Foundations of Quantum Mechanics.

Single-particle Schrödinger Equation.

$H\Psi(\underline{r},t) = i\hbar \frac{\partial \Psi}{\partial t}$. $H = T + V = -\frac{\hbar^2}{2m}\nabla^2 + V(\underline{r})$

For a stationary state, $\Psi(\underline{r},t) = e^{-iEt/\hbar}\psi(\underline{r})$, $H\psi = E\psi$.

Ψ and ψ are wavefunctions in coordinate space.

Momentum Space Wavefunction.

Suppose first that $V=0$. A trivial solution for $\psi(\underline{r})$ is: $e^{i\underline{p}\cdot\underline{r}/\hbar}$ with $E = \frac{\underline{p}^2}{2m}$.

This corresponds to a state where the particle's momentum is known to be $\underline{p}$:

$\underbrace{(-i\hbar\underline{\nabla})}_{\text{operator corresponding to momentum}} e^{i\underline{p}\cdot\underline{r}/\hbar} = \underline{p}e^{i\underline{p}\cdot\underline{r}/\hbar}$. So $e^{i\underline{p}\cdot\underline{r}/\hbar}$ is an eigenfunction of the momentum operator, with eigenvalue $\underline{p}$.

For $V \neq 0$, these plane waves are not solutions of $H\psi = E\psi$, but we can build up solutions as superpositions of them: $\psi(\underline{r}) = \frac{1}{(2\pi\hbar)^{3/2}}\int d^3p\, \varphi(\underline{p})\, e^{i\underline{p}\cdot\underline{r}/\hbar}$;

ie we write $\psi(\underline{r})$ as a Fourier Transform.

Reminder about Fourier Transforms: applies to almost any function that does not grow too fast when $|\underline{r}| \to \infty$. The essential fact is: $\int dx\, e^{ikx} = 2\pi\,\delta(k)$.

Also, $\delta(f(k)) = \sum_i \delta(k-k_i)\cdot\frac{1}{|f'(k_i)|}$, where k_i are the zeroes of f.

In particular, $\delta(ak) = \frac{1}{|a|}\delta(k)$

From this, we get: $\varphi(\underline{p}) = \frac{1}{(2\pi\hbar)^{3/2}}\int d^3r\, \psi(\underline{r})\, e^{-i\underline{p}\cdot\underline{r}/\hbar}$

To show this: the RHS $= \frac{1}{(2\pi\hbar)^{3/2}}\int d^3r \left(\frac{1}{(2\pi\hbar)^{3/2}}\int d^3p'\, \varphi(\underline{p}')\, e^{i\underline{p}'\cdot\underline{r}/\hbar}\right) e^{-i\underline{p}\cdot\underline{r}/\hbar}$

$= \frac{1}{(2\pi\hbar)^3}\int d^3p'\, \varphi(\underline{p}')\int d^3r\, e^{i(\underline{p}'-\underline{p})\cdot\underline{r}/\hbar} = \frac{1}{(2\pi\hbar)^3}\int d^3p'\, \varphi(\underline{p}')\,(2\pi\hbar)^3\,\delta^{(3)}(\underline{p}-\underline{p}') = \varphi(\underline{p})$

If ψ is normalised to unity, then so is φ. (Ie, $\int d^3r\, |\psi(\underline{r})|^2 = 1 \iff \int d^3p\, |\varphi(\underline{p})|^2 = 1$)

To show this: $\int d^3p\, |\varphi(\underline{p})|^2 = \int d^3p\, \varphi(\underline{p})\varphi^*(\underline{p}) = \frac{1}{(2\pi\hbar)^3}\int d^3p \int d^3r_1 d^3r_2\, \psi(\underline{r}_1)\psi^*(\underline{r}_2)\, e^{-i\underline{p}\cdot(\underline{r}_1-\underline{r}_2)/\hbar}$

$= \int d^3r_1 d^3r_2\, \psi(\underline{r}_1)\psi^*(\underline{r}_2)\,\delta^{(3)}(\underline{r}_1-\underline{r}_2)$

$|\psi(\underline{r})|^2 d^3r$ = the probability that a measurement of the particle's coordinate gives an answer within the infinitessimal volume element of coordinate space in the neighbourhood of $\underline{r}$.

$|\varphi(\underline{p})|^2 d^3p$ = ——— " ——— momentum

——— " ———

momentum ——— " ——— $\underline{p}$.

This follows naturally because of the symmetry between ψ and φ in the previous equations - if we have normalised ψ to unity so that there is unit probability of getting some answer for the measurement of $\underline{r}$, then there is also unit probability of getting some answer for $\underline{p}$. This is why we introduced the factor $1/(2\pi\hbar)^{3/2}$.

Knowledge of either ψ or φ provides a complete description description of the particle's state.

Ψ and φ are defined only for stationary states. More generally, we define
$\Phi(\underline{p},t) = \frac{1}{(2\pi\hbar)^{3/2}} \int d^3r\, \Psi(\underline{r},t)\, e^{-i\underline{p}\cdot\underline{r}/\hbar}$.

Analogous situation: in classical mechanics, vectors can be represented in different ways in different coordinate systems. Any representation gives complete information about the vectors. We write "vector equations", independent of the coordinate system.

Example: $m\ddot{\underline{r}} = \underline{F}$, but they take different concrete form in different representations.

Similarly, in Quantum Mechanics, we can think of the physical states of a system independently of what sort of wavefunction we choose to represent them. We write equations that are true in any representations, but take different concrete forms in different representations - both the wavefunctions and the operator.

Example: Suppose that, in the coordinate-space representation, $H = -\frac{\hbar^2}{2m}\nabla^2 + \underline{\xi}\cdot\underline{r}$, then in momentum-space, $H = \frac{p^2}{2m} + \underline{\xi}\cdot\left(i\hbar\frac{\partial}{\partial \underline{p}}\right)$.
For then the momentum-space realisation of the Schrödinger equation is: $\left(\frac{p^2}{2m} + \underline{\xi}\cdot i\hbar\frac{\partial}{\partial \underline{p}}\right)\varphi(\underline{p}) = E\varphi(\underline{p})$, which is derived from $\left(-\frac{\hbar^2}{2m}\nabla^2 + \underline{\xi}\cdot\underline{r}\right)\Psi(\underline{r}) = E\Psi(\underline{r})$ by applying to it: $\frac{1}{(2\pi\hbar)^{3/2}}\int d^3r\, e^{i\underline{p}\cdot\underline{r}/\hbar}$.

Bras and Kets.

Introduce a ket $|m\rangle$ which corresponds to a state. m is a label, or a set of labels.
Superposition principle: if $|m\rangle$ and $|n\rangle$ are two possible states of a given system, then so is $|X\rangle = \lambda|m\rangle + \mu|n\rangle$, where λ, μ are complex numbers.

If, in coordinate-space, $|m\rangle$ and $|n\rangle$ are described by $\Psi_m(\underline{r},t)$ and $\Psi_n(\underline{r},t)$, then $|X\rangle$ is by definition described by $\lambda\Psi_m(\underline{r},t) + \mu\Psi_n(\underline{r},t)$; by applying $\int d^3r\, e^{i\underline{p}\cdot\underline{r}/\hbar}$ to the wavefunctions, we get a precisely similar situation between the three momentum-space wavefunctions.

The various states $|m\rangle$ accessible to a system span an abstract vector space - an (infinite-dimensional) Hilbert space.
Define a dual space of bras. Write the bra corresponding to the ket $|m\rangle$ as $\langle m|$.
By definition, $\langle X| = \lambda^*\langle m| + \mu^*\langle n|$.
For any bra and any ket, define a scalar product which is a (complex) number, by
$\langle m|n\rangle = \int d^3r\, \Psi_m^*(\underline{r},t)\,\Psi_n(\underline{r},t) = \int d^3p\, \Phi_m^*(\underline{p},t)\,\Phi_n(\underline{p},t) = \langle n|m\rangle^*$.
Evidently, $\langle m|m\rangle = \int d^3r\, |\Psi_m(\underline{r},t)|^2 = \int d^3p\, |\Phi_m(\underline{p},t)|^2 \geq 0$.
Actually, this is >0, because if $\Psi_m = 0$ everywhere, it does not describe a state.
If $\langle m|m\rangle = C^2$, then by dividing Ψ or Φ by $Ce^{i\delta}$ for any real constant δ, we obtain a new ket such that $\langle m|m\rangle = 1$, and the state is "normalised to unity."
For any constant λ, both $|m\rangle$ and $\lambda|m\rangle$ describe the same physics.
If $\langle m|n\rangle = 0 = \langle n|m\rangle$, we say that $|m\rangle$ and $|n\rangle$ are orthogonal.

Linear Operators.

Operators map $\left\{\begin{smallmatrix}\text{bras}\\ \text{kets}\end{smallmatrix}\right\}$ into other $\left\{\begin{smallmatrix}\text{bras}\\ \text{kets}\end{smallmatrix}\right\}$. We consider linear operators:

$L|x\rangle = L(\lambda|m\rangle + \mu|n\rangle) = \lambda L|m\rangle + \mu L|n\rangle$.

$\langle x|L = (\lambda^*\langle m| + \mu^*\langle n|)L = \lambda^*\langle m|L^* + \mu^*\langle n|L$

Define a sum of operators $(L+M)$ such that for any ket $|\rangle$, $(L+M)|\rangle = L|\rangle + M|\rangle$ and $\langle|(L+M) = \langle|L + \langle|M$, and a product, $LM|\rangle = L(M|\rangle)$ and $\langle|LM = (\langle|L)M$.

Usually $LM \neq ML$.

Example of a linear operator: $|b\rangle\langle a|$, defined such that when we apply it to any ket $|\rangle$, $(|b\rangle\langle a|)|\rangle = |b\rangle.\langle a|\rangle$, ie, the ket $|b\rangle$ times the number $\langle a|\rangle$.
Also, $\langle|(|b\rangle\langle a|) = \langle|b\rangle.\langle a|$, ie, the number $\langle|b\rangle$ times the bra $\langle a|$.

Orthonormal Basis.

Select a set of kets such that $\langle n|m\rangle = \delta_{nm} = \langle m|n\rangle$. Suppose that the set is complete: ie, any ket $|\alpha\rangle$ can be expanded as a linear combination: $|\alpha\rangle = \sum_r \alpha_r |r\rangle$.

Then, $\langle n|\alpha\rangle = \sum_r \alpha_r \langle n|r\rangle = \sum_r \alpha_r \delta_{nr} = \alpha_n$. $\therefore |\alpha\rangle = \sum_r |r\rangle\langle r|\alpha\rangle$.

So, when applied to any ket $|\alpha\rangle$, the operator $\sum_r |r\rangle\langle r|$ gives back the same ket.

So, by definition, $\sum_r |r\rangle\langle r| = 1$. This is called the completeness relation.

For any product of operators, $LM = \sum_r L|r\rangle\langle r|M$.

Also, $\langle\alpha| = \sum_r \langle\alpha|r\rangle\langle r| = \sum_r \langle r|\alpha_r^*$

Hermitian Operators.

Write $\langle n|(L|m\rangle) = \langle n|L|m\rangle$, the matrix element of L between the states m, n. ($|t \in \mathbb{C}$).

For example, $\langle n|H|m\rangle = \int d^3r\, \Psi_n^*(\underline{r},t)\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\underline{r})\right)\Psi_m(\underline{r},t)$.

Define the hermitian conjugate, L^+, of L such that the bra corresponding to $L|m\rangle$ is $\langle m|L^+$.

Then, $\langle m|L^+|n\rangle = \langle n|L|m\rangle \;\forall\; m,n$. If $L^+ = L$, then L is hermitian.

Example: H is hermitian within the space of physical states. (ie, those for which the wavefunction goes to zero sufficiently rapidly, as $|\underline{r}| \to \infty$, for then $\int d^3r\, \Psi_n^* \nabla^2 \Psi_m = \int d^3r\, \Psi_n^* \overleftarrow{\nabla}^2 \Psi_m$. Also, V is real).

Note: $(LM)^+ = M^+L^+$

Eigenstates.

If $L|a\rangle = a|a\rangle$ (a - a number), we say that $|a\rangle$ is an eigenstate of L with eigenvalue a. Then also, $\langle a|L^+ = a^*$

If $L = L^+$, so if L is hermitian, then a is real. For then, $\langle a|L|a\rangle = \langle a|L^+|a\rangle^* = \langle a|L|a\rangle^*$

$\therefore \langle a|a\rangle a = \langle a|a\rangle a^*$, and so, since $\langle a|a\rangle > 0$, we have $a = a^*$.

Suppose also that $L|b\rangle = b|b\rangle$, with $b \neq a$. Then one can deduce $\langle b|a\rangle = 0$.
If $b=a$, we do not necessarily have $\langle b|a\rangle = 0$. But, in this case, $|x\rangle = |a\rangle + \lambda|b\rangle$ $(\lambda \in \mathbb{C})$ is also an eigenstate of L, with the same eigenvalue. We can choose λ such that $|x\rangle$ is orthogonal to $|a\rangle$. Ie, we can choose an orthogonal pair of kets in this 2-dimensional subspace of eigenstates of L with eigenvalue a.

