Quantum Mechanics I

Summary

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1 Quantum behavior

Two Slit experiment

- With **bullets**, if only one hole (1 or 2) is open we see a Gaussian $P_{1,2}$ centered around the hole. If both holes are open these Gaussians simply add: $P_{12} = P_1 + P_2$.
- With **waves**, if only one hole (1 or 2) is open we find that the intensity $I_{1,2} \sim |A|^2$ is a function centered around the hole. If both holes are open we find an interference pattern $I_{12} \neq I_1 + I_2$. The amplitude after the double slit is given by $A_{12} = A_1 + A_2$. Therefore the total intensity is
$$I_{12} = |A_1|^2 + |A_2|^2 + 2|A_1||A_2|\cos\delta = I_1 + I_2 + \underbrace{2|A_1||A_2|\cos\delta}_{\text{interference}}.$$
- Now, with **electrons** that pass through a double slit, we interestingly also see an interference pattern in the probability of arrival $P_{12} \neq P_1 + P_2$, even though each electron arrives at the detector as a single particle (can reconstruct its full energy, tracks a curve of charge one in B-field, etc.).

  Further, if we put two light sources behind the two hole such that we see which hole the electrons went through, the interference pattern is destroyed and we have $P_{12} = P_1 + P_2$ again.

  If we dim the light and/or adjust the wavelength of the light we can partially restore the interference patter, as either not every electron hits a photon or the light gets too fuzzy and we can't tell which hole the light came from because the wavelength is comparable to the hole distance.

Probability and probability amplitudes

- The probability P of an event is given by the square of the absolute probability amplitude ϕ:
$$P = |\phi|^2.$$
  If an event can occur in several ways, there is interference:
$$\phi = \phi_1 + \phi_2 \qquad P = |\phi_1 + \phi_2|^2.$$
  If an experiment can determine which alternative happened, the interference is destroyed:
$$P = P_1 + P_2.$$
- **Heisenberg's uncertainty principle**: $(\Delta x)(\Delta p_x) = h$.
- "**bra-ket**" notation of Dirac:
$$\langle \text{final condition} | \text{initial condition} \rangle .$$
  For $\langle \text{arrives at } x | \text{leaves at } s \rangle$, or short $\langle x|s\rangle$ the probability is
$$P = |\langle x|s\rangle|^2.$$
  If an event can occur in multiple ways, we sum the amplitudes:
$$\langle x|s\rangle = \langle x|s\rangle_{\text{slit 1}} + \langle x|s\rangle_{\text{slit 2}} .$$
  Sequences of events factorize:
$$\langle x|s\rangle_{\text{slit 1}} = \langle x|\text{slit 1}\rangle \langle \text{slit 1}|s\rangle .$$
- Let a particle transition from position $\mathbf{x}_1$ to $\mathbf{x}_2$ with some intermediate position $\mathbf{y}$. The corresponding amplitude is $\langle \mathbf{x}_2|\mathbf{x}_1\rangle = \langle \mathbf{x}_2|\mathbf{y}\rangle \langle \mathbf{y}|\mathbf{x}_1\rangle$. The transition amplitude of a free particle from a position $\mathbf{x}$ to a position $\mathbf{y}$ is
$$\mathcal{M}_{x\to y} \sim \frac{e^{-\frac{i}{\hbar}\mathbf{p}\cdot(\mathbf{x}-\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}.$$

2 Quantum Measurement and Quantum States

Stern-Gerlach Experiment We can describe atoms as small magnetic dipoles μ. If we direct such a beam towards an inhomogeneous magnetic field with gradient in the z-direction, we would expect the beam to spread out in the z-direction according to the (assumed continuous) value of μ_z. But this is not what happens. Instead the beam splits into n discrete beams, depending on the *spin* of the atoms. Atoms with spin-j split into $n = 2j+1$ beams.

