Intrinsic Parity

Each particle has an intrinsic parity, for instance an electron has $\eta_e = +1$, so it would look the same in a mirror. The overall parity of an ensemble of particles is the same before and after a reaction[5]. The overall parity is the product of the parities of the individual particles and the parity of the spatial wavefunction $(-1)^\ell$. This can provide a further constraint on the possible values of ℓ, and hence (via exchange symmetry) on the possible spin states.

[4] There will be a radial component to this but it is not relevant here.

[5] . . . usually.

5 Perturbation Theory

5.1 Time-Independent

For a Hamiltonian $\hat{H}$ which is similar to a familiar $\hat{H}_0$, we define the perturbation $\Delta\hat{H}$ by

$$\hat{H} \equiv \hat{H}_0 + \Delta\hat{H}$$

Rather than trying to solve this Hamiltonian, we instead try to solve the λ-parametrised

$$\hat{H}_\lambda = \hat{H}_0 + \lambda\Delta\hat{H}$$

with the assumption that the Hamiltonian and its eigenstates are analytic in λ. We write

$$\hat{H}_\lambda |E_\lambda\rangle = E(\lambda)|E_\lambda\rangle \qquad (\lambda\text{TISE})$$

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \qquad |E_\lambda\rangle = |\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \dots$$

Substituting $E(\lambda)$, $|E_\lambda\rangle$, and $\hat{H}_\lambda$ into (λTISE), and equating terms of the same order:

$$(\hat{H}_0 + \lambda\Delta\hat{H})\big(|\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \dots\big) = \big(E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots\big)\big(|\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \dots\big)$$

$$\hat{H}_0|\alpha\rangle = E^{(0)}|\alpha\rangle \qquad (\lambda^0)$$

$$\hat{H}_0|\beta\rangle + \Delta\hat{H}|n\rangle = E_n|\beta\rangle + E_n^{(1)}|n\rangle \qquad (\lambda^1)$$

$$\hat{H}_0|\gamma\rangle + \Delta\hat{H}|\beta\rangle = E_n|\gamma\rangle + E_n^{(1)}|\beta\rangle + E_n^{(2)}|n\rangle \qquad (\lambda^2)$$

- λ^0: $|\alpha\rangle$ is an eigenstate of the familiar Hamiltonian. We can rewrite $|\alpha\rangle = |n\rangle$ where this is an eigenstate of $\hat{H}_0$ energy $E^{(0)} = E_n$, and seek the perturbations from this state and its energy.
- λ^1: Acting with $\langle n|$ gives the first-order energy modification

  $$\underbrace{\langle n|\hat{H}_0}_{E_n\langle n|}|\beta\rangle + \left\langle\Delta\hat{H}\right\rangle = E_n\langle n|\beta\rangle + E_n^{(1)} \qquad \Rightarrow \qquad E_n^{(1)} = \left\langle\Delta\hat{H}\right\rangle$$

  Acting with $\langle m|$ st $\langle m|n\rangle = 0$ gives the components $\langle m|\beta\rangle$ of $|\beta\rangle$

  $$\underbrace{\langle m|\hat{H}_0}_{E_m\langle m|}|\beta\rangle + \langle m|\Delta\hat{H}|n\rangle = E_n\langle m|\beta\rangle \qquad \Rightarrow \qquad \langle m|\beta\rangle = \frac{\langle m|\Delta\hat{H}|n\rangle}{E_n - E_m}$$

  thus provided the eigenstates of $\hat{H}_0$ are non-degenerate, we have found $|\beta\rangle$ as the first order state correction, as $|\beta\rangle = \sum_{m\neq n}|m\rangle\langle m|\beta\rangle$ (n is excluded from the sum because $\langle n|\beta\rangle$ turns out to be 0).

- λ^2: Acting with $\langle n|$ gives:

$$E_n \langle n|\gamma\rangle + \langle n|\Delta\hat{H}|\beta\rangle = E_n \langle n|\gamma\rangle + \left\langle \Delta\hat{H} \right\rangle \underbrace{\langle n|\beta\rangle}_{0} + E_n^{(2)}$$

$$\Rightarrow \qquad E_n^{(2)} = \langle n|\Delta\hat{H}|\beta\rangle = \sum_{m\neq n} \frac{\langle m|\Delta\hat{H}|n\rangle \langle n|\Delta\hat{H}|m\rangle}{E_n - E_m} = \sum_{m\neq n} \frac{\left|\langle m|\Delta\hat{H}|n\rangle\right|^2}{E_n - E_m}$$

This is an important formula, as it is the order at which interesting physical effects usually come in. This is as high as we go in the perturbation series. Hence:

$$E_n(\lambda) = E_n + \lambda \langle n|\Delta\hat{H}|n\rangle + \lambda^2 \sum_{m\neq n} \frac{\left|\langle m|\Delta\hat{H}|n\rangle\right|^2}{E_n - E_m} + \mathcal{O}(\lambda^3)$$

For the case that $E_n \neq E_m \forall m \neq n$. The radius of convergence of this function is the smallest λ for which the perturbation causes the physical situation to functionally change.