So we have an orthonormal set of eigenstates of L. We confine ourselves to considering those operators L whose eigenstates are complete. (This is not simple to investigate in an infinite-dimensional space!)

We define a function $f(L)$ of L such that, for any of the complete set of eigenstates of L, $f(L)|a\rangle = f(a)|a\rangle$. This has to be true when $f(L)$ is a power series (or a polynomial); otherwise it is just definition.

Reminder about Observables.

(i) Observables are associated with hermitian linear operators.
(ii) When the value of an observable Q is known to be q, the system must be in an eigenstate of Q with eigenvalue q: $Q|q\rangle = q|q\rangle$.
(iii) When we measure Q in a general state $|x\rangle$, the probability of getting its eigenvalue q as its value is $|\langle q|x\rangle|^2$, provided $\langle x|x\rangle = 1$.

Check that assumption (iii) is consistent. The total probability of getting some value is:
$\sum_q |\langle q|x\rangle|^2 = \sum_q \langle x|q\rangle\langle q|x\rangle = \langle x|x\rangle = 1$, so the completeness relation is important for the consistency.

If we prepare the state $|\rangle$ many times, and each time measure Q, the average value is: $\sum_r q_r |\langle q_r|\rangle|^2 = \sum_r q_r \langle|q_r\rangle\langle q_r|\rangle = \sum_r \langle|q_r\rangle\langle q_r|Q|\rangle = \langle|Q|\rangle$, the <u>expectation value</u> of Q in the state $|\rangle$. If the state $|\rangle$ is not normalised to unity, this becomes: $\frac{\langle|Q|\rangle}{\langle|\rangle}$.
This is a number - for example, using momentum-space wavefunctions, it is: $\frac{\int d^3p\, \Phi^*(p,t)\, Q\, \Phi(p,t)}{\int d^3p\, \Phi^*(p,t)\, \Phi(p,t)}$, with Q expressed in its concrete momentum-space version.

Continuum states.

So far we have explicitly assumed a discrete spectrum of states, for example the bound states of an electron in an atom, or a free particle confined within a box. $(k_i = \frac{2\pi n}{L})$
In the continuum limit $L \to \infty$, the orthonormality relation becomes $\langle m|n\rangle = \delta(m-n)$, instead of δ_{mn}. The completeness relation becomes: $\int dm\, |m\rangle\langle m| = 1$. Check this:
$\langle m|n\rangle = \langle m|1|n\rangle = \int dr\, \langle m|r\rangle\langle r|n\rangle = \int dr\, \delta(m-r)\,\delta(r-n) = \delta(m-n)$.

If m stands for a set of labels, some continuous and others discrete, $\langle m|n\rangle$ is a product of δ-functions for the continuous ones and Kronecker δ's for the discrete ones, and the completeness relation is a combination of integrations and summations.

If the observable Q has continuous eigenvalues q, $Q|q\rangle = q|q\rangle$, we can write a general state as $|\rangle = \int dq\, |q\rangle\langle q|\rangle$, from the completeness relation.
Now, $|\langle q|\rangle|^2$ is a relative probability, because the probability in the continuum case of getting any particular value is 0. Rather, the probability of ~~get~~ getting an answer in the interval $(q, q+dq)$ is: $\frac{|\langle q|\rangle|^2 dq}{\langle|\rangle}$. As a check, the integral of this over all q is 1, so there is unit probability of getting some answer.

Sets of Observables.

Generally, a state is not labelled uniquely by the eigenvalue of just one observable. How do we choose a set of observables whose eigenvalues uniquely label all the states?

(i) If Q, R are two commuting observables, ie, $[Q,R]=0$, and $f(R)$ is a hermitian function of R, then $[Q, f(R)] = 0$. For, let $|a\rangle$, $|b\rangle$ be eigenstates of R, with $R|a\rangle = a|a\rangle$, $R|b\rangle = b|b\rangle$, so $\langle a|R = \langle a|a$, $\langle b|R = \langle b|b$.
Then, $0 = \langle b|QR - RQ|a\rangle = (a-b)\langle b|Q|a\rangle$. So either $a=b$ or $\langle b|Q|a\rangle = 0$.
$\therefore\ 0 = (f(a) - f(b))\langle b|Q|a\rangle = \langle b|Qf(R) - f(R)Q|a\rangle$. Since this vanishes for any $|a\rangle, |b\rangle$ from a complete set of states (assume), $Qf(R) - f(R)Q = 0$.

(ii) If $[Q,R]=0$, they have a complete set of common eigenstates, ie. enough to span the whole space of states. For let $|q_i\rangle$ be the (assumed complete) set of eigenstates of Q. Then, $R|q_i\rangle = R\cdot\frac{1}{q_i}Q|q_i\rangle = \frac{1}{q_i}QR|q_i\rangle$. [We need not worry about the case $q_i = 0$, for then we can work instead with $Q+C$, with C a complex number]
So, $R|q_i\rangle$ is an eigenstate of Q with eigenvalue q_i.
There are two possibilities:
(a) there is only one independent eigenstate of Q with eigenvalue q_i, and $R|q_i\rangle = \text{const.} \times |q_i\rangle$, whence $|q_i\rangle$ is also an eigenstate of R.
(b) the eigenvalue q_i of Q belongs to several eigenstates, $|q_{i1}\rangle, |q_{i2}\rangle, \ldots, |q_{in}\rangle$ (ie, there is degeneracy). Then R maps this subspace of states into itself. Because R is hermitian, there is a linear transformation that diagonalises this mapping: $|\bar{q}_{ir}\rangle = \sum_{s=1}^{n} \lambda_{rs} |q_{is}\rangle$, with $R|\bar{q}_{ir}\rangle = \text{const.} \times |\bar{q}_{ir}\rangle$.

In the first case, where an eigenstate of Q is not degenerate, its eigenvalue specifies the state uniquely. In the second case, some of the degenerate states (having the same eigenvalue for Q) may be specified uniquely by saying also what is the eigenvalue of R. The rest fall into classes, such that within each class each state is an eigenstate of both Q and R, with the same pair of eigenvalues. To distinguish these from one another, we introduce a third observable which commutes with both Q and R, and repeat the argument.
Continue introducing commuting observables until all degeneracy is resolved.
How many such observables do we need?

(iii) Define a complete set of commuting observables, $Q^{(i)}$, such that any observable that commutes with all of them is a function of them. Let $|q^{(1)}, q^{(2)}, ..\rangle$ be a common eigenstate of all the $Q^{(i)}$. So, $Q^{(i)}|q^{(1)}, q^{(2)}, ..\rangle = q^{(i)}|q^{(1)}, q^{(2)}, ..\rangle$.
This is unique. For, suppose there are two such states, $|1\rangle$ and $|2\rangle$, orthogonal to each other. Define the operator Ω by: $\Omega|1\rangle = |1\rangle$, $\Omega|\rangle = 0$, where $|\rangle$ is any other state of the basis orthogonal to $|1\rangle$, including $|2\rangle$.
Then, $(\Omega Q^{(i)} - Q^{(i)}\Omega)|1\rangle = (q^{(i)} - q^{(i)})|1\rangle = 0 = (\Omega Q^{(i)} - Q^{(i)}\Omega)|\rangle$.
So, $[\Omega, Q^{(i)}] = 0$ when applied to any state of the basis, so Ω is a function of the $Q^{(i)}$.
But, this cannot be, as $f(Q^{(1)}, Q^{(2)}, ..)|1\rangle = f(q^{(1)}, q^{(2)}, ..)|1\rangle$, and $f(Q^{(1)}, Q^{(2)}, ..)|2\rangle = f(q^{(1)}, q^{(2)}, ..)|2\rangle$, contradicting the definition of Ω.

Conclusion: a state is uniquely labelled by the eigenvalues of a complete set of commuting observables.

Unitary Transformations.

Let U be a unitary operator, ie $U^{-1} = U^{+}$, $UU^{+} = I = U^{+}U$. Transform all observables, $Q \to UQU^{-1}$, and all states: $|\rangle \to U|\rangle$, $\langle| \to \langle|U^{+}$. Then, any matrix element $\langle B|Q|A\rangle \to \langle B|U^{+}UQU^{-1}U|A\rangle = \langle B|Q|A\rangle$. Ie, the experimental quantities are unchanged. So, by making the transformation we obtain different operators and state vectors, but describing the same physics as before. Making such a transformation is called changing the picture.

Schrödinger Picture.

This is the familiar picture: most of the observables correspond to operators that do not depend explicitly on t, but the state vectors vary with t, and obey the Schrödinger equation: $H|t\rangle = i\hbar \frac{\partial}{\partial t}|t\rangle$, so that $|t\rangle = e^{-iHt/\hbar}|0\rangle$. $-(*)$

[Check this solution by substituting it back into the differential equation, using $\frac{\partial}{\partial t} e^{-iHt/\hbar} = \frac{-iH}{\hbar} e^{-iHt/\hbar} = e^{-iHt/\hbar}\left(\frac{-iH}{\hbar}\right)$, as H commutes with any function of H.]

We call $e^{-iHt/\hbar}$ the Schrödinger-picture time-evolution operator. If $|0\rangle$ is an eigenstate of H, $|t\rangle = e^{-iEt/\hbar}|0\rangle$ and the time-dependence is trivial (stationary state)
Most matrix elements $\langle B|Q|A\rangle$ of observables vary with t because the state vectors do.

Heisenberg Picture

Choose $U = U(t) = e^{iHt/\hbar}$, so that $|t\rangle_H = e^{iHt/\hbar}|t\rangle_S = |0\rangle_S$, by $(*)$. Ie, the state vectors in the Heisenberg picture are independent of t. $Q_H = e^{iHt/\hbar} Q_S e^{-iHt/\hbar}$, so the Heisenberg picture observables mostly have explicit dependence on t. If $\dot{Q}_S = 0$, $\dot{Q}_H = \frac{iH}{\hbar} Q_H + Q_H\left(\frac{-iH}{\hbar}\right) = \frac{i}{\hbar}[H, Q_H]$ which is the equation of motion in the Heisenberg picture.

Remarks: (i) H is the same in both pictures: $H_H = e^{iH_s t/\hbar} H_s e^{-iH_s t/\hbar} = H_s$.

(ii) If $[Q_s, R_s] = C$ (a number), then also $[Q_H, R_H] = C$.

(iii) The two pictures coincide at $t=0$. If we use instead $V(t) = e^{iH(t-t_0)/\hbar}$, we obtain another Heisenberg picture, which coincides with the Schrödinger picture at $t = t_0$.

Quantisation Conditions.

Dirac tried to build up Quantum Mechanics as a generalisation of classical mechanics (although not all quantum systems have a classical analogue).
Classical mechanics: introduce generalised coordinates q_r and conjugate momenta p_r.
For any two dynamical variables, L, M, define their Poisson Bracket as:
$\{L, M\} = \frac{\partial L}{\partial q_r}\cdot\frac{\partial M}{\partial p_r} - \frac{\partial L}{\partial p_r}\cdot\frac{\partial M}{\partial q_r}$.

It has the properties:

(a) $\{L, M\} = -\{M, L\}$.

(b) If C does not depend on the dynamics of the system and is independent of p's and q's, then $\{C, L\} = 0$.

(c) $\{L_1 + L_2, M\} = \{L_1, M\} + \{L_2, M\}$.

(d) $\{L_1 L_2, M\} = \{L_1, M\} L_2 + L_1 \{L_2, M\}$

(e) $\{L, \{M, N\}\} + \{M, \{N, L\}\} + \{N, \{L, M\}\} = 0$ (Jacobian identity)

(f) The Poisson brackets is independent of the particular choice of generalised coordinates q_r.

All of these properties remain true if we replace the Poisson bracket with commutators of the hermitian operators that correspond to quantum-mechanical observables:
$\{L, M\} \to \frac{1}{i\hbar}[L, M]$, where $\hbar$ is some constant, which is real if the RHS is hermitian.
$\left([L,M]^+ = (LM - ML)^+ = ML^+ - L^+M^+ = ML - LM = -[L,M]\right)$. Experiment fixes the value of $\hbar$.

Choose Cartesian coordinates: $\{x_i, x_j\} = 0 = \{p_i, p_j\}$.
So, $[x_i, x_j] = 0 = [p_i, p_j]$, $\{x_i, p_j\} = \delta_{ij}$ and $[x_i, p_j] = i\hbar\delta_{ij}$.
So $\hbar$ is the familiar quantity: in coordinate space, $p_j = -i\hbar\,\partial/\partial x_j$, and for any wavefunction $\Psi[\underline{r}, t]$, $[x_i, p_j]\Psi = i\hbar\Psi\delta_{ij}$. However, $\{x^2, p_x^2\} = 4xp_x$. But, $\frac{1}{i\hbar}[x^2, p_x^2] = 4xp_x - 2i\hbar$, so we only get the stated correspondance in the limit.
Classically, $\dot{p}_r = -\partial H/\partial q_r = -\{H, p_r\}$, $\dot{q}_r = \partial H/\partial p_r = \{q_r, H\}$ (Hamilton's equations)
$\to \dot{p}_r = \frac{1}{i\hbar}[H, p_r]$, $\dot{q}_r = \frac{1}{i\hbar}[H, q_r]$ - the Heisenberg picture equation of motion.