- For spin-1 particles the beam splits into three, corresponding to the states $|\hat z,+\rangle$, $|\hat z,0\rangle$ and $|\hat z,-\rangle$.
- By sending each beam through a gate and then apply an opposite magnetic field to recombine the beams we can build a filter. Chaining these filters we can measure how many particles make it through:
$$\begin{aligned}&\langle \hat z,+|\hat z,+\rangle = \langle \hat z,0|\hat z,0\rangle = \langle \hat z,-|\hat z,-\rangle \quad = 1,\\ &\langle \hat z,+|\hat z,0\rangle = \langle \hat z,0|\hat z,+\rangle = \langle \hat z,+|\hat z,-\rangle\\ &= \langle \hat z,-|\hat z,+\rangle = \langle \hat z,0|\hat z,-\rangle = \langle \hat z,-|\hat z,0\rangle = 0.\end{aligned}$$
- If the second filter is tilted by θ along $\mathbf{n}$ we find that all transitions are possible $\langle \hat n,a|\hat z,b\rangle \neq 0$, for $a,b \in \{+,0,-\}$. Further, the transition from some $|\hat z,a\rangle$ to any $|\hat n,b\rangle$ always takes place:
$$\begin{aligned}|\langle \hat n,+|\hat z,+\rangle|^2 + |\langle \hat n,0|\hat z,+\rangle|^2 + |\langle \hat n,-|\hat z,+\rangle|^2 = 1,\\ |\langle \hat n,+|\hat z,0\rangle|^2 + |\langle \hat n,0|\hat z,0\rangle|^2 + |\langle \hat n,-|\hat z,0\rangle|^2 = 1,\\ |\langle \hat n,+|\hat z,-\rangle|^2 + |\langle \hat n,0|\hat z,-\rangle|^2 + |\langle \hat n,-|\hat z,-\rangle|^2 = 1,\end{aligned}$$
- If we take three filters, the first aligned with the z-axis and filtering $|\hat z,+\rangle$ states, the second one tilted by θ along $\mathbf{n}$ and filtering $|\hat n,0\rangle$ states and the third also aligned along the z-direction. When the particles arrive at the third filter, we find that they transition through all the states $|\hat z,\{+,0,-\}\rangle$, despite the fact that they have once been in a pure $|\hat z,+\rangle$ state.

  The ratio of probabilities of the two transitions $\langle \hat z,+|\hat n,0\rangle \langle \hat n,0|\hat z,+\rangle$ and $\langle \hat z,-|\hat n,0\rangle \langle \hat n,0|\hat z,+\rangle$ is independent of the state prior to the second filter:
$$\frac{|\langle \hat z,+|\hat n,0\rangle \langle \hat n,0|\hat z,+\rangle|^2}{|\langle \hat z,-|\hat n,0\rangle \langle \hat n,0|\hat z,+\rangle|^2} = \frac{|\langle \hat z,+|\hat n,0\rangle|^2}{|\langle \hat z,-|\hat n,0\rangle|^2}.$$
- If we setup the filter to filter $|\hat z,+\rangle \to |\hat n,0\rangle \to |\hat z,-\rangle$, we find that $N \times |\langle \hat z,-|\hat n,0\rangle|^2$ atoms exit the last filter, where N is the number of atoms entering the setup. If we open the second filter to let through all atoms, no atoms make it out, as $\langle \hat z,+|\hat z,-\rangle = 0$. It follows:
$$\langle \chi|\phi\rangle = \sum_{\text{all } i} = \langle \chi|i\rangle \langle i|\phi\rangle . \tag{1}$$
- Atomic systems can be decomposed into **base states** by a filtering process, with the following properties:
  - If a system is in a base state then the future evolution is independent of the past.
  - Base states states satisfy eqn. (1).
  - Base states are completely different from each other:
$$\langle i|j\rangle = \delta_{ij}.$$
- Further we require: $\langle \phi|\chi\rangle^* = \langle \chi|\phi\rangle$.
- An atom which is prepared at state $|\chi\rangle$ and is subjected to a physical process A that transitions it into state $|\phi\rangle$ is denoted by $\langle \phi| A |\chi\rangle$.