Degenerate perturbation theory is a scam. For a degenerate set of states, the perturbed states will not have contributions from any state outside of that set. One can think of this as degenerate states having the smallest energy differences (0!) and so the smallest denominators in the state expansion for $\langle m|\beta\rangle$ above.

For problems with degenerate perturbation theory, one doesn't really need any perturbation theory. The dimension of the degenerate space is small enough that finding the perturbed states essentially reduces to a simple eigenvalue problem.

Some examples follow, first for the non-degenerate cases of 1D QHOs and the fine structure of hydrogen (this has degeneracy but that turns out not to matter), then for the degenerate cases of the linear and quadratic Stark effect.

5.1.1 Perturbed 1D Harmonic Oscillators

$$\hat{H}_\lambda = \frac{\hat{P}^2}{2m} + \frac{1}{2}m\omega^2\hat{X}^2 + \underbrace{\begin{cases} -\lambda m\omega^2 x_0 \hat{X} \\ \frac{1}{2}\lambda m\omega^2 \hat{X}^2 \end{cases}}_{\Delta\hat{H}}$$

In both cases the spectrum is in fact known, as the potentials can be rewritten in terms of those of other harmonic oscillators:

$$\frac{1}{2}m\omega^2\hat{X}^2 - \lambda m\omega^2 x_0 \hat{X} = \frac{1}{2}m\omega^2(\hat{X} - \lambda x_0)^2 - \frac{\lambda^2}{2}m\omega^2 x_0^2 \quad \Rightarrow E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{\lambda^2}{2}m\omega^2 x_0^2$$

$$\frac{1}{2}m\omega^2\hat{X}^2 + \frac{1}{2}\lambda m\omega^2\hat{X}^2 = \frac{1}{2}m\left(\omega\sqrt{1+\lambda}\right)^2\hat{X}^2 \quad \Rightarrow E_n = \left(n + \frac{1}{2}\right)\hbar\omega\sqrt{1+\lambda}$$

The first case is thus simply an oscillator which has been translated and lowered; the second is a strengthened oscillator. The radii of convergence are ∞ and 1, as when $\lambda = -1$ the second potential becomes unstable. We now see how perturbation theory gives the right expansions.

Translated:

$$E_n(\lambda) = \left(n + \frac{1}{2}\right)\hbar\omega - \lambda m\omega^2 x_0 \underbrace{\langle n|\hat{X}|n\rangle}_{0 \text{ by parity}} + \lambda^2 m^2\omega^4 x_0^2 \sum_{m\neq n} \frac{\left|\langle m|\hat{X}|n\rangle\right|^2}{(n-m)\hbar\omega} + \mathcal{O}(\lambda^3)$$

Using $\hat{X} = \sqrt{\hbar/2m\omega}(\hat{A} + \hat{A}^\dagger)$, we have

$$\langle m|\hat{X}|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}\delta_{m,n+1} + \sqrt{n}\delta_{m,n-1}\right)$$

$$\begin{aligned}\Rightarrow E_n(\lambda) &= \left(n+\frac{1}{2}\right)\hbar\omega + \lambda^2 m^2\omega^4 x_0^2\left(\frac{(n+1)}{-\hbar\omega} + \frac{n}{\hbar\omega}\right)\frac{\hbar}{2m\omega} + \mathcal{O}(\lambda^3)\\ &= \left(n+\frac{1}{2}\right)\hbar\omega - \frac{\lambda^2}{2}m\omega^2 x_0^2 + \mathcal{O}(\lambda^3)\end{aligned}$$

Strengthened: Similar (though more boring) calculations give:

$$E_n(\lambda) = \left(n+\frac{1}{2}\right)\hbar\omega\left(1 + \frac{\lambda}{2} - \frac{\lambda^2}{8} + \mathcal{O}(\lambda^3)\right)$$

which of course agrees with the expansion of $\sqrt{1+\lambda}$.