Linear Harmonic Oscillator.

$H = p^2/2m + \frac{1}{2}m\omega^2 x^2$. Define $a = \frac{i}{\sqrt{2m\hbar\omega}}(p - im\omega x)$ - a dimensionless operator.
Then, $[a, a^+] = 1$. $\left(a^+ = \frac{-i}{\sqrt{2m\hbar\omega}}(p + im\omega x),\ [x,p] = i\hbar\right)$. So, $H = \hbar\omega(a^+a + \frac{1}{2})$
Let $|n\rangle$ be an eigenstate of H, $H|n\rangle = (n + \frac{1}{2})\hbar\omega|n\rangle$, with $\langle n|n\rangle = 1$
Then, $Ha|n\rangle = aH|n\rangle + [H, a]|n\rangle$, and $[H, a] = \hbar\omega[a^+a, a] = \hbar\omega[a^+, a]a = -\hbar\omega a$.
$\therefore Ha|n\rangle = \left((n+\frac{1}{2})\hbar\omega - \hbar\omega\right)a|n\rangle = (n - \frac{1}{2})\hbar\omega a|n\rangle$

So either $a|n\rangle = 0$, or it is an eigenstate of H with eigenvalue $(n-\frac{1}{2})\hbar\omega$.
$\therefore\ a|n\rangle = c_n|n-1\rangle$, where c_n is a constant, and $\langle n-1|n-1\rangle = 1$.
Argue similarly with $a|n-1\rangle$, etc. Each time we get an eigenvalue which is $\hbar\omega$ smaller than before. We show that this sequence of eigenvalues must terminate, at $\frac{1}{2}\hbar\omega$, and therefore n has to be a non-negative integer.
The norm of $a|n\rangle$ is: $\langle n|a^+.a|n\rangle = |c_n|^2\langle n-1|n-1\rangle = |c_n|^2$.
Also, $\langle n|a^+a|n\rangle = \langle n|\frac{H}{\hbar\omega} - \frac{1}{2}|n\rangle = n\langle n|n\rangle = n$. So $n = |c_n|^2$, so $n \geq 0$, with $n=0$ corresponding the case $a|n\rangle = 0$.
So, because unless the sequence terminates we arrive at negative n, and because we have shown that $n \geq 0$, the sequence must terminate by our hitting $n=0$, and so we must have started with a non-negative integer n.

Now, $c_n = \sqrt{n}\, e^{i\theta_n}$. We can choose the relative phases of $|n-1\rangle$ and $|n\rangle$ so that $\theta_n = 0$.
Ie, $a|n\rangle = \sqrt{n}|n-1\rangle$.
Then, $\langle n|a^+ = \sqrt{n}\langle n-1|$ $\therefore\ \langle n|a^+|n'\rangle = \sqrt{n}\langle n-1|n'\rangle = \sqrt{n}\,\delta_{n-1,n'}$.
$\therefore\ a^+|n'\rangle = \sum_n |n\rangle\langle n|a^+|n'\rangle = \sum_n |n\rangle\sqrt{n}\,\delta_{n-1,n'} = \sqrt{n'+1}\,|n'+1\rangle$.

<u>Conclusions:</u> H has a lowest eigenstate $|0\rangle$, with eigenvalue $\frac{1}{2}\hbar\omega$. The other normalised eigenstates are: $|n\rangle = \frac{1}{\sqrt{n!}}(a^+)^n|0\rangle$, with eigenvalue $(n+\frac{1}{2})\hbar\omega$.

The state may be degenerate, and we need other labels to specify it uniquely. Then all the states $|n\rangle$ will be similarly degenerate, because a^+ does not affect the other labels.
a^+ is called a <u>creation operator</u>: it creates a quantum $\hbar\omega$ of energy.
a is called an <u>annihilation operator</u>: it annihilates a quantum $\hbar\omega$ of energy.

Define $N = a^+a$, so that $N|n\rangle = \left(\frac{H}{\hbar\omega} - \frac{1}{2}\right)|n\rangle = n|n\rangle$. N is the <u>number operator</u>, whose eigenvalues n are the number of quantum $\hbar\omega$ of energy above the ground state energy.

<u>3-dimensional Harmonic Oscillator.</u>

$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2$.
The Schrödinger equation, $H\Psi(\underline{r}) = E\Psi(\underline{r})$ is: $\sum_{i=1}^{3}\left\{-\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial x_i}\right)^2 + \frac{1}{2}m\omega^2 x_i^2\right\}\Psi(\underline{r}) = E\Psi(\underline{r})$.
When H is a sum like this, there are elementary solutions $\Psi(\underline{r}) = \Psi_1(\underline{x}_1)\Psi_2(\underline{x}_2)\Psi_3(\underline{x}_3)$, with $H_i\Psi_i = E_i\Psi_i$, with $H_i = \{\cdots\}_i$ and $E = E_1 + E_2 + E_3$.
So, $E_i = (n_i + \frac{1}{2})\hbar\omega$, and the eigenstates are: $|n_1 n_2 n_3\rangle = |n_1\rangle|n_2\rangle|n_3\rangle$, a <u>direct product</u> or <u>tensor product</u> of kets, which by definition has factorised wavefunction.

Introduce $a_i = \frac{i}{\sqrt{2m\hbar\omega}}(p_i - im\omega x_i)$, $i = 1, 2, 3$.
Then, $[a_i, a_j^+] = \delta_{ij}$, and $|n_1 n_2 n_3\rangle = \frac{1}{\sqrt{n_1!\,n_2!\,n_3!}}(a_1^+)^{n_1}(a_2^+)^{n_2}(a_3^+)^{n_3}|0\rangle$, where $|0\rangle$ is the ground state $|000\rangle$.
$H = (N + \frac{3}{2})\hbar\omega$, $N = \sum_{i=1}^{3} a_i^+ a_i$.

Time-Independent Perturbation Theory.

Used for solving stationary-state problems.
Let $H = H_0 + \varepsilon H_1$, and $H_0 |0_j\rangle = E_{0j} |0_j\rangle$, $j = 1, 2, 3, \ldots$ Assume that the eigenstates and eigenvalues of H may be expanded in powers of ε. $H|i\rangle = E_i |i\rangle$

Case (i): no degeneracy.

As $\varepsilon \to 0$, each state $|i\rangle \to$ one of the eigenstates of H_0, and we can choose the labelling such that $|i\rangle \to |0_i\rangle$

Expand $|i\rangle = \sum_j a_{ij} |0_j\rangle$:

$a_{ii} = 1 + \varepsilon b_{ii} + \varepsilon^2 c_{ii} + \ldots$ (not summation convention here!)

$a_{ij} = \varepsilon b_{ij} + \varepsilon^2 c_{ij} + \ldots$

$E_i = E_{0i} + \varepsilon \Delta_i^{(1)} + \varepsilon^2 \Delta_i^{(2)} + \ldots$

$H|i\rangle = E_i |i\rangle$ gives: $(H_0 + \varepsilon H_1) \left\{ (1 + \varepsilon b_{ii} + \varepsilon^2 c_{ii} + \cdots) |0_i\rangle + \sum_{j \neq i} (\varepsilon b_{ij} + \varepsilon^2 c_{ij} + \cdots) |0_j\rangle \right\}$

$$= (E_{0i} + \varepsilon \Delta_i^{(1)} + \varepsilon^2 \Delta_i^{(2)} + \cdots) \{ \cdots \}.$$

Terms of order ε^0: $H_0 |0_i\rangle = E_{0i} |0_i\rangle$.

ε^1: $\cancel{E_{0i} b_{ii} |0_i\rangle} + H_1 |0_i\rangle + \sum_{j \neq i} b_{ij} E_{0j} |0_j\rangle = \cancel{E_{0i} b_{ii} |0_i\rangle} + \Delta_i^{(1)} |0_i\rangle + \sum_{j \neq i}' b_{ij} E_{0i} |0_j\rangle$

Take scalar product with $\langle 0_i|$: $\langle 0_i | H_1 | 0_i \rangle = \Delta_i^{(1)}$

with $\langle 0_k|$, $k \neq i$: $b_{ik} = \dfrac{\langle 0_k | H_1 | 0_i \rangle}{E_{0i} - E_{0k}}$

ε^2: $H_0 c_{ii} |0_i\rangle + \sum_{j \neq i} b_{ij} H_1 |0_j\rangle = E_{0i} \sum_{\text{all } j} c_{ij} |0_j\rangle + \Delta_i^{(1)} \sum_{j \neq i} b_{ij} |0_j\rangle + \Delta_i^{(2)} |0_i\rangle$.

Take scalar product with $\langle 0_i|$: get $\Delta_i^{(2)} = \sum_{j \neq i} b_{ij} \langle 0_i | H_1 | 0_j \rangle = \sum_{j \neq i} \dfrac{\langle 0_j | H_1 | 0_i \rangle \langle 0_i | H_1 | 0_j \rangle}{E_{0i} - E_{0j}}$

So, $E_i = \langle 0_i | H | 0_i \rangle + \sum_{j \neq i} \dfrac{|\langle 0_i | H | 0_j \rangle|^2}{E_{0i} - E_{0j}} + O(\varepsilon^3)$

In practice, this gives a good approximation if the shift in the levels E_{0i} caused by adding H_1 $\ll$ to H_0 $\ll$ spacing between the levels.
If there is degeneracy, one or more of the denominators vanish!

Simplest Example of Nondegenerate Perturbation Theory.

Consider a particle in one dimension confined to $0 \leq x \leq a$, with possible wavefunction $\psi_n(x) = c_n \sin \frac{n\pi x}{a}$, energy $\frac{\hbar^2 n^2 \pi^2}{2ma^2}$. To apply the theory, it is important to normalise the wavefunction: $c_n = \left\{ \int_0^a dx \sin^2 \frac{n\pi x}{a} \right\}^{1/2}$.
Apply a constant electric field in the x-direction, so that a potential $-q\mathcal{E}x$ is added to the original Hamiltonian. To lowest order in q, the energy levels shift by $\int_0^a dx\, |c_n|^2 \sin^2 \frac{n\pi x}{a} (-q\mathcal{E}x)$.

Example: The Anharmonic Oscillator.

$H = H_0 + \varepsilon x^3$, $H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$. Use the eigenstates $|n\rangle$ of H_0, $E_{0n} = (n + \frac{1}{2})\hbar\omega$.
To lowest order in ε, the eigenvalues of H are: $\langle n | H | n \rangle = E_{0n} + \varepsilon \langle n | x^3 | n \rangle$.

Write $a = \frac{i}{\sqrt{2m\hbar\omega}}(p - im\omega x)$, $a^+ = \frac{-i}{\sqrt{2m\hbar\omega}}(p + i\omega m x)$. $\Rightarrow x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^+)$.

$\langle n | \varepsilon x^3 | n \rangle = \varepsilon \left(\frac{\hbar}{2m\omega}\right)^{3/2} \langle n | (a+a^+)^3 | n \rangle$.

$(a+a^+)^3 = a^3 + (a^2 a^+ + a a^+ a + a^+ a^2) + (a a^{+2} + a^+ a a^+ + a^{+2} a) + a^{+3}$.

Use $a|n\rangle = \sqrt{n}|n-1\rangle$, $a^+|n\rangle = \sqrt{n+1}|n+1\rangle$.

In order to get a non-vanishing expectation value, we need terms that have an equal number of a and a^+ multiplied together. For example, $\langle n | a^3 | n \rangle \propto \langle n | n-3 \rangle = 0$.

$\therefore \langle n | x^3 | n \rangle = 0$ for all n, and therefore the energy shift caused by adding εx^3 to H_0 is $O(\varepsilon^2)$

[For εx^4 instead of εx^3, we get $O(\varepsilon)$].

For εx^3, the $O(\varepsilon^2)$ term in the energy shift is: $\varepsilon^2 \left(\frac{\hbar}{2m\omega}\right)^3 \cdot \sum_{m \neq n} \frac{|\langle m | (a+a^+)^3 | n \rangle|^2}{(n-m)\hbar\omega}$.

The terms in the sum that contribute are $m = n \pm 3$ from a^3 and a^{+3}, and $m = n \pm 1$ from the other terms.

Degenerate Perturbation Theory.

If there is degeneracy of the eigenstates of H_0, the calculation of the energy shift for any nondegenerate state goes through as before. But for a set of degenerate states, adding in εH_1 to H_0 is likely to separate them in energy, and we cannot immediately identify which states $|0_i\rangle$ of the degenerate subspace is associated with each eigenstate $|i\rangle$ of H.