3 Quantum Mechanics and Linear Algebra

- Amplitudes are the inner products of vectors in the **ket space** of physical states:
$$\langle b|a\rangle \leftrightarrow \mathbf{b}\cdot\mathbf{a}.$$
$$|\alpha\rangle + |\beta\rangle = |\gamma\rangle, \qquad c\,|\chi\rangle \text{ and } |\chi\rangle \ \to\ \text{same physical state.}$$
- Changes in physical states are represented by the action of **operators** on kets:
$$A\,|\psi\rangle = |\phi\rangle .$$
  Operators A have eigenstates $|i\rangle$, which correspond to base states with eigenvalues λ_i:
$$A\,|i\rangle = \lambda_i\,|i\rangle$$
  Any physical state $|\phi\rangle$ can be represented as a superposition of base states:
$$\forall\,|\phi\rangle\ \exists\{c_i\}: \quad |\phi\rangle = \sum_i c_i\,|i\rangle , \quad \text{where } c_i = \langle i|\phi\rangle .$$
- The dual space of **bra states** $\langle\phi|$ is the set of "final conditions", where as the ket space is set of "initial conditions". For a general superposition of ket states the bra dual reads:
$$c_1\,|a_1\rangle + \cdots + c_n\,|a_n\rangle \ \leftrightarrow\ c_1^*\,\langle a_1| + \ldots + c_n^*\,\langle a_n| .$$
- The dual bra-space defines probability amplitudes as **inner products** $\langle a|b\rangle$ with
$$\langle a|b\rangle = \langle b|a\rangle^* \qquad \langle\phi|\phi\rangle \geq 0,\ \forall\,|\phi\rangle ,$$
  and $\sqrt{\langle\phi|\phi\rangle}$ is the norm of the state $|\phi\rangle$. We can normalize all states without altering the physics:
$$|\phi\rangle \to \left|\tilde\phi\right\rangle = \frac{|\phi\rangle}{\sqrt{\langle\phi|\phi\rangle}}, \quad \text{where } \left\langle\tilde\phi\middle|\tilde\phi\right\rangle = 1.$$
- Properties of operators:
  i) Two operators are equal, $X = Y$, if
$$X\,|\phi\rangle = Y\,|\phi\rangle , \quad \forall\,|\phi\rangle .$$
  ii) An operator is zero, $X = 0$, if $X\,|\phi\rangle = 0 \quad \forall\,|\phi\rangle$.
  iii) $X+Y = Y+X \quad X+(Y+Z) = (X+Y)+Z = X+Y+Z$
  iv) $X(YZ) = (XY)Z = XYZ$
  v) $XY \neq YX$
- The **outer product** $|b\rangle\langle a|$ is an operator turning a generic state $|\phi\rangle$ to a state $|b\rangle$:
$$\begin{aligned}(|b\rangle\langle a|)\,|\phi\rangle &= |b\rangle\,(\langle a|\phi\rangle) = (\langle a|\phi\rangle)\,|b\rangle\\ (\text{operator})\,|\text{state}\rangle = \ldots \quad &= (\text{number})\,|\text{new state}\rangle\end{aligned}$$
- $X^\dagger$ is the **hermitian adjoint**. Operators with $X^\dagger = X$ are called **hermitian operators**. We have $(XY)^\dagger = Y^\dagger X^\dagger$.
- For general operator X and hermitian operator H we have:
$$\langle a|\,X\,|b\rangle = \langle b|\,X^\dagger\,|a\rangle \qquad \langle a|\,H\,|b\rangle = \langle b|\,H\,|a\rangle .$$
  i) The eigenvalues of a Hermitian operator are real.
  ii) The eigenstates of a Hermitian operator with non-degenerate eigenvalues are orthogonal.