5.1.2 Hydrogen Fine Structure

This has never been examined (in astro), so maybe don't worry about the, ahem, *finer* details.

$$\hat{H}_0 = \frac{\hat{\mathbf{P}}^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0\hat{R}} \qquad \left(\mu = \tfrac{m_e m_p}{m_e+m_p}\right)$$

The "Gross Structure" energies are

$$E_n(0) = -\frac{1}{2}\mu c^2\left(\frac{\alpha}{n}\right)^2 \qquad \left(\alpha = \tfrac{e^2}{4\pi\epsilon_0\hbar c} \approx \tfrac{1}{137}\right)$$

These are independent of ℓ, m, spin etc. There are three effects contributing at order α^4:

- Relativistic KE
- Spin-Orbit Coupling
- Darwin term

Relativistic KE: $\hat{\mathbf{P}}^2/2\mu$ is a non-relativistic approximation to the kinetic energy from

$$\sqrt{\hat{\mathbf{P}}^2c^2 + \mu^2c^4} \approx \mu c^2 + \frac{\hat{\mathbf{P}}^2}{2\mu} - \underbrace{\frac{\hat{\mathbf{P}}^4}{8\mu^3c^2}}_{\Delta\hat{H}}$$

One might think that because the system is degenerate the second-order terms with $E_n - E_m$ on the denominator of the sum might blow up, however the numerator is also zero for degenerate states, as we now derive. Two degenerate states can be written $|n,\ell,m\rangle$ and $|n,\ell',m'\rangle$, with either $\ell \neq \ell'$ or $m \neq m'$. Also, it can easily be shown that $\left[\Delta\hat{H}, \hat{\mathbf{L}}^2\right] = \left[\Delta\hat{H}, \hat{L}_z\right] = 0$. Thus

$$\begin{aligned}0 &= \left\langle n,\ell',m'\right|\left(\Delta\hat{H}\hat{\mathbf{L}}^2 - \hat{\mathbf{L}}^2\Delta\hat{H}\right)\left|n,\ell,m\right\rangle & 0 &= \left\langle n,\ell',m'\right|\left(\Delta\hat{H}\hat{L}_z - \hat{L}_z\Delta\hat{H}\right)\left|n,\ell,m\right\rangle\\ &= (\ell(\ell+1) - \ell'(\ell'+1))\hbar^2\left\langle n,\ell',m'\right|\Delta\hat{H}\left|n,\ell,m\right\rangle & &= (m-m')\hbar\left\langle n,\ell',m'\right|\Delta\hat{H}\left|n,\ell,m\right\rangle\end{aligned}$$

Thus whether $\ell \neq \ell'$ or $m \neq m'$, we find that for different states[6] $|n\rangle \neq |m\rangle$, $\langle m|\Delta\hat{H}|n\rangle = 0$. As such, when we go back to the derivation in λ^2, we have $\langle n|\Delta\hat{H}|\beta\rangle = 0$ and thus $E_n^{(2)} = 0$, so the energy doesn't run away.

[6] with apologies for confusing use of the letter m

We now have to evaluate

$$E^{(1)}_{n\ell} = \left\langle n,\ell,m\middle|\Delta\hat{H}\middle|n,\ell,m\right\rangle = \left\langle \Delta\hat{H}\right\rangle$$

Firstly, note that we can write

$$\Delta\hat{H} \equiv -\frac{\hat{\mathbf{P}}^4}{8\mu^3c^2} = -\frac{\left(\hat{H}_0 - V(\hat{R})\right)^2}{2\mu c^2} = -\frac{\hat{H}_0^2 - \hat{H}_0V(\hat{R}) - V(\hat{R})\hat{H}_0 + V(\hat{R})^2}{2\mu c^2}$$

$$E^{(1)}_{n\ell} = -\frac{1}{2\mu c^2}\left(E_n^2 - 2E_n\left\langle V(\hat{R})\right\rangle + \left\langle V(\hat{R})^2\right\rangle\right)$$

From the Virial Theorem, $\langle V\rangle = -2\langle T\rangle = E_n - \langle T\rangle \Rightarrow \langle T\rangle = -E_n \Rightarrow \langle V\rangle = 2E_n$. Also, it can be shown that to first order,

$$\left\langle V(\hat{R})^2\right\rangle = \frac{4nE_n^2}{\ell+\frac{1}{2}}$$

and so on substituting into these two terms gives

$$E^{(1)}_{n\ell} = -\frac{E_n^2}{2\mu c^2}\left(\frac{4n}{\ell+\frac{1}{2}} - 3\right) = -\frac{1}{2}\mu c^2\left(\frac{n}{\ell+\frac{1}{2}} - \frac{3}{4}\right)\frac{\alpha^4}{n^4}$$

where we find that the degeneracy between states of different ℓ has been lifted.