Pick some orthonormal basis $|0_j\rangle$, $j = 1, .., N$ in the subspace. For the states associated with them, expand: $|i\rangle = \sum_{j \leq N} \lambda_{ij} |0_j\rangle + \varepsilon \sum_{j > N} b_{ij} |0_j\rangle + O(\varepsilon^2)$, $i = 1, .., N$.

By confining the summation in the second term to $j > N$, we have included any $O(\varepsilon)$ contributions from $j \leq N$ in the first term.

Call the energy level of the degenerate states E_0. Also expand for the altered levels: $E_i = E_0 + \varepsilon \Delta_i^{(1)} + O(\varepsilon^2)$

Insert these expansions into $H|i\rangle = E|i\rangle$, then up to $O(\varepsilon)$ one obtains:

$$\sum_{j=1}^{N} H_1 \lambda_{ij} |0_j\rangle + \sum_{j>N} b_{ij} E_{0j} |0_j\rangle = \Delta_i^{(1)} \sum_{j=1}^{N} \lambda_{ij} |0_j\rangle + E_0 \sum_{j>N} b_{ij} |0_j\rangle.$$

Take the scalar product with $\langle 0_k |$, $k \leq N$: $\sum_{j \geq 1}^{N} \lambda_{ij} \langle 0_k | H_1 | 0_j \rangle = \Delta_i^{(1)} \lambda_{ik}$.

These are homogeneous simultaneous equations for the λ.

To get a nontrivial solution, need $\det(\langle 0_k | H_1 | 0_j \rangle - \Delta_i^{(1)} \delta_{jk}) = 0$

The determinant is $N \times N$, so the equation is degree N in $\Delta_i^{(1)}$ and usually has N different solutions. The solutions are real because H_1 is hermitian.

One can diagonalise $\langle 0_k | H_1 | 0_j \rangle$ by a linear transformation, so getting a different orthonormal basis in the subspace. These are the states out of which the eigenstates $|i\rangle$ of H grow directly when we switch on the term εH_1.

Example: The Stark Effect.

Hydrogen atom in an electric field: $H = H_0 - e\varphi$. For a uniform field, $\varphi = \underline{\mathcal{E}}\cdot\underline{r}$.
In practice, the distance scale on which $\underline{\mathcal{E}}$ varies $\gg$ the radius of the atom, so it is a good approximation to suppose $\underline{\mathcal{E}}$ is uniform. In practice also, $|\underline{\mathcal{E}}| \ll$ the electric field inside the atom, which $\approx 10^{10}\ \mathrm{Vm}^{-1}$.

$H = H_0 + e\,\underline{\mathcal{E}}\cdot\underline{r}$

Therefore, one expects perturbation theory to give a good approximation to the near energy levels.
Non-degenerate perturbation theory gives the lowest order energy shift as $e\,\underline{\mathcal{E}}\cdot\langle 0_i|\underline{r}|0_i\rangle$

But, $H_0(\underline{r}) = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0|\underline{r}|} = H_0(-\underline{r})$
So one can form solutions to the Schrödinger equation having definite parity, $\psi_{0i}(\underline{r}) = \pm\psi_{0i}(-\underline{r})$ and these solutions form a complete set.
For these $\int d^3r\,|\psi_{0i}(\underline{r})|^2\,\underline{r} = 0$, and so the energy shift is $O(\varepsilon^2)$.

Recall that, for the hydrogen atom with hamiltonian H_0, we have eigenstates of definite orbital angular momentum l and definite parity $(-1)^l$. Recall also that the energy levels depend only on the "principal quantum number" n, and are $\propto 1/n^2$.
Ground state is: $n=1$, $l=0$ - not degenerate.
Next is: $n=2$, $l = 0$ or 1 - degenerate.
So the result is that the energy shift $O(\varepsilon^2)$ applies to the ground state, and for the excited states we must use instead degenerate perturbation theory.
For $n=2$, the perturbed states correspond to superpositions of the $l=0$ and $l=1$ unperturbed states (found by solving the determinant equation). These superpositions do not have definite parity, and the energy shift is $O(\varepsilon)$.

Angular momentum.

Orbital angular momentum of a particle, $\hbar\underline{L} = \underline{r}\wedge\underline{p}$. It has the properties:
(i) $\underline{L}^+ = \underline{L}$ (because $\underline{r}, \underline{p}$ are both hermitian).
(ii) In the coordinate-space representation, where $\underline{p} = -i\hbar\underline{\nabla}$, $\underline{L}^2$ is that part of $\underline{r}^2\underline{\nabla}^2$ which involves the polar angles θ and φ.
(iii) $[\underline{L}^2, L_z] = 0$, so $\underline{L}^2$ and L_z have simultaneous eigenfunctions, which are $Y_{lm}(\theta,\varphi) = \text{cst.}\ P_l^m(\theta)\,e^{im\varphi}$, corresponding to eigenvalues $l(l+1)$ and m.
In order that $P_l^m(\theta)$ behaves at $\theta = 0, \pi$, need: (a) $l = 0, 1, 2, \ldots$, (b) $m = -l, -l+1, \ldots, l$

Analysis from commutation relations.

$[L_1, L_2] = \frac{1}{\hbar^2}[x_2p_3 - x_3p_2,\ x_3p_1 - x_1p_3] = \frac{1}{\hbar^2}x_2[p_3, x_3]p_1 + \frac{1}{\hbar^2}x_1[x_3, p_3]p_2 = \frac{-i}{\hbar}x_2p_1 + \frac{i}{\hbar}x_1p_2 = iL_3$.
(Using $[x_i, p_j] = i\hbar\delta_{ij}$). Get two other relations by cyclic permutations.
So, $[L_i, L_j] = i\varepsilon_{ijk}L_k$, or, $\underline{L}\wedge\underline{L} = i\underline{L}$.
Note: better to write $\underline{L} = \underline{r}\wedge\underline{p}$. Then this is $[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k$.

From these commutation relations, one finds $[\underline{L}^2, L_i] = 0$, so $\underline{L}^2$ and any one of the components L_i have common eigenstates. Conventionally, we choose $\underline{L}^2$ and L_3
Define $|l,m\rangle$ such that $\underline{L}^2|l,m\rangle = l(l+1)|l,m\rangle$, $L_3|l,m\rangle = m|l,m\rangle$.
Note that $l(l+1)$ is unchanged under $l \mapsto -l-1$, so we can define $l \geq -\frac{1}{2}$.

Define $L_\pm = L_1 \pm iL_2 = L_\mp^\dagger$. Then, $[\underline{L}^2, L_\pm] = 0$, and $[L_3, L_\pm] = \pm L_\pm$.
So, $\underline{L}^2(L_\pm|l,m\rangle) = L_\pm \underline{L}^2|l\,m\rangle = l(l+1)(L_\pm|l\,m\rangle)$.
$L_3(L_\pm|l\,m\rangle) = \{L_\pm L_3 + [L_3, L_\pm]\}|l\,m\rangle = (m\pm1)(L_\pm|l\,m\rangle)$
So either $L_\pm|l\,m\rangle = 0$ or $L_\pm|l\,m\rangle = c_{lm}^{(\pm)}|l, m\pm1\rangle$.
But, $0 \leq |c_{lm}^{(-)}|^2 = \langle lm|L_+L_-|lm\rangle = \langle lm|(L_1+iL_2)(L_1-iL_2)|lm\rangle = \langle lm|L_1^2+L_2^2+i[L_2,L_1]|lm\rangle$
$= \langle lm|\underline{L}^2 - L_3^2 + L_3|lm\rangle = l(l+1) - m^2 + m = (l+\frac{1}{2})^2 - (m-\frac{1}{2})^2$
Similarly, $0 \leq |c_{lm}^{(+)}|^2 = (l+\frac{1}{2})^2 - (m+\frac{1}{2})^2$. So m cannot be $>l$ or $<-l$.

So if we apply L_+ or L_- repeatedly, we must hit a value of m for which $c_{lm}^{(+)}$ or $c_{lm}^{(-)} = 0$, so that the sequence terminates and we do not reach forbidden values for m. The sequences terminate at $m=l$ and $m=-l$, and the allowed values of m are between these and separated from them by integers:
$m = -l, -l+1, \ldots, l$, so $2l$ must be an integer, ie, either l is an integer, and also m, with $|m| \leq l$, or l is half an odd integer, and also m, with $|m| \leq l$.

Defining arbitrary phase factors to be 1, $L_\pm|lm\rangle = \sqrt{(l+\frac{1}{2})^2 - (m\pm\frac{1}{2})^2}\,|l, m\pm1\rangle$.
We call $L_\pm$ <u>ladder operators.</u>
When l is half an odd integer, it cannot correspond to orbital angular momentum, ie, it is not associated with the motion of the particle, but rather is intrinsic to it. We call this intrinsic angular momentum <u>spin</u>.
Unlike in classical physics, even pointlike particles can carry spin angular momentum.

Electrons have spin $\frac{1}{2}$, ie, $l = \frac{1}{2}$, but write $s = \frac{1}{2}$, as do muons, protons, neutrons, quarks. Pions have spin 0. Photons have spin 1, as do w, z.
[We use $\underline{S}$ for spin, $\underline{L}$ for orbital angular momentum, and the total angular momentum is $\underline{J} = \underline{L} + \underline{S}$]

<u>Spin ½.</u>

In the special case of spin-½ particles, we write $\underline{S} = \frac{1}{2}\underline{\sigma}$, where $\underline{\sigma}$ = Pauli spin matrix. or, $\underline{S} = \frac{1}{2}\hbar\underline{\sigma}$.
$\underline{S}^2 = \frac{1}{4}\underline{\sigma}^2$ has eigenvalue $s(s+1) = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}$, so $\underline{\sigma}^2$ has eigenvalue 3. It makes sense to introduce to the operator $\underline{\sigma}$ only if we apply it to a state of a spin-½ particle. We write $\underline{\sigma}^2 = 3$, (by which we mean that $\underline{\sigma}^2$ and 3 have the same effect when applied to these states)
Now, $\underline{\sigma}^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2$, but S_3 has eigenvalues $\frac{1}{2}$ and $-\frac{1}{2}$, so S_3^2 has eigenvalue ¼, and so σ_3^2 has eigenvalue 1. So $\sigma_3^2 = 1$ (in the same sense as before).
Because any direction can be chosen as the z-axis, $\sigma_1^2 = \sigma_2^2 = 1$ also.

Could have: $\underline{S} = \frac{1}{2}\hbar\underline{\sigma}$, $[S_i, S_j] = i\hbar\varepsilon_{ijk}S_k$. Rest follows through.

$\underline{S} = \frac{1}{2}\underline{\sigma}$. $[S_i, S_j] = i\varepsilon_{ijk}S_k \Rightarrow [\sigma_i, \sigma_j] = 2i\varepsilon_{ijk}\sigma_k$.

$\sigma_1\sigma_2 - \sigma_2\sigma_1 = 2i\sigma_3$ $-(*)$ $\Rightarrow$ $\sigma_2 - \sigma_1\sigma_2\sigma_1 = 2i\sigma_1\sigma_3$ and $\sigma_1\sigma_2\sigma_1 - \sigma_2 = 2i\sigma_3\sigma_1$

Adding $\Rightarrow$ $\sigma_1\sigma_3 + \sigma_3\sigma_1 = 0$, or $\{\sigma_1, \sigma_3\} = 0 = [\sigma_1, \sigma_3]_+$ - the <u>anticommutator</u>.

Generally, $[\sigma_i, \sigma_j]_+ = 0$, $i \neq j$. In particular, $-\sigma_1\sigma_2 = \sigma_2\sigma_1$, so $\sigma_1\sigma_2 = i\sigma_3$ (from $(*)$).

We can write everything together as: $\sigma_i\sigma_j = i\varepsilon_{ijk}\sigma_k + \delta_{ij}$

The usual representation of this algebra, with σ_3 diagonal, is:

$\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$, $\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$.

<u>Example</u>: $|s = 1/2, s_3 = +1/2\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $|\frac{1}{2}, -\frac{1}{2}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

A general state is a linear combination of basis states: $u = \begin{pmatrix} \psi_1(\underline{r}) \\ \psi_2(\underline{r}) \end{pmatrix}$, a two-component <u>spinor</u>.

Normalise: $\int d^3r\, u^\dagger u = 1 = \int d^3r\, (\psi_1^* \psi_2^*)\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \int d^3r\, (|\psi_1|^2 + |\psi_2|^2)$

This equals = (probability that a measurement gives $s_3 = +\frac{1}{2}$) + (probability that it gives $s_3 = -\frac{1}{2}$)

<u>Addition of Angular Momenta.</u>

$\underline{J} = \underline{J}^{(1)} + \underline{J}^{(2)}$. Suppose that $\underline{J}^{(1)}$ and $\underline{J}^{(2)}$ refer to independent degrees of freedom, such as the spin and orbital angular momentum of a particle, or the orbital angular momenta of two separate particles, so that $[J_i^{(1)}, J_j^{(2)}] = 0$.