  Eigenstates of Hermitian operators are typically orthonormal: $\langle i|j\rangle = \delta_{ij}$.
- For every state $|\phi\rangle$:
$$|\phi\rangle = \sum_i (\langle i|\phi\rangle)\,|i\rangle \Leftrightarrow |\phi\rangle = (\sum_i |i\rangle\langle i|)\,|\phi\rangle \Leftrightarrow 1 = \sum_{\text{all } i} |i\rangle\langle i| .$$
- For every normalized state $|\phi\rangle$ we have
$$1 = \langle\phi|\phi\rangle = \sum_i \langle\phi|i\rangle\,\langle i|\phi\rangle \ \Rightarrow\ 1 = \sum_i |\langle i|\phi\rangle|^2,$$
  which is consistent with the interpretation of associating $\langle i|\phi\rangle$ the probability $P(|\phi\rangle \to |i\rangle) = |\langle i|\phi\rangle|^2$ for a transition from state $|\phi\rangle$ to $|i\rangle$.
- The operator $\Lambda_i \equiv |i\rangle\langle i|$ projects a general state onto the eigenstate $|i\rangle$ and has the defining property of a projector:
$$\Lambda_i\,|\phi\rangle = (|i\rangle\langle i|)\,|\phi\rangle = (\langle i|\phi\rangle)\,|i\rangle \quad \text{and} \quad \Lambda_i\Lambda_j = \Lambda_i\delta_{ij}.$$
- States and operators can be represented by vectors and matrices. The eigenstates $\{|i\rangle \mid i = 1,\ldots,N\}$ of a Hermitian operator A, with $\langle i|j\rangle = \delta_{ij}$ can be represented as vectors:
$$|1\rangle := \begin{pmatrix}1\\0\\\vdots\\0\end{pmatrix}, \quad |2\rangle := \begin{pmatrix}0\\1\\\vdots\\0\end{pmatrix}, \quad \ldots \quad , \quad |N\rangle := \begin{pmatrix}0\\0\\\vdots\\1\end{pmatrix}.$$
  And the dual bra-eigenstates as:
$$\langle 1| := (1,0,\ldots,0), \quad \ldots \quad , \quad \langle N| := (0,0,\ldots,1).$$
- A general state $|\phi\rangle$ satisfies:
$$|\phi\rangle = \sum_i \langle i|\phi\rangle\,|i\rangle = \begin{pmatrix}\langle 1|\phi\rangle\\ \langle 2|\phi\rangle\\ \ldots\\ \langle N|\phi\rangle\end{pmatrix}.$$
  And for a bra-state $\langle\phi|$:
$$\langle\phi| = \sum_i \langle i|\phi\rangle^*\,\langle i| = (\langle 1|\phi\rangle^*, \langle 2|\phi\rangle^*, \ldots, \langle N|\phi\rangle^*).$$

- The inner product is $\langle a|b\rangle = \sum_i \langle i|a\rangle^* \langle i|b\rangle$.
- The outer product operator is represented as

$$|a\rangle\langle b| = \begin{pmatrix} \langle 1|a\rangle\langle 1|b\rangle^* & \langle 1|a\rangle\langle 2|b\rangle^* & \cdots & \langle 1|a\rangle\langle N|b\rangle^* \\ \langle 2|a\rangle\langle 1|b\rangle^* & \langle 2|a\rangle\langle 2|b\rangle^* & \cdots & \langle 1|a\rangle\langle N|b\rangle^* \\ \vdots & \vdots & \ddots & \vdots \\ \langle N|a\rangle\langle 1|b\rangle^* & \langle N|a\rangle\langle 2|b\rangle^* & \cdots & \langle N|a\rangle\langle N|b\rangle^* \end{pmatrix}.$$

- A general operator can be written as

$$X = \sum_{ij} |i\rangle\langle i| X |j\rangle\langle j| = \begin{pmatrix} \langle 1|X|1\rangle & \langle 1|X|2\rangle & \cdots & \langle 1|X|N\rangle \\ \langle 2|X|1\rangle & \langle 2|X|2\rangle & \cdots & \langle 2|X|N\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle N|X|1\rangle & \langle N|X|2\rangle & \cdots & \langle N|X|N\rangle \end{pmatrix}.$$