Spin-Orbit Coupling and the Darwin Term. An electron moving at relativistic speeds will see the electric field be converted to magnetic field, and thus feel a perturbative force, with a potential energy $-\mathbf{m_e}\cdot\mathbf{B}$. The dipole moment of the electron $\mathbf{m_e} = e\mathbf{S}/2\mu$, and the $\mathbf{B}$ field can be found from:

$$\mathbf{B} = \gamma\mathbf{v}\times\mathbf{E} = \frac{\mathbf{p}}{\mu}\times\frac{e}{4\pi\epsilon_0}\frac{\mathbf{x}}{|\mathbf{x}|^3} = -\frac{e}{4\pi\mu\epsilon_0}\frac{\mathbf{L}}{R^3} \;\Rightarrow\; \Delta\hat{H} = \frac{e^2}{8\pi\mu^2\epsilon_0}\frac{\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}}{R^3}$$

$\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$ can be written $\frac{1}{2}\left(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right)$. Clearly we have $\left\langle\Delta\hat{H}\right\rangle = 0$ if $\ell = 0$, so we are just considering $\ell \geq 1$[7]. For convenience we relabel the state $|n,\ell,m\rangle\otimes|\updownarrow\rangle \to |n,j,m_j,\ell\rangle$, where the possible values for j are $\ell\pm 1/2$ (no absolute signs because $\ell\geq 1$). The remaining steps in the calculation are not particularly insightful, so the answer is just given below:

$$E^{(1),\mathrm{SO}}_{nj\ell} = -\frac{1}{2}\alpha^4\mu c^2\frac{1}{2n^3\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}\begin{cases}\ell & \text{if } j=\ell+\frac{1}{2}\\ -\ell-1 & \text{if } j=\ell-\frac{1}{2}\end{cases}$$

Overall we then end up with

$$E^{(1)}_{n,j} = -\frac{1}{2}\alpha^2\mu c^2\left[\frac{1}{n^2} - \frac{\alpha^2}{n^3}\left(\frac{3}{4n} - \frac{1}{j+\frac{1}{2}}\right)\right] + \mathcal{O}(\alpha^6)$$

[7] However, if $\ell = 0$, the Darwin term then applies, and this turns out to give the exact same energy

5.1.3 Stark Effect

When a H atom is placed in a small constant homogeneous external $\mathbf{E}$ field, we have

$$\Delta\hat{H} = -e\Phi = e\mathbf{E}\cdot\mathbf{X} = eEX_3$$

where wlog we have put $\mathbf{E} \parallel \hat{\mathbf{z}}$. In general, atoms are distorted by electric fields into dipoles $\mathbf{D}$, the energy of which is

$$E_{\text{dip}} = -\frac{1}{2}\mathbf{D}\cdot\mathbf{E}$$

It will be useful to consider parity operations, under which $X_3 \to -X_3$ and $|n,\ell,m\rangle \to (-1)^\ell |n,\ell,m\rangle$. For example $\langle 100|X_3|100\rangle = 0$, as the integral is odd over even bounds ($\mathbb{R}^3$). Thus at first order the ground state is unaffected. The first excited state has quadruple degeneracy:

$$\{|200\rangle, |211\rangle, |210\rangle, |21-1\rangle\}$$

Again, by parity we have $\langle 2\ell 0|X_3|2\ell 0\rangle = 0$ as the integrand is odd. Also, $\left[\hat{L}_z, X_3\right] = 0$, so

$$0 = \left\langle 200\middle|\left(\hat{L}_z X_3 - X_3\hat{L}_z\right)\middle|21\pm 1\right\rangle = \mp\hbar\langle 200|X_3|21\pm 1\rangle$$

so $\langle 200|X_3|21\pm 1\rangle = 0$. The only non-zero matrix elements are then $\langle 200|X_3|210\rangle$ and its cc, which can be shown to be equal to $-3a_0$. The perturbation can then be written

$$\left[\Delta\hat{H}_{n=2}\right] = -3eEa_0\begin{pmatrix} 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{pmatrix}$$

To recap, all of the $n=2$ states are eigenstates of the unperturbed Hamiltonian $\hat{H}_0$ with the same energy eigenvalue, as is any linear combination of these states. However, only those states which are eigenstates of $\Delta\hat{H}_{n=2}$ (represented by the above matrix) will be eigenstates of the new overall Hamiltonian. The eigenstates of $\Delta\hat{H}_{n=2}$ are

$$\frac{|200\rangle \pm |210\rangle}{\sqrt{2}}, |211\rangle, |21-1\rangle \qquad\qquad E_2^{(1)} = \mp 3e|\mathbf{E}|a_0, 0, 0$$

and so these are the eigenstates of the overall perturbed Hamiltonian. There will thus be a splitting in the energies as the $\ell = 0$ states mix together. The splitting is linear in $|\mathbf{E}|$, so this is the linear Stark effect.

Although unperturbed at first order, the second-order perturbation to the ground state energy E_1 is non-zero. No states are degenerate with $|100\rangle$, so we can use non-degenerate perturbation theory again. Applying the 2nd-order formula,

$$E_1^{(2)} = \sum_{n=2}^{\infty}\sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell} e^2|\mathbf{E}|^2\frac{|\langle n,\ell,m|X_3|100\rangle|^2}{E_1 - E_n}$$

It turns out that only terms with $\ell = 1$ and $m = 0$ will contribute to the sum, so

$$E_1^{(2)} = e^2|\mathbf{E}|^2\sum_{n=2}^{\infty}\frac{|\langle n,1,0|X_3|100\rangle|^2}{E_1 - E_n}$$

which is more tractable; it turns out to be equal to $-\frac{9}{4}a_0^3|\mathbf{E}|^2$

5.2 Time-Dependent

Time-dependent perturbation theory usually arises from a quiescent system being perturbed by a thing, leading to

$$\hat{H}_0 \to \hat{H}_0 + \Delta(t)$$

Also, we are more interested in the transition rates between the eigenstates of $\hat{H}_0$, denoted $\{|n\rangle\}$.