Eigenvalues: $\underline{J}^{(1)2}$ has eigenvalues $j_1(j_1+1)$, $J_3^{(1)}$ has eigenvalues m_1,
$\underline{J}^{(2)2}$ has eigenvalues $j_2(j_2+1)$, $J_3^{(2)}$ has eigenvalues m_2,
$\underline{J}^2$ has eigenvalues $j(j+1)$, J_3 has eigenvalues m.

Eigenstates: $|j_1 m_1\rangle$, $|j_2 m_2\rangle$, $|jm\rangle$.

Consider the states $|j_1 m_1\rangle|j_2 m_2\rangle = |j_1 m_1; j_2 m_2\rangle$. (The wavefunction in any representation is a product of wavefunctions)

Now, $J_3 = J_3^{(1)} + J_3^{(2)}$, $\therefore$ $J_3|j_1 m_1; j_2 m_2\rangle = (m_1 + m_2)|j_1 m_1; j_2 m_2\rangle$.

So $|j_1 m_1; j_2 m_2\rangle$ is an eigenstate of J_3 with eigenvalue $m = m_1 + m_2$.

Now, $\underline{J}^2 = (\underline{J}^{(1)} + \underline{J}^{(2)})^2 = \underline{J}^{(1)2} + \underline{J}^{(2)2} + 2\underline{J}^{(1)}\cdot\underline{J}^{(2)} = \underline{J}^{(1)2} + \underline{J}^{(2)2} + 2J_3^{(1)}J_3^{(2)} + J_+^{(1)}J_-^{(2)} + J_-^{(1)}J_+^{(2)}$.

If we apply this to the product state, the last two terms change $m_1 \to m_1 \pm 1$, $m_2 \to m_2 \mp 1$ (unless they give zero). So, in most cases, the product state is not an eigenstate of $\underline{J}^2$.

To get the simultaneous eigenstates $|jm\rangle$ of $\underline{J}^2$ and J_3, we need suitable linear combinations of the product states $|j_1 m_1; j_2 m_2\rangle$, involving different values of m_1 and m_2 with $m_1 + m_2 = m$.

[The conventional notation $|jm\rangle$ is incomplete: it is understood that the state is also an eigenstate of $\underline{J}^{(1)2}$ and $\underline{J}^{(2)2}$, ie, the states in the linear combination all have the same j_1 and all have the same j_2]

Consider the state $|j_1 j_1; j_2 j_2\rangle$. Because $J_+^{(1)}$ and $J_+^{(2)}$ annihilate the state, this state is an eigenstate of $\underline{J}^2$. Then,

$$\underline{J}^2|j_1 j_1; j_2 j_2\rangle = (j_1(j_1+1) + j_2(j_2+1) + 2j_1 j_2)|j_1 j_1; j_2 j_2\rangle = (j_1+j_2)(j_1+j_2+1)|j_1 j_1; j_2 j_2\rangle$$

Write this eigenvalue as $j(j+1)$, whence $j = j_1 + j_2$, ie, $|j_1+j_2, j_1+j_2\rangle = |j_1 j_1 ; j_2 j_2\rangle$.

Recall, $J_\pm |jm\rangle = \sqrt{(j+\frac{1}{2})^2 - (m \pm \frac{1}{2})^2}\, |j, m\pm 1\rangle$

Now, $J_- |j_1+j_2, j_1+j_2\rangle = \sqrt{(j_1+j_2+\frac{1}{2})^2 - (j_1+j_2-\frac{1}{2})^2}\, |j_1+j_2, j_1+j_2-1\rangle = \sqrt{2(j_1+j_2)}\, |j_1+j_2, j_1+j_2-1\rangle$

Also, this equals $(J_-^{(1)} + J_-^{(2)}) |j_1 j_1 ; j_2 j_2\rangle = \sqrt{2j_1}\, |j_1 j_1 - 1 ; j_2 j_2\rangle + \sqrt{2j_2}\, |j_1 j_1 ; j_2 j_2 - 1\rangle$

$$\therefore |j_1+j_2, j_1+j_2-1\rangle = \sqrt{\frac{j_1}{j_1+j_2}}\, |j_1 j_1 - 1 ; j_2 j_2\rangle + \sqrt{\frac{j_2}{j_1+j_2}}\, |j_1 j_1 ; j_2 j_2 - 1\rangle$$

The sum of the squares of the coefficients is 1 - the state is normalised to 1.

The orthogonal linear combination of the same two product states is (with a choice of phase): $\sqrt{\frac{j_2}{j_1+j_2}}\, |j_1 j_1 - 1 ; j_2 j_2\rangle - \sqrt{\frac{j_1}{j_1+j_2}}\, |j_1 j_1 ; j_2 j_2 - 1\rangle$

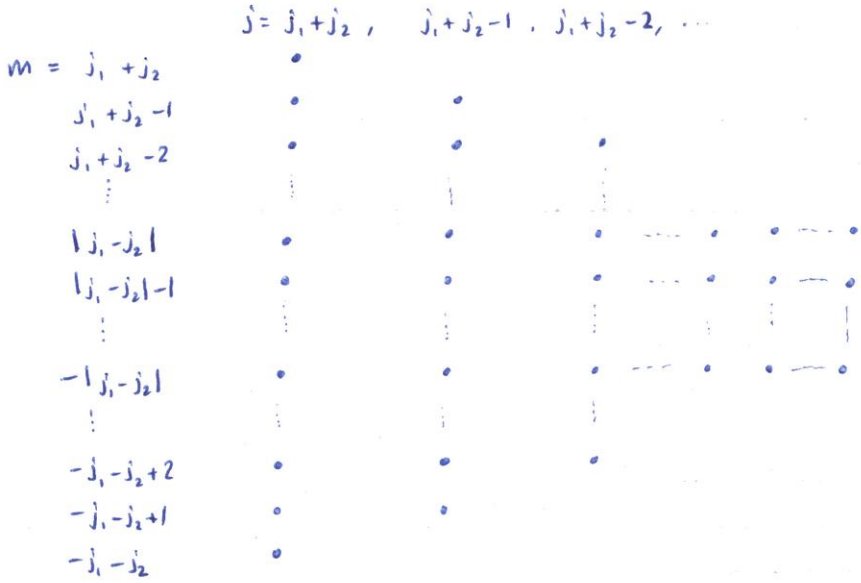
This is also an eigenstate of J_3, with eigenvalue $m = j_1 + j_2 - 1$. It must correspond to $j \geq j_1 + j_2 - 1$, not including $j = j_1 + j_2$.

But, $J_+ |\rangle = (J_+^{(1)} + J_+^{(2)}) |\rangle = (\cdot\cdot) |j_1 j_1 ; j_2 j_2\rangle - (\cdot\cdot) |j_1 j_1 ; j_2 j_2\rangle = 0$

So we identify the state as $|j_1+j_2-1, j_1+j_2-1\rangle$. This can be seen also from the fact that we cannot have $j > j_1 + j_2$ because the maximum value for m is $\max J_3^{(1)} + \max J_3^{(2)} = j_1 + j_2$.

Now apply $J_- = J_-^{(1)} + J_-^{(2)}$ to $|j_1+j_2, j_1+j_2-1\rangle$ and to $|j_1+j_2-1, j_1+j_2-1\rangle$, giving $|j_1+j_2, j_1+j_2-2\rangle$ and $|j_1+j_2-1, j_1+j_2-2\rangle$ as linear combinations of $|j_1 j_1 - 2 ; j_2 j_2\rangle$, $|j_1 j_1 - 1 ; j_2 j_2 - 1\rangle$, and $|j_1 j_1 ; j_2 j_2 - 2\rangle$.

The third linear combination of these three product states, orthogonal to these, must be $|j_1+j_2-2, j_1+j_2-2\rangle$. Continue until all product states have been used.



← the value of m for which the number of product states stops increasing when we apply J_-

As a check, we calculate the number of independent states:

The number of states $|jm\rangle$ is: $\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1)$ ← the number of values of m between $-j$ and $+j$.

The number of product states is: $(2j_1+1)(2j_2+1)$

So, $j_1 + j_2 \geq j \geq |j_1 - j_2|$, just as in classical physics.

Example: $1+1 = 0, 1,$ or 2. $\quad \frac{1}{2}+\frac{1}{2}+1 = (0 \text{ or } 1) + 1 = 0, 1,$ or 2.

$\frac{1}{2}+\frac{1}{2} = 0$ or 1. $\quad 29 + 0 = 29$.

Although the notation does not say so explicitly, the states $|jm\rangle$ are eigenstates of $\underline{J}^{(1)2}$ and $\underline{J}^{(2)2}$. Within the subspace of such states, we have the completeness relation:
$\sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 m_1 ; j_2 m_2\rangle\langle j_1 m_1 ; j_2 m_2| = 1.$

These are Clebsch-Gordon coefficients.

Apply this to $|jm\rangle$: $|jm\rangle = \sum_{m_1,m_2} |j_1 m_1 ; j_2 m_2\rangle\langle j_1 m_1 ; j_2 m_2 | jm\rangle$
We calculated $\langle j_1 j_1 -1 ; j_2 j_2 | j_1+j_2-1, j_1+j_2-1\rangle = \sqrt{\frac{j_2}{j_1+j_2}}$, etc.

By construction, and by choice of arbitrary phases, the Clebsch-Gordon coefficients are real. They are calculated from the algebra of angular momentum, and so are unaffected by the introduction of any other labels to describe the state:
$|jm;\alpha\rangle = \sum_{m_1,m_2} |j_1 m_1 ; j_2 m_2 ; \alpha\rangle\langle j_1 m_1 ; j_2 m_2 | jm\rangle$

Example: $\frac{1}{2}+\frac{1}{2}$. Write the single-particle states, $|s=\frac{1}{2}, s_3=\frac{1}{2}\rangle = |\uparrow\rangle$, $|s=\frac{1}{2}, s_3=-\frac{1}{2}\rangle = |\downarrow\rangle$.
Here, $\sqrt{\frac{j_1}{j_1+j_2}} = \sqrt{\frac{j_2}{j_1+j_2}} = 1/\sqrt{2}$.

$$\left.\begin{aligned} &|\uparrow\rangle|\uparrow\rangle = |s=1, s_3=1\rangle \\ &\tfrac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle) = |s=1, s_3=0\rangle \\ &|\downarrow\rangle|\downarrow\rangle = |s=1, s_3=-1\rangle \end{aligned}\right\} \text{Triple states: symmetric under particle interchange}$$

$$\tfrac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle) = |s=0, s_3=0\rangle \quad \} \text{ Singlet state: antisymmetric.}$$

Identical Particles.

Consider two particles, alike in all respects except $m_1 \neq m_2$. Solve for their motion and let $m_1 \to m_2$. In classical physics, one obtains the solution for identical particles, but not in quantum mechanics. Basic reason, here, the trajectory of a particle is not well-defined, because of the uncertainty principle. If we know its position precisely, we cannot also know its momentum, so we cannot know where it has just come from. So a pair of identical particles have no individuality; we cannot say that this one came from here and the other from there, and vice versa.

Let $|a\,b\rangle$ be a state of two identical particles, where 'a' denotes position and spin for one of the particles, and 'b' for the other. Then, the states $|a\,b\rangle$ and $|b\,a\rangle$ are physically equivalent. The simplest way to realise this is to decree that $|b\,a\rangle = e^{i\theta}|a\,b\rangle$, with θ constant. Then, $|a\,b\rangle = e^{i\theta}|b\,a\rangle$, and $e^{2i\theta}=1$, so $e^{i\theta}=\pm 1$, and the two-particle state is either symmetric or antisymmetric under particle interchange. All two-particle states of a particular pair of identical particles must have the same symmetry, because otherwise superpositions of states would lose symmetry.

For two identical particles, $H(1,2) = H(2,1)$, and so the change $\Delta|a,b\rangle$ when time Δt elapses, $\Delta|a,b\rangle = \frac{\Delta t}{i\hbar} H|a,b\rangle$ has the same symmetry as $|ab\rangle$.

Experiment: states of two identical particles whose spin is an integer are symmetric - Bosons.
——— " ——— $\frac{1}{2}$ an odd integer are antisymmetric - Fermions

Examples of fermions are: e, p, n, ν, q, and any bound state that consists of an odd number of fermions (because the total angular momentum of the bound state is the "sum" of the spins - in the state we have been describing - and the orbital angular momentum (which are integers)). For example, a He^3 nucleus, ppn, is a fermion.

For fermions, $|a\,a\rangle = -|a\,a\rangle$ and so $|a\,a\rangle = 0$ - Pauli exclusion principle.
Two identical fermions cannot occupy the same two-particle state.
Examples of bosons: γ, π, bound states of an even number of fermions (such as a He nucleus)

For states containing N particles, $|a_{P_1} \ldots a_{P_N}\rangle = |a_1 \ldots a_N\rangle$ for bosons, $= \sigma(P)|a_1 \ldots a_N\rangle$ for fermions, where $\sigma(P)$ is the signature of the permutation P.