If $\hat{H}_0$ were the entire Hamiltonian, the time evolution of a general state $|\psi(0)\rangle = \sum_n a_n |n\rangle$ would be

$$|\psi(t)\rangle = \sum_n a_n e^{-iE_n t/\hbar} |n\rangle$$

for constant a_n and $\hat{H}_0 |n\rangle = E_n |n\rangle$. However, the perturbation means this is not what it would be. We instead write

$$|\psi(t)\rangle = \sum_n a_n(t) e^{-iE_n t/\hbar} |n\rangle$$

the "interaction picture" state, where $a_n(t)$ are now time-dependent quantities, representing the probability amplitudes for each state at a time t. From the TDSE,

$$\begin{aligned} i\hbar \sum \left(\dot{a}_n - \frac{iE_n}{\hbar} a_n \right) e^{-iE_n t/\hbar} |n\rangle &= \sum (a_n E_n + a_n \Delta(t)) e^{-iE_n t/\hbar} |n\rangle \\ (i\hbar \dot{a}_k + a_k E_k) e^{-iE_k t/\hbar} &= a_k E_k e^{-iE_k t/\hbar} + \sum a_n e^{-iE_n t/\hbar} \langle k|\Delta|n\rangle \\ \dot{a}_k &= -\frac{i}{\hbar} \sum a_n(t) e^{i(E_k - E_n)t/\hbar} \langle k|\Delta|n\rangle \end{aligned}$$

where $\dot{a}_k \equiv \mathrm{d}a_k/\mathrm{d}t$ and we have multiplied by $\langle k|$ in the second step. For a small perturbation the quantity $\langle k|\Delta|n\rangle$ is expected to be small. Integrating, we find

$$a_k(t) = a_k(t_0) - \frac{i}{\hbar} \int_{t_0}^{t} \sum a_n(t') e^{i(E_k - E_n)t'/\hbar} \langle k|\Delta(t')|n\rangle \, \mathrm{d}t'$$

which is no more tractable but easier to approximate. Ordinarily we would Matryoshka this equation into itself forever, giving a Dyson series, but this would give ever larger products of $\langle k|\Delta(t_i)|n\rangle$, and as this is small we decide not to do this and instead approximate $a_n(t') \approx a_n(t_0)$. This gives

$$a_k(t) \approx a_k(t_0) - \frac{i}{\hbar} \int_{t_0}^{t} \sum a_n(t_0) e^{i\omega_{kn} t'} \langle k|\Delta(t')|n\rangle \, \mathrm{d}t'$$

where we have defined $\omega_{kn} \equiv (E_k - E_n)/\hbar$. Now suppose the system starts at t_0 in an eigenstate $|m\rangle \neq |k\rangle$, so that $a_n(t_0) = \delta_{nm}$. The integral becomes:

$$\boxed{a_k(t) = -\frac{i}{\hbar} \int_{t_0}^{t} e^{i\omega_{km} t'} \langle k|\Delta(t')|m\rangle \, \mathrm{d}t'}$$

which is about as far as we can go without specifying a $\Delta(t)$.

5.2.1 Forced QHO $\Delta(t) = -F_0\hat{X}e^{-t^2/\tau^2}$.

Suppose our system starts in the state $|0\rangle$ at $t = -\infty$. For other excited states $|k\rangle$ at large times $t = \infty$, we have

$$\begin{aligned} a_k(\infty) &= -\frac{i}{\hbar}\int_{-\infty}^{\infty} e^{i\omega_{k0}t'}\,\langle k|-F_0\hat{X}e^{-t'^2/\tau^2}|0\rangle\,\mathrm{d}t' \\ &= \frac{iF_0}{\hbar}\,\langle k|\hat{X}|0\rangle\int_{-\infty}^{\infty} e^{i\omega_{k0}t'}e^{-t'^2/\tau^2}\,\mathrm{d}t' \end{aligned}$$

Writing $\hat{X}$ in terms of ladder operators and evaluating the integral,

$$\begin{aligned} &= \frac{iF_0}{\hbar}\left[\sqrt{\frac{\hbar}{2m\omega}}\left\langle k\middle|\left(\hat{A}+\hat{A}^\dagger\right)\middle|0\right\rangle\right]\left[\sqrt{\pi}\tau e^{-\omega_{k0}^2\tau^2/4}\right] \\ &= \frac{iF_0}{\hbar}\sqrt{\frac{\pi\hbar}{2m\omega}}\delta_{k1}\tau e^{-\omega_{10}^2\tau^2/4} \end{aligned}$$

So there is no probability (to first order) of excitation to anything but the first excited state, and the probability of reaching that state is

$$|a_1(\infty)|^2 = \frac{F_0^2\pi}{2m\hbar\omega}\tau^2 e^{-\omega_{10}^2\tau^2/2}$$

which is largest if $\tau \sim 1/\omega_{10}$.

5.2.2 Switching on a time-independent perturbation:

$$\Delta(t) = \begin{cases} 0 & t \le 0 \\ \Delta(\hat{X}, \hat{P}, \ldots, \not{t}) & t > 0 \end{cases}$$

Suppose now that $|\psi(t<0)\rangle = |m\rangle$. For $a_{k\neq m}$, we find

$$\begin{aligned} a_k(t) &= -\frac{i}{\hbar}\int_0^t e^{i\omega_{km}t'}\,\langle k|\Delta(\not{t})|m\rangle\,\mathrm{d}t' \\ &= -\frac{1}{\hbar\omega_{km}}\left(e^{i\omega_{km}t}-1\right)\langle k|\Delta|m\rangle \\ |a_k(t)|^2 &= \frac{4|\,\langle k|\Delta|m\rangle|^2}{\hbar^2}\frac{\sin^2(\omega_{km}t/2)}{\omega_{km}^2} \end{aligned}$$

We would like to find how this depends on what the state $|k\rangle$ is at large times. First consider the function $\sin^2(\omega t/2)/\omega^2 t$, which is the second fraction above divided by t. Its integral over all ω is equal to $\pi/2$ (for any t), and for any $\omega \neq 0$, its value for large t tends to 0. Thus it must be equal to $(\pi/2)\delta(\omega)$. We can then write:

$$\lim_{t\to\infty}|a_k(t)|^2 = \frac{4|\,\langle k|\Delta|m\rangle|^2}{\hbar^2}t\frac{\pi}{2}\delta(\omega_{km})$$

And thus the transition rate at large times is

$$\Gamma_{mk} = \frac{2\pi}{\hbar^2}|\,\langle k|\Delta|m\rangle|^2\delta(\omega_{km}) = \frac{2\pi}{\hbar}|\,\langle k|\Delta|m\rangle|^2\delta(E_k - E_m)$$

where we have used $\delta(x/\hbar) = \hbar\delta(x)$ to convert between delta functions of ω and E. So for a time-independent perturbation, transitions can only be between degenerate states.

5.2.3 Monochromatic Perturbations:

$$\Delta(t) = \begin{cases} 0 & t \leq 0 \\ \Delta e^{-i\omega t} + \Delta^\dagger e^{i\omega t} & t > 0 \end{cases}$$

for some Δ which is indep of time. As always, beginning in the state $|m\rangle$, we find

$$\begin{aligned} a_k(t) &= -\frac{i}{\hbar}\left[\langle k|\Delta|m\rangle \int_0^t e^{i(\omega_{km}-\omega)t'}\,\mathrm{d}t' + \langle k|\Delta^\dagger|m\rangle \int_0^t e^{i(\omega_{km}+\omega)t'}\,\mathrm{d}t' \right] \\ &= -\frac{\langle k|\Delta|m\rangle}{\hbar(\omega_{km}-\omega)}\left[e^{i(\omega_{km}-\omega)t}-1\right] - \frac{\langle k|\Delta^\dagger|m\rangle}{\hbar(\omega_{km}+\omega)}\left[e^{i(\omega_{km}+\omega)t}-1\right] \end{aligned}$$

We expect that transitions will only take place when $\omega = \pm\omega_{km}$, corresponding to absorption or stimulated emission respectively. Indeed one term will begin to dominate at large times, so we will have either

$$|a_k(t)|^2 = \frac{4}{\hbar^2}\frac{\left|\langle k|\Delta^{(\dagger)}|m\rangle\right|^2}{(\omega_{km}\mp\omega)^2}\sin^2\left(\frac{(\omega_{km}\mp\omega)t}{2}\right)$$

and so at large times, from similar considerations about δ functions in the previous subsubsection, we will obtain

$$\Gamma_{mk} = \frac{2\pi}{\hbar}\left|\langle k|\Delta^{(\dagger)}|m\rangle\right|^2\delta(E_k - E_m \mp \hbar\omega) \qquad \text{(Golden)}$$

known as Fermi's Golden Rule. This means that *purely* monochromatic light can't cause transitions between bound states (at rest); to cause transitions we therefore need to use a range of frequencies.

Depending on the form of Δ, there may be some selection rules that apply, making certain transitions impossible. Parity considerations can often be useful in deciding this.