This symmetry or antisymmetry is only required if the particles are all identical. So, for example, the bound state of p+n has no particular symmetry.

Aside: The proton and neutron are bound states of quarks: $p = uud$, $n = ddu$. They have spin ½. There is a bound state uuu (the Δ^{++}), where the three quarks all occupy the same single-particle state, which the Pauli exclusion principle forbids. Explanation: there is a new label, "color", which takes three possible values, and in the Δ^{++} each of the u quarks has different colour. If one includes the color label the state vector does not have the antisymmetry appropriate for fermions; there is a color wavefunction ε_{ijk} which multiplies the wavefunction composed of the other labels, which is symmetric.

Non-interacting Identical Particles.

$H = T_1 + V_1(\underline{r}_1) + T_2 + V_2(\underline{r}_2)$. For the electrons in the He atom, neglecting the interaction between them, is: $\frac{p_1^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0 r_2}$.

Let the single-particle wavefunction be $u_\alpha(\underline{r})$: $(T + V(\underline{r}))\, u_\alpha(\underline{r}) = E_\alpha\, u_\alpha(\underline{r})$.
Eigenstates of H: $u_\alpha(\underline{r}_1) u_\beta(\underline{r}_2)$, with eigenvalue $E_\alpha + E_\beta$. But these do not have the right symmetry. We need: $\Psi(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2}}\left[u_\alpha(\underline{r}_1) u_\beta(\underline{r}_2) \pm u_\beta(\underline{r}_1) u_\alpha(\underline{r}_2)\right]$ for $\left\{\begin{matrix}\text{bosons}\\ \text{fermions}\end{matrix}\right\}$.

If u_α, u_β are normalised to 1, the $1/\sqrt{2}$ makes Ψ normalised: $\int d^3\underline{r}_1\, d^3\underline{r}_2\, |\Psi|^2 = 1$.
This assume $\alpha \neq \beta$. If $\alpha = \beta$, for bosons the normalised wavefunction is $u_\alpha(\underline{r}_1) u_\alpha(\underline{r}_2)$, while for fermions there is no allowed wavefunction.

Generalise to N particles: $u_{\alpha_1}(\underline{r}_1) u_{\alpha_2}(\underline{r}_2) \ldots u_{\alpha_n}(\underline{r}_N)$ are solutions of the Schrödinger equation. For bosons, sum over all permutations of the labels, and divide by a normalisation factor; $(\text{number of terms})^{-1/2}$, which will depend on how many of the labels are different. For fermions, : $\Psi(\underline{r}_1, \ldots, \underline{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_{\alpha_1}(\underline{r}_1) & \cdots & u_{\alpha_N}(\underline{r}_1) \\ \vdots & & \vdots \\ u_{\alpha_N}(\underline{r}_1) & \cdots & u_{\alpha_N}(\underline{r}_N) \end{vmatrix}$ - Slater determinant.

Reminder: this is required only for identical particles.

Effects Of Spin.

Suppose H is independent of spin, such as with the He atom when we neglect the spin-orbit interaction arising from the interaction between the electron's magnetic moment, $\mu \underline{\sigma}$, with the magnetic field generated by its orbital motion.
Then there are elementary solutions to the Schrödinger equation:
(function of the space-coordinates) × (spin wavefunction).
H_0 is the whole wavefunction, that must have the appropriate symmetry. For example, for a pair of electrons, there are two possibilies:

$$\begin{pmatrix}\text{antisymmetric}\\ \text{space wavefunction}\end{pmatrix} \times \begin{pmatrix}\text{triplet spin}\\ \text{function}\end{pmatrix} \quad \text{or} \quad \begin{pmatrix}\text{symmetric space}\\ \text{wavefunction}\end{pmatrix} \times \begin{pmatrix}\text{singlet spin}\\ \text{function}\end{pmatrix}$$

Helium atom.

Neglect spin interactions and electron-electron interactions, so that the elementary eigenfunctions of H are products of hydrogen-like single-particle wavefunctions. These single-particle wavefunctions are Ψ_{nl}, with single-particle energies $E_{nl} \propto \frac{-1}{n^2}$ (independent of l), and for $n = 1, 2, 3, \ldots$, $l = 0, 1, \ldots, (n-1)$. The tightest binding is for $n=1, l=0$ and so the ground state for He has wavefunction
$\Psi_{10}(\underline{r}_1)\Psi_{10}(\underline{r}_2) \times$ (singlet spin function), with energy $2E_{10}$.
The angular momentum of this state is $(l=0) + (l=0) \Rightarrow$ total $l=0$. $s=0$, so total angular momentum $j=0$ (for the electrons!)

Jargon: $l=0$ - "S-wave", $l=1$ - "P-wave", $l=2$ - "D-wave".
So the He-atom ground state is ^1S (singlet S)
The next hydrogen-like level is $n=2$, $l=0$ or 1, energy $E_{20} = E_{21}$. So there are four excited states of the He atom, all having energy $E_{10} + E_{20}$:
$\frac{1}{\sqrt{2}}(\Psi_{10}(\underline{r}_1)\Psi_{20}(\underline{r}_2) + \Psi_{20}(\underline{r}_1)\Psi_{10}(\underline{r}_2)) \times$ (singlet). $l = 0+0 = 0$, $s=0$, so $j=0$. Have ^1S.
$\frac{1}{\sqrt{2}}(\Psi_{10}\Psi_{20} - \Psi_{20}\Psi_{10}) \times$ (triplet). $l=0$, $s=1$, so $j=1$. Now have ^3S.
$\frac{1}{\sqrt{2}}(\Psi_{10}\Psi_{21} + \Psi_{21}\Psi_{10}) \times$ (singlet). $l = 0+1 = 1$, $s=0$, $j=1$. Have ^1P.
$\frac{1}{\sqrt{2}}(\Psi_{10}\Psi_{21} - \Psi_{21}\Psi_{10}) \times$ (triplet). $l=1$, $s=1$, so $j = 0, 1,$ or 2. Have ^3P.

The largest correction is the electrostatic potential $\frac{e^2}{4\pi|\underline{r}_1 - \underline{r}_2|}$ between the electrons.
Including this splits the levels:

Normally the atom is in its ground state. If we heat the gas, there are collisions between atoms and some of their thermal kinetic energy can be transfered into an atom and excite one or more of the electrons into a higher state. The atom then "decays" into a lower state, by photon emission.
The photon energy, $\hbar\omega = \Delta E$, where ΔE = difference between energies of the atom before and after the decay. There are selection rules which determine which transitions are allowed (or at least, likely).

* Periodic System of the Elements.

Consider the ground states of multi-electron atoms. If we neglect the interaction between the electrons, the elementary wavefunctions are products of single-particle ones. For each single-electron wavefunction there are two spin states.
We count the multi-electron states:

$n=1$	$l=0$	$m=0$	2 single-particle states.	H, He
$n=2$	$l=0$	$m=0$	2 states	Li, Be
	$l=1$	$m=-1,0,1$	6 states	B, C, N, O, F, Ne
$n=3$	$l=0$	$m=0$	2 states	Na, ..
	$l=1$	$m=-1,0,1$	6 states	., ., ., ., ., A.
	$l=2$	$m=-2,..,2$	10 states	....

He, Ne, A are all very stable. Li, Na have similar chemistry. For Larger Z, electron-electron interactions become important. *.

Selection Rules

In a transition, certain quantities are preserved for deep reasons.
(i) momentum, (ii) energy, (iii) total angular momentum.
These conservation laws are consequences of the invariance of space under translation, time and rotation. For example, if $\underline{x}$ is the position of the centre of mass of a system which is closed (unaffected by outside forces), the Hamiltonian or Lagrangian will not depend explicitly on $\underline{x}$. So, $\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{\underline{x}}}\right) - \frac{\partial \mathcal{L}}{\partial x} = 0$.
These three laws led Pauli to predict the existence of the neutrino: $n \to p + e + \bar{\nu}$.
The sum of the mass and the energies of the p and e varies from event to event, and their total angular momentum is $(s=\frac{1}{2}) + (s=\frac{1}{2}) + (\text{integral } l) = \text{integer}$, while the n itself has spin $\frac{1}{2}$ (which is its total angular momentum when it is at rest). The $\bar{\nu}$ carries off the missing energy, which is extremely small, so its mass must be extremely small. Its charge is 0. It has spin $1/2$.

(iv) Electric charge: This is closely related to the gauge invariance of electrodynamics - the hamiltonian or lagrangian is invariant under the gauge transformation: $A^\mu \mapsto A^\mu + \partial\Lambda/\partial x_\mu$
(v) Baryon number: $p \not\to \pi^+ \nu$, though $p\bar{p} \to \pi^+\pi^-$.
(vi) Lepton number: $e^- p \not\to n\pi^0$.

Some other quantities are not conserved absolutely, but may be conserved depending which force is at work. There are four forces:
electromagnetic, strength measured by $\frac{e^2}{4\pi\varepsilon_0\hbar c^2} = \frac{1}{137}$ (dimensionless)
nuclear, strength 1 (range 10^{-15} m)
weak (eg. $n \to pe\bar{\nu}$), strength 10^{-5}
gravity, strength 10^{-40}.

Parity.

Classically, $m\ddot{\underline{r}} = \underline{F} = -\frac{\partial V}{\partial \underline{r}}$. Perform the mathematical operation: $\underline{r} \mapsto -\underline{r}$ (space reflection). If $V(\underline{r}) = V(-\underline{r})$, such as $\frac{e^2}{4\pi\varepsilon_0|\underline{r}|}$, we say V is a scalar. If $V(\underline{r}) = -V(-\underline{r})$, V is a pseudoscalar.

For scalar V, the equation of motion is unchanged under space reflection, and the space-reflected of any solution $\underline{r} = \underline{r}(t)$ will also be a solution.

For scalar V, $\underline{F} \to -\underline{F}$ under $\underline{r} \to -\underline{r}$, and we say $\underline{F}$ is a vector. For pseudoscalar V, $\underline{F} \to \underline{F}$, and $\underline{F}$ is an axial vector or pseudovector.

The electromagnetic and nuclear forces satisfy scalar V, but not the weak.

Wu experiment (1956): In the β-decay of C_0^{60} the electrons are emitted preferentially in the hemisphere opposite to the spin $\underline{S}$.

Space reflection:

Under space reflection, $\underline{S} \to \underline{S}$ (axial vector), because it transforms like $\underline{r} \wedge \underline{p}$.

So the space-reflected version of what is observed is not what is observed. So the potential contains a pseudoscalar term, such as $\underline{S}\cdot\underline{p}$, and the force contains an axial vector part. Experiments finds that the weak force is a mixture of vector and axial vector, with equal strengths.

Parity for Stationary States.

For the nuclear and electromagnetic interactions, H is a scalar: $H(\underline{r}) = H(-\underline{r})$. Then, if $H(\underline{r})\Psi(\underline{r}) = E\Psi(\underline{r})$, have $H(-\underline{r})\Psi(-\underline{r}) = E\Psi(-\underline{r})$ by renaming the argument of Ψ. So, $H(\underline{r})\Psi(-\underline{r}) = E\Psi(-\underline{r})$. Ie, if $\Psi(\underline{r})$ is an eigenstate of $H(\underline{r})$, then so is $\Psi(-\underline{r})$, with the same eigenvalue. If there is no degeneracy, $\Psi(-\underline{r}) = C\Psi(\underline{r})$, C a constant. Renaming $\underline{r}$, get $\Psi(\underline{r}) = C\Psi(-\underline{r})$, and so $C^2 = 1$; $C = \pm 1$ is the parity of the state.

If there is degeneracy, the solutions need not have definite parity, but linear combinations of them do: for example, if we have a solution $\Psi(\underline{r})$, take $\frac{1}{\sqrt{2}}(\Psi(\underline{r}) \pm \Psi(-\underline{r}))$

The Deuteron (n,p bound state).

The nuclear force has scalar potential $V(\underline{r}_1 - \underline{r}_2)$, which is spin-independent to a first approximation. $H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\underline{r}_1 - \underline{r}_2)$, where $m_1 \approx m_2 =: m$.

Introduce centre-of-mass coordinates: $\underline{r} = \underline{r}_1 - \underline{r}_2$, $\underline{R} = \frac{m_1\underline{r}_1 + m_2\underline{r}_2}{m_1 + m_2}$.

Then, $-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2$, where $M = m_1 + m_2$, $\mu = \frac{m_1 m_2}{m_1 + m_2}$ (reduced mass)

In the case $m_1 = m_2 = m$, have $M = 2m$, $\mu = \frac{1}{2}m$.

So there are eigenfunctions $\Psi(\underline{r})e^{i\underline{K}\cdot\underline{R}}$ corresponding to kinetic energy $\frac{\hbar^2 K^2}{2M}$, associated with the centre of mass energy, with Ψ satisfying $\left[-\frac{\hbar^2}{2\mu}\nabla_{\underline{r}}^2 + V(\underline{r})\right]\Psi(\underline{r}) = E\Psi(\underline{r})$

So, as classically, the centre of mass moves freely like a particle of mass $M = m_1 + m_2$ and the relative motion is like that of a single particle of reduced mass μ.

In the rest frame of the centre of mass, $\underline{p}_1 = -\underline{p}_2 =: \underline{p}$; the total angular momentum is: $\hbar \underline{L} = \underline{r}_1 \wedge \underline{p}_1 + \underline{r}_2 \wedge \underline{p}_2 = (\underline{r}_1 - \underline{r}_2) \wedge \underline{p} = \underline{r} \wedge \underline{p}$.

If we neglect spin interactions, $V = V(|\underline{r}|)$ because there is no ~~pe~~ preferred direction. Then, $[\underline{L}^2, H] = 0$ and the eigenstates of H can be taken to be eigenstates of $\underline{L}^2$, with wavefunctions $\Psi(\underline{r}) = R(r)\, Y_{lm}(\theta, \varphi)$ such that

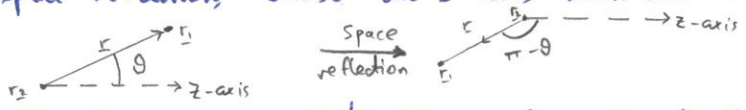
$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} rR + \left(V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right) rR = E_r R$$

Here, $\hbar^2 l(l+1)/2\mu r^2$ behaves like an addition to V (the centrifugal potential), which corresponds to a repulsive potential. We expect the tightest bound state to be $l=0$ so that the repulsion is absent.

Experiment finds that the deuteron ground state has total angular momentum $j=1$. So if $l=0$, have $s=1$. But one can calculate the deuteron's magnetic moment as a function of l and s. For $l=0, s=1$, it almost agrees with experiment. The remedy is to include spin interaction, so that ~~term~~ terms such as $\underline{S}\cdot\underline{r}$ appear in H, and then $[\underline{L}^2, H] \neq 0$ and so l is not a good quantum number. The ground state is: $\begin{pmatrix} \text{mainly} \\ l=0, s=1 \end{pmatrix} + \begin{pmatrix} \text{linear combinations of} \\ l=1, s=0,1 \text{ or } l=2, s=1 \end{pmatrix}$

We need the state to have definite parity, because there is no degeneracy (according to experiment).

Recall that $Y_{lm}(\theta, \varphi) = \text{const.}\, P_l^m(\theta)\, e^{im\varphi}$. To investigate how these behave under space reflection, choose the z-axis such that $m=0$. Then this becomes const. $P_l(\theta)$



ie, $\theta \to \pi - \theta$, $\cos\theta \to -\cos\theta$.

So, $P_l \to (-1)^l P_l$.

So the parity is $(-1)^l$. The main part of the wavefunction therefore has parity $+1$, and the extra piece must also have parity $+1$, which excludes $l=1$. Experiment finds: S-wave + 4% D-wave.

Transitions

$H\Psi = i\hbar\dot{\Psi}$, so if $H(\underline{r}) = H(-\underline{r})$, the change $\Delta\Psi$ in time Δt has the same parity as Ψ. Thus if it is the electromagnetic or nuclear force that causes a transition, parity is conserved.

Example: pn scattering.

Work in the centre-of-mass frame, where the total momentum is 0. Suppose, for example, that the initial state is singlet (total $s=0$). Then, $j=l$ and $p=(-1)^l$. Conservation of total angular momentum allows the final states:

singlet, same l, $p=(-1)^l$.

triplet, $l-1, l, l+1$ (except when $l=0$, when triplet, l is the only possibility).

Parity conservation rules out orbital angular momentum changing by one unit.

For pp-scattering, the same applies, but also the state must be antisymmetric. So in the original state we need l even, which excludes triplet-l in the final state, so singlet-l → singlet-l.

Intrinsic Parity.

Bound states have a parity which we may calculate, but elementary particles may also have an intrinsic parity obtained from experiment.

$$\begin{pmatrix}\text{parity}\\ \text{of a state}\end{pmatrix} = \begin{pmatrix}\text{parity due to}\\ \text{orbital motion}\end{pmatrix} \times \begin{pmatrix}\text{product of the intrinsic}\\ \text{parities of the particles}\end{pmatrix}.$$

This matters only if particles are created or destroyed in the transition, because otherwise the intrinsic parity factor just cancels in the parity conservation equation. For the photon, we may calculate this intrinsic parity. Since it has zero mass, if there is no interaction, $E = c\sqrt{p^2 + c^2m^2}$ gives $E - c^2p^2 = 0$. To get a wave equation, use the same correspondance as gives the time-independent Schrödinger equation, $\underline{p} \to -i\hbar\underline{\nabla}$ and $E \to i\hbar\,\partial/\partial t$, we get $\left(\frac{\partial^2}{\partial t^2} - \nabla^2\right)A = 0$. It is natural to identify the wavefunction A with the classical vector potential (more than one component because the photon has spin 1). In the presence of interaction, $\left(\frac{\partial^2}{\partial t^2} - \nabla^2\right)A = \underline{j}$. Under space reflection, $\underline{j} \to -\underline{j}$, so $A \to -A$, and photons have negative intrinsic parity, as confirmed by experiment.

Excitation and decay of the hydrogen atom

———— $n=2,\ L=1,\ j=\frac{1}{2}$ or $\frac{3}{2},\ p=-$

———— $n=2,\ L=0,\ j=1/2,\ p=+$

———— $n=1,\ L=0,\ j=\frac{1}{2},\ p=+$ - for the electron.

We ignore the electron's intrinsic parity because it is present in both the initial and final states (also the proton). Consider the excitation/decay of the atom by photon absorption/decay. Two-photon transitions occur with a probability suppressed by a factor of $\frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137}$. The transition occurs most readily for $L=0$ photons, so that there is no centrifugal barrier.

$(j=3/2,\ p=-1) \leftrightarrow (j=1/2,\ p=+1) + \gamma$. j, p can be conserved.

$(j=1/2,\ p=-1) \leftrightarrow (j=1/2,\ p=+1) + \gamma$ ——— " ———

$(j=1/2,\ p=+1) \leftrightarrow (j=1/2,\ p=+1) + \gamma$ j is conserved but not p.

The last transition can occur, with $L=1$ for the photon, but not so readily. So the absorption of such a photon from the ground state to this excited state occurs fairly rarely, and when it does the state has rather long lifetime.

Summary.

(i) Parity is conserved for nuclear-force and electromagnetic transitions, but not for weak interactions.

(ii) Unless there is degeneracy, when parity is conserved, stationary states have definite parity.

(iii) Spin is an axial vector, and is therefore unaffected by space reflection. The parity of a state is determined by orbital motion and the intrinsic parities of the particles.

(iv) In the centre-of-mass frame of a pair of particles, the parity associated with the orbital motion is $(-1)^l$.

(v) For an identical pair of particles there is an extra condition from the requirement on the symmetry or antisymmetry of the wavefunction. The space part of the wavefunction has symmetry $(-1)^l$. For two spin-$\frac{1}{2}$ particles, the singlet $(s=0)$ wavefunction is antisymmetric and the triplet $(s=1)$ is symmetric.

Variational Principle.

If Ψ is any wavefunction, $\langle H\rangle = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0$, where E_0 is the ground-state energy. Expand $|\Psi\rangle$ in terms of the (unknown) eigenstates of H:
$|\Psi\rangle = \sum_i c_i|i\rangle$. Then, $\langle H\rangle = \sum_i |c_i|^2 E_i / \sum_i |c_i|^2$.
The stationary values of $\langle H\rangle$ when we vary $\mathrm{Re}\, c_i$ and $\mathrm{Im}\, c_i$, or equivalently c_i and c_i^*, obtained from $\frac{\partial\langle H\rangle}{\partial c_i} = 0 = \frac{\partial\langle H\rangle}{\partial c_i^*}$ for all i, are just the eigenvalues E_i.
To use this, make an intelligent guess for Ψ, including in it one or more adjustable parameters λ. The stationary values of $\langle H\rangle$ when we vary the λ's are approximations to the eigenvalues of H. Varying the λ's corresponds to varying the expansion coefficients c_i. Normally, the number of λ's $\ll$ the number of c_i, so the variation of the c_i corresponding to the variation of the λ's is subject to a lot of constraints. So usually we do not achieve the exact eigenvalues E_i. But if we choose Ψ intelligently, we can hope to get near one. One will not usually end up with the true function Ψ, but if Ψ is "wrong" by $O(\varepsilon)$, then the calculated energy is wrong only by $O(\varepsilon^2)$. For if all the $c_i = O(\varepsilon)$ except for $i=I$,
$$\langle H\rangle = \frac{|c_I|^2 E_I + O(\varepsilon^2)}{|c_I|^2 + O(\varepsilon^2)} = E_I + O(\varepsilon^2)$$
So even a poor wavefunction can give quite a good estimate of the energy eigenvalue.

Example: the Helium Atom

$H = H_0(\underline{r}_1) + H_0(\underline{r}_2) + \frac{e^2}{r_{12}}$. $r_{12} = |\underline{r}_1 - \underline{r}_2|$. (units where $4\pi\varepsilon_0 = 1$)
$H_0(\underline{r}) = \frac{p^2}{2m} - \frac{2e^2}{r}$.
One could use perturbation theory, although it is hard to argue that $\frac{e^2}{r_{12}}$ is small compared with $-2e^2/r_1$ and $-2e^2/r_2$. It gives the energy correct to within 6% (1st order).
To use the variational principle, use a product-like wavefunctions, corresponding to nuclear charge Ze:
$$\Psi = \Psi_1\Psi_2 = \frac{Z^3}{\pi a_0^3} e^{-Zr_1/a_0} \cdot e^{-Zr_2/a_0}, \quad \text{where } \left(\frac{p^2}{2m} - \frac{Ze^2}{r}\right)\Psi_i(\underline{r}) = \frac{-e^2Z^2}{2a_0}\Psi_i.$$
a_0 = hydrogen Bohr radius.
The physical intuition which suggests that this is useful is that one electron partially screens the nuclear charge from the other. If we take Z as the variational parameter, we expect we will end up with $Z<2$.
Find $\langle H\rangle = \frac{e^2}{2a_0}\left[-2Z^2 + 4Z(Z-2) + \frac{5}{4}Z\right]$.
$\frac{\partial\langle H\rangle}{\partial Z} = 0$ gives $Z = 2 - 5/16$, giving value for $\langle H\rangle$ correct to within 2%.

We get only one stationary value, and because we have used ground-state hydrogen-like wavefunctions, we expect the resulting value for $\langle H \rangle$ to be closer to E_0 rather than one of the higher E_i. To get the higher E_i we must use a different trial wavefunction, Ψ, such that it has a chance, for suitable values of the parameters we include in it, to come close to one of the Ψ_i.

Translation Operators

There are two kinds of translation: (a) of the apparatus that produces the state; (b) of the apparatus that measures the state.

Suppose that, under (a), $|\rangle \to D(\underline{a})|\rangle$ and $\langle| \to \langle| D^\dagger(\underline{a})$.
For any two states, want $\langle A|B\rangle = \int d^3r\, \Psi_A^*(\underline{r})\Psi_B(\underline{r})$ to be unchanged: $\langle A|B\rangle = \langle A|D^\dagger(\underline{a})D(\underline{a})|B\rangle$.
If this is true for all $|A\rangle, |B\rangle$, then $D^\dagger(\underline{a})D(\underline{a}) = 1$, so $D(\underline{a})$ is unitary.
If we translate through $\underline{a}$ and then through $-\underline{a}$, we should return to the initial state: $|\rangle \to D(-\underline{a})D(\underline{a})|\rangle = |\rangle$ for all $|\rangle$. $\therefore D(-\underline{a})D(\underline{a}) = 1$. Ie. $D(-\underline{a}) = D^{-1}(\underline{a}) = D^\dagger(\underline{a})$.

If we make both kinds of translation, the results of measurements (ie, matrix elements) should be unchanged. So, if moving the measuring apparatus makes $Q \to Q'$, then
$\langle B|Q|A\rangle \to \langle B|D^{-1}(\underline{a})\, Q'\, D(\underline{a})|A\rangle = \langle B|Q|A\rangle$ for all $|A\rangle, |B\rangle$. $\therefore Q' = D(\underline{a})\, Q\, D^{-1}(\underline{a})$

We shall not translate the measuring apparatus. Then the matrix elements do change: $\langle B|Q|A\rangle \to \langle B|D^{-1}(\underline{a})\, Q\, D(\underline{a})|A\rangle$. We can achieve this if, instead of changing the states when the production apparatus, we change the operators: $Q \to D^{-1}(\underline{a})\, Q\, D(\underline{a})$.