6 Interpreting QM

[Note: The content in this section has only been examined in Astro once (2020, P4, Q6X(i)), and even then it was only about the basics, and only in the smaller first half of the question. As such, I haven't bothered to painstakingly understand and type up everything the lecturer talked about (much of which, like von Neumann entropy, wasn't in the Schedules).]

6.1 Density Operators

When the state of a system is uncertain, such as with 10^{23} atoms, or with a non-isolated system, we need a new framework. Rather than describing the system with a state vector, we describe it using a *density operator* ρ. If the *Classical* probabilities of the system being in state $|\alpha\rangle$ are p_α, the density operator is written

$$\rho = \sum_\alpha p_\alpha\,|\alpha\rangle\langle\alpha|$$

This is **not** to say that the system is in the state

$$|\phi\rangle = \sum_\alpha \sqrt{p_\alpha}\,|\alpha\rangle$$

The system is **not** in a specific state, we *don't know what state the particle is in.* All we know is the *probabilities* that the particle is in a given state. *Each of those states* will in turn have particular probabilities of giving particular results on measuring particular properties, but we don't generally know what the state is. In this sense, the probabilities are not objective, they are practical. In the special case that we *do* know what state the system is in (say $|\chi\rangle$), the density operator is then just $\rho = |\chi\rangle\langle\chi|$ and said to be *pure.*

ρ is defined by being Hermitian ($\rho = \rho^\dagger$), non-negative ($\langle\psi|\rho|\psi\rangle \geq 0 \; \forall \, |\psi\rangle$), and complete ($\operatorname{Tr}\rho = 1$). This corresponds to probabilities being real, non-negative, and summing to 1. Any operator satisfying these is a valid density operator. Note that the *probabilities* p_α are generally different from the density operator's *eigenvalues*, which do not usually have much significance, though in order for ρ to be non-negative, its eigenvalues must all be positive, and for $\operatorname{Tr}\rho = 1$, they must all be between 0 and 1.

ρ is pure $\iff \rho^2 = \rho$. To prove this, write $\rho = |\chi\rangle\langle\chi|$. Then

$$\rho^2 = |\chi\rangle\langle\chi|\,|\chi\rangle\langle\chi| = |\chi\rangle\langle\chi| = \rho$$

so ρ pure $\Rightarrow \rho^2 = \rho$. For the converse, $\rho^2 = \rho \Rightarrow \rho(\rho - 1) = 0$, so ρ has eigenvalues that are all either 1 or 0. But $\operatorname{Tr}\rho = 1$, so exactly one of its eigenvalues are 1 and the rest 0. Thus $\rho = |\chi\rangle\langle\chi|$ with eigenstate $|\chi\rangle$.

6.2 Trace of Operators

For a matrix $\mathbf{A}$, the trace is given by the sum of its eigenvalues λ_i. If $\mathbf{A}$ is Hermitian, then the eigenvectors can be chosen $\{\mathbf{v}_i\}$ orthonormal and form an orthonormal basis. As such the quantity

$$\sum_i \mathbf{v}_i^\dagger \mathbf{A} \mathbf{v}_i = \sum_i \lambda_i \mathbf{v}_i^\dagger \mathbf{v}_i = \sum_i \lambda_i = \operatorname{Tr}\mathbf{A}$$

Also, the trace is conserved under a similarity transformation $\mathbf{A} \to \mathbf{U}^\dagger\mathbf{A}\mathbf{U}$ for general unitary $\mathbf{U}$, as $\operatorname{Tr}\left(\mathbf{U}^\dagger\mathbf{A}\mathbf{U}\right) = \operatorname{Tr}\left(\mathbf{U}\mathbf{U}^\dagger\mathbf{A}\right) = \operatorname{Tr}\mathbf{A}$. Thus

$$\operatorname{Tr}\mathbf{A} = \operatorname{Tr}\left(\mathbf{U}^\dagger\mathbf{A}\mathbf{U}\right) = \sum_i \mathbf{v}_i^\dagger \mathbf{U}^\dagger \mathbf{A}\mathbf{U}\mathbf{v}_i = \operatorname{Tr}\left(\mathbf{u}_i^\dagger \mathbf{A}\mathbf{u}_i\right)$$

where the $\mathbf{u}_i = \mathbf{U}\mathbf{v}_i$ are *not* eigenvalues of $\mathbf{A}$, but are simply members of some general orthonormal basis. In a similar way, the trace of an operator $\hat{Q}$ is

$$\operatorname{Tr}\hat{Q} = \sum_\alpha \langle\alpha|\hat{Q}|\alpha\rangle$$

for *any* orthonormal basis $\{|\alpha\rangle\}$. Also, the trace is linear.