To Find $D(\underline{a})$

When we move the apparatus that prepares the state, a particle coordinate operator $\langle \underline{x} \rangle \to \langle \underline{x} + \underline{a} \rangle$ which we achieve by leaving the bra and ket unchanged, and making $\underline{x} \to \underline{x} + \underline{a}$. Ie, $D^{-1}(\underline{a})\, \underline{x}\, D(\underline{a}) = \underline{x} + \underline{a}$
Consider first an infinitessimal translation, $\underline{a} = \delta\underline{a}$, and expand: $D(\delta\underline{a}) = 1 + i\,\underline{d}.\delta\underline{a} + O(\delta\underline{a}^2)$.
Then, $D^\dagger(\delta\underline{a})D(\delta\underline{a}) = (1 - i\underline{d}^\dagger.\delta\underline{a} + O(\delta\underline{a}^2))(1 + i\underline{d}.\delta\underline{a} + O(\delta\underline{a}^2)) = 1 + i(\underline{d} - \underline{d}^\dagger).\delta\underline{a} + O(\delta\underline{a}^2)$
$\therefore \underline{d} = \underline{d}^\dagger$, ie $\underline{d}$ is hermitian. It is the <u>generator</u> of the translation.

$(1 - i\underline{d}^\dagger.\delta\underline{a} + O(\delta\underline{a}^2))\,\underline{x}\,(1 + i\underline{d}.\delta\underline{a} + O(\delta\underline{a}^2)) = \underline{x} + \delta\underline{a}$, giving: $-i[d_j, x_i]\,\delta a_j = \delta a_i$, or, $[d_j, x_i] = i\delta_{ij}$, because this is to be true for all $\delta\underline{a}$.

A solution to this is $\underline{d} = -\underline{p}/\hbar$, where $\underline{p}$ is the total momentum of the system, ie the sum of all the momenta of all the separate particles. In order to establish that this is the correct $\underline{d}$, we must check that all the other observables needed to make a complete set also transform correctly. These are particle momenta, and internal variables such as particles spins and charges.

They all satisfy $\delta Q = -i[d_j, Q]\delta a_j = 0$, and $\underline{d} = -\underline{p}/\hbar$ does give this. Let Q be any observable. Suppose that, under translation $\underline{a}$, $Q \to Q(\underline{a})$. Under a further infinitessimal translation, $Q(\underline{a}) \to Q(\underline{a}) + \delta Q(\underline{a})$, with $\delta Q = \frac{i}{\hbar}[\underline{p}_j, Q(\underline{a})]\delta a_j = \frac{i}{\hbar}[\underline{p}, Q(\underline{a})]\cdot\delta\underline{a}$.

Or, $\frac{\partial Q}{\partial \underline{a}} = \frac{i}{\hbar}[\underline{p}, Q]$, or $\frac{\partial Q}{\partial \underline{a}} = -\frac{i}{\hbar}\underline{p}Q + \frac{i}{\hbar}Q\underline{p} = 0$.

Or, $\frac{\partial}{\partial \underline{a}}\left(e^{-i\underline{p}\cdot\underline{a}/\hbar} Q e^{i\underline{p}\cdot\underline{a}/\hbar}\right) = 0$. $\therefore Q(\underline{a}) = e^{i\underline{p}\cdot\underline{a}/\hbar} Q(0) e^{-i\underline{p}\cdot\underline{a}/\hbar}$. So $D(\underline{a}) = e^{-i\underline{p}\cdot\underline{a}/\hbar}$.

Notice the "group property": $D(\underline{a})D(\underline{b}) = e^{-i\underline{p}\cdot\underline{a}/\hbar} e^{-i\underline{p}\cdot\underline{b}/\hbar} = e^{-i\underline{p}\cdot(\underline{a}+\underline{b})/\hbar} = D(\underline{a}+\underline{b})$

For a closed system, H depends only on the separations between the particles in it and so is translation invariant. $\therefore D^{-1}HD = H$ for all $\underline{a}$, and $[\underline{d}, H] = 0$, ie, $[\underline{p}, H] = 0$.

In the Heisenberg picture, where the bras and kets do not vary with t, this gives $\dot{\underline{p}} = 0$. So the conservation of total momentum of a closed system follows from translation invariance.

Rotations.

Introduce $D(R)$ corresponding to a rotation R, analogous to $D(\underline{a})$. $D^{+}(R)D(R) = 1$, $D(R^{-1}) = D^{-1}(R)$.

Two types of rotation about the same axis:

(a) of the equipment that prepares the state: either $|\rangle \to D(R)|\rangle$ or $Q \to D^{-1}(R)\,Q\,D(R)$

(b) of the apparatus that measures the observables: $Q \to D(R)\,Q\,D^{-1}(R)$.

To find D, consider type (a). For the coordinate of any particle, let $D^{-1}(R)\underline{x}D(R) = \underline{x}_{rot}$.

Let R_1 be an infinitessimal rotation about the x_1-axis, through angle $\delta\varphi_1$.

$$\underline{x}_{rot} = \begin{pmatrix} x_1 \\ x_2\cos\delta\varphi_1 - x_3\sin\delta\varphi_1 \\ x_3\cos\delta\varphi_1 + x_2\sin\delta\varphi_1 \end{pmatrix} = \underline{x} + \begin{pmatrix} 0 \\ -x_3 \\ x_2 \end{pmatrix}\delta\varphi_1 + O(\delta\varphi_1^2)$$

Expand $D(R_1)$ as: $1 + iI_1\delta\varphi_1 + \cdots$, so $D^{-1}(R_1)\,x_i\,D(R_1) = x_i - i\delta\varphi_1[I_1, x_i] + \cdots$

$\therefore [I_1, x_1] = 0$, $[I_1, x_2] = -ix_3$, $[I_1, x_3] = ix_2$.

Solution: $I_1 = -J_1$, where $\underline{J}$ is the total angular momentum

$$\underline{J} = \sum_{\text{particles}}(\underline{S} + \underline{L}) = \sum_{\text{particles}}\left(\underline{S} + \frac{1}{\hbar}\underline{x}\wedge\underline{p}\right)$$

$\underline{S}$ commutes with each x_i, as do the contributions to $\underline{L}$ from all the other particles. When $\underline{x}, \underline{p}$ refer to the same particle, $[\frac{1}{\hbar}(\underline{x}\wedge\underline{p})_i, x_j] = i\varepsilon_{ijk}x_k$.

We must check that the remaining members of a complete set of observables transform correctly.

Under a rotation, all vectors have their components mixed up similarly, so in particular we want $[I_1, p_1] = 0$, $[I_1, p_2] = -ip_3$, $[I_1, p_3] = ip_2$ – likewise for s_i.

Just as for any particle, $[L_i, x_j] = i\varepsilon_{ijk}x_k$, so also $[L_i, p_j] = i\varepsilon_{ijk}p_k$, by explicit calculation, and $[S_i, S_j] = i\varepsilon_{ijk}S_k$ from the defining algebra of (spin) angular momentum operators.

There is nothing special about the 1-direction. For an infinitessimal rotation through angle $\delta\varphi$ about an axis in the direction $\delta\underline{\varphi}$, $D(R) = 1 + i\underline{I}\cdot\delta\underline{\varphi} + \cdots = 1 - i\underline{J}\cdot\delta\underline{\varphi} + \cdots$

From this, $D(R) = e^{-i\underline{J}.\underline{\varphi}}$ for a non-infinitessimal rotation. For a closed system, there is no preferred direction and so H is rotation invariant. Thus $[H, \underline{I}] = 0 = [H, \underline{J}]$. So in the Heisenberg picture, $\dot{\underline{J}} = 0$. So for a closed system, the total angular momentum $\underline{J}$ is conserved, as a consequence of the rotation-invariance of space.

The Rotation Group.

Two successive rotations, R_1 then R_2 are equivalent to a single rotation $R_2 R_1$.
Under R_1, $|\rangle \to D(R_1)|\rangle$, which under R_2 becomes $D(R_2)D(R_1)|\rangle$, for any $|\rangle$.
So $D(R_2R_1) = D(R_2)D(R_1)$, and the $D(R)$ obey the same algebra as the rotations R.
We say that the operators $D(R)$ form a representation of the group of rotations R.
The group is non-abelian: generally, $D(R_1R_2) \neq D(R_2R_1)$, ie $e^{-i\underline{J}.\underline{\varphi}_1} e^{-i\underline{J}.\underline{\varphi}_2} \neq e^{-i\underline{J}.\underline{\varphi}_2} e^{-i\underline{J}.\underline{\varphi}_1}$.
(This is because the components of $\underline{J}$ do not commute with each other)

Consider $D(R)|jm\rangle$. It is the state of total angular momentum j for which it is known that the component of $\underline{J}$ in the direction got by rotating the z-axis through R is m.
So $\langle j'm'|D(R)|jm\rangle = 0$ for $j \neq j'$.
Define $\langle jm'|D(R)|jm\rangle = D^j_{m'm}(R)$, a $(2j+1)\times(2j+1)$ matrix for given j.
The product of two such matrices:

$$[\underline{D}^j(R_1)\,\underline{D}^j(R_2)]_{m'm} = \sum_{m''} D^j_{m'm''}(R_1)\,D^j_{m''m}(R_2) = \sum_{m'',j''} \langle jm'|D(R_1)|j''m''\rangle\langle j''m''|D(R_2)|jm\rangle$$

(only $j''=j$ contributes) $\quad = \langle jm'|D(R_1)D(R_2)|jm\rangle$ (by completeness)

$$= \langle jm'|D(R_1R_2)|jm\rangle = D^j_{m'm}(R_1R_2)$$

So the matrices also form a representation of the rotation group - the $(2j+1)$-dimensional unitary irreducible representation. It is irreducible because $D(R)|jm\rangle = \sum_{m',j'} |j'm'\rangle\langle j'm'|D(R)|jm\rangle = \sum_{m'} |jm'\rangle D^j_{m'm}(R)$, and for general R all the m' are needed. - There is no subspace that is invariant under all the rotations.
A reducible representation is such that, after suitable linear transformation on the states, all the matrices have the form $\begin{pmatrix} \underline{D}^a & 0 \\ 0 & \underline{D}^b \end{pmatrix}$ - ie it is made up of two representations of lower dimension,

Irreducible Tensor Operators.

Define an irreducible tensor operator of rank k: a set of $(2k+1)$ operators T^k_κ with $\kappa = -k, \dots, k$, such that $D^{-1}(R)\,T^k_\kappa\,D(R) = \sum_{\kappa'=-k}^{k} T^k_{\kappa'} D^k_{\kappa'\kappa}(R^{-1})$.
The simplest example is $k=1$, a vector operator. Under a rotation, the Cartesian components of a vector are mixed up in the same way as for the prototype vector $\underline{x}$: we have $[J_i, V_j] = i\varepsilon_{ijk}V_k$.
Its spherical components V_k are: $V_{+1} = -\frac{1}{\sqrt{2}}(V_x + iV_y)$, $V_0 = V_z$, $V_{-1} = \frac{1}{\sqrt{2}}(V_x - iV_y)$
Consider the particular case $\underline{V} = \underline{x}$ - the coordinate of a particle. One can show that a state $T^k_\kappa|j=0, m=0\rangle$, unless it vanishes, transforms like $|k\kappa\rangle$, ie the tensor operator creates total angular momentum k, z-component κ.

So, $x_{+1}|0\rangle = \frac{-1}{\sqrt{2}}(x+iy)|0\rangle = \frac{-1}{\sqrt{2}} r\sin\theta\, e^{i\varphi}|0\rangle$ has $j=1$, $m=1$.

$x_0|0\rangle = z|0\rangle = r\cos\theta|0\rangle$ has $j=1$, $m=0$.

$x_{-1}|0\rangle = \frac{1}{\sqrt{2}}(x-iy) = \frac{1}{\sqrt{2}} r\sin\theta\, e^{-i\varphi}|0\rangle$ has $j=1$, $m=-1$.

Obviously $\underline{x}$ creates orbital angular momentum rather than spin.
Up to a constant factor, $\sin\theta\, e^{i\varphi} = Y_1^1(\theta,\varphi) = P_1^1(\theta)e^{i\varphi}$.

$$\cos\theta = Y_0^1(\theta,\varphi) = P_0^1(\cos\theta)$$

$$\sin\theta\, e^{-i\varphi} = Y_{-1}^1(\theta,\varphi) = P_1^1(\theta)e^{-i\varphi}.$$

Consider a hydrogen atom in a uniform electric field: $H = H_0 + e\mathcal{E}z$. If the atom were originally in an eigenstate $|1\rangle$ of H_0, after time Δt, the change in the state $\propto H|1\rangle$, and the probability of finding that the atom is now in a different eigenstate $|2\rangle$ is proportional to $|\langle 2|H|1\rangle|^2$.
But $\langle 2|H|1\rangle = \langle 2|H_0 + e\mathcal{E}z|1\rangle = e\mathcal{E}\langle 2|z|1\rangle$
Since z is the $k=0$ component of a vector, it creates (orbital) angular momentum 1, with z-component 0.
If $|1\rangle = |L_1 m_1$ & other labels$\rangle$, and $|2\rangle = |L_2 m_2$ & other labels$\rangle$, the matrix element is 0 unless $L_2 = L_1 - 1, L_1$, or $L_1 + 1$ and $m_1 = m_2$.