Expectation values can also be evaluated using the trace. For a system in a definite state $|\psi\rangle$ and an orthonormal basis $\{|\beta\rangle\}$, the expectation value of an operator $\hat{Q}$ is given by

$$\left\langle\hat{Q}\right\rangle_\psi = \langle\psi|\hat{Q}|\psi\rangle = \sum_\beta \langle\psi|\hat{Q}|\beta\rangle\langle\beta|\psi\rangle = \sum_\beta \langle\beta|\psi\rangle\,\langle\psi|\hat{Q}|\beta\rangle = \operatorname{Tr}\left(|\psi\rangle\langle\psi|\,\hat{Q}\right)$$

For an observable $\hat{Q}$, the expectation value is naturally $\sum_\alpha p_\alpha \langle\alpha|\hat{Q}|\alpha\rangle$. This can be written in terms of the density operator:

$$\left\langle\hat{Q}\right\rangle = \sum_\alpha p_\alpha \langle\alpha|\hat{Q}|\alpha\rangle = \sum_\alpha p_\alpha \operatorname{Tr}\left(|\alpha\rangle\langle\alpha|\,\hat{Q}\right) = \operatorname{Tr}\left(\sum_\alpha p_\alpha |\alpha\rangle\langle\alpha|\,\hat{Q}\right) = \operatorname{Tr}\left(\rho\hat{Q}\right)$$

where we have used the linearity of Tr.

6.3 Two-Spin System

Consider the basis $\{|\uparrow\rangle, |\downarrow\rangle\}$, corresponding to spins maximally aligned along $\hat{\mathbf{z}}$. If the system is definitely in $|\uparrow\rangle$, the density operator is $\rho = |\uparrow\rangle\langle\uparrow|$. If the system is equally likely to be in either state, the density operator becomes

$$\rho = \frac{1}{2}(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|) = \frac{1}{2}$$

This could equally be written as $\frac{1}{2}(|\uparrow_x\rangle\langle\uparrow_x| + |\downarrow_x\rangle\langle\downarrow_x|)$, which is in the basis of aligned spins along $\hat{\mathbf{x}}$ and also equal to 1/2. This density operator admits no information at all about the system, as all states are equally likely.

Any 2×2 Hermitian matrix is a linear combination of $\{I_{2\times 2}, \sigma_i\}$, so a general *density matrix* (a matrix representation of the *density operator* in this two-dimensional vector space, basis $\{|\uparrow\rangle, |\downarrow\rangle\}$) describing the orientation of the spin of a spin-$\frac{1}{2}$ particle is

$$\rho = \frac{1}{2}(I_{2\times 2} + \mathbf{b}\cdot\boldsymbol{\sigma}) = \frac{1}{2}\begin{pmatrix} 1+b_z & b_x - ib_y \\ b_x + ib_y & 1-b_z \end{pmatrix}$$

for some real vector $\mathbf{b}$ which we constrain below. The factor of $\frac{1}{2}$ is to ensure that $\operatorname{Tr}\rho = 1$; all the σ_i are traceless. The determinant of this density matrix, equal to the *product* of the eigenvalues, is $\frac{1}{4}\left(1 - |\mathbf{b}|^2\right)$, but as all the eigenvalues of the density matrix must be between 0 and 1, the determinant must also be between 0 and 1. As such, we require $|\mathbf{b}| \leq 1$, defining a *Bloch Ball* of possible values of $\mathbf{b}$ corresponding to possible density operators to describe this system.

- $|\mathbf{b}| = 1$: the determinant is 0, so the eigenvalues are 0 and 1 and ρ is pure
- $|\mathbf{b}| = 0$: $\rho = \frac{1}{2}I_{2\times 2}$ and any pair orthogonal states (say $|\uparrow\rangle$ and $|\downarrow\rangle$, or $|\uparrow_x\rangle$ and $|\downarrow_x\rangle$) are equally likely
- $0 < |\mathbf{b}| < 1$: the state is impure (*mixed*), but preferentially aligned along $\mathbf{b}$

6.4 Entanglement

Suppose a system has multiple parts described by $\mathcal{H}_1$ and $\mathcal{H}_2$. A state $|\Psi\rangle \in \mathcal{H}_1 \otimes \mathcal{H}_2$ is said to be *entangled* if it cannot be written $|\Psi\rangle = |\phi\rangle \otimes |\chi\rangle$ for $|\phi\rangle \in \mathcal{H}_1$ and $|\chi\rangle \in \mathcal{H}_2$. For a state to be entangled means that its subsystems are correlated, and in a sense "talking" to one another.

It can sometimes be difficult to determine whether a state can be written in this way or not. It becomes easier with *reduced density operators*, which involve taking the trace of the *joint* density operator over just $\mathcal{H}_2$, say (that is, multiplying on both sides by an orthonormal basis of *this* space and summing). If the system is entangled, the reduced density matrices will be mixed, and vice versa.