- Hermitian operators are called **compatible**, if they commute:

$$[A, B] \coloneqq AB - BA = 0.$$

- For two compatible operators A, B, $[A, B] = 0$, where A has a spectrum of eigenstates $|i\rangle$ with non-degenerate eigenvalues $A|i\rangle = \lambda_i |i\rangle$, i) B is a diagonal matrix in the representation of the $|i\rangle$ basis, ii) the set of $|i\rangle$ states is also a set of eigenstates of B.
- If two operators do not commute $[A, B] \neq 0$, their common eigenstates do not form a complete set.
- The **expectation value** of a Hermitian operator A corresponding to the average of infinite measurements for a physical observable (energy, momentum, position, etc.) is

$$\langle A\rangle = \langle\phi| A |\phi\rangle = \sum_i \lambda_i |\langle i|\phi\rangle|^2 = \sum_i \lambda_i \operatorname{Prob}(|\phi\rangle \to |i\rangle).$$

  The **uncertainty** in such measurements is given by

$$\left\langle(\Delta A)^2\right\rangle \coloneqq \left\langle(A - \langle A\rangle \mathbf{1})^2\right\rangle = \left\langle A^2\right\rangle - \langle A\rangle^2.$$

  The uncertainty for a system in an eigenstate of A is zero.
- **Uncertainty principle**: $\left\langle(\Delta A)^2\right\rangle\left\langle(\Delta B)^2\right\rangle \geq \frac{1}{4}|\langle[A, B]\rangle|^2$.
- The **anti-commutator** is defined as $\{X, Y\} \coloneqq XY + YX$, and the (anti-)commutator of operators is also hermitian:

$$\{X, Y\}^\dagger = \{X, Y\}, \qquad [A, B]^\dagger = -[A, B]$$

- The expectation value of a Hermitian operator is real, while it is imaginary for anti-Hermitian operators.
- Incompatible operators A and B offer different sets of base states $\{|a_i\rangle\}$ and $\{|b_i\rangle\}$. The unitary **change of basis** operator U, with $UU^\dagger = 1$, is given by

$$U = \sum_k |b_k\rangle\langle a_k| \quad \to \quad U|a_i\rangle = |b_i\rangle, \; U^\dagger |b_i\rangle = |a_i\rangle.$$

$$\begin{pmatrix} \vdots \\ \langle b_i|\phi\rangle \\ \vdots \end{pmatrix} = \begin{pmatrix} \ddots & \vdots & \cdot^{\cdot^{\cdot}} \\ \cdots & \langle a_i| U^\dagger |a_k\rangle & \cdots \\ \cdot^{\cdot^{\cdot}} & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ \langle a_i|\phi\rangle \\ \vdots \end{pmatrix}$$

$$\Big(\langle b_j| X |b_i\rangle\Big) = \Big(\langle a_j| U^\dagger |a_k\rangle\Big)\Big(\langle a_k| X |a_l\rangle\Big)\Big(\langle a_l| U |a_i\rangle\Big)$$

- The **trace** $\operatorname{tr}(X) = \sum_i \langle a_i| X |a_i\rangle$ is independent of the representation. Also, $\operatorname{tr}(|c\rangle\langle b|) = \langle b|c\rangle$.
- Two operators A, B are equivalent if they can be related by a unitary transformation $\quad B = UAU^\dagger, \quad U^\dagger = U^{-1}$.

4 Time Evolution

- For a state which evolves in time $|\phi, t_0\rangle \to |\phi, t\rangle$ for $t \geq t_0$ we introduce the **time evolution operator** $U(t - t_0)$ with the following properties:

$$|\phi, t\rangle = U(t - t_0)|\phi, t_0\rangle.$$

  i) To keep the normalization, U has to be unitary:

$$U^\dagger(t - t_0)U(t - t_0) = 1.$$

  ii) A time evolution $t_0 \to t_1 > t_0$ followed by $t_1 \to t_2 > t_1$ is equivalent to $t_0 \to t_2$:

$$U(t_2 - t_1)U(t_1 - t_0) = U(t_2 - t_0).$$

  iii) $\lim_{t \to t_0} U(t - t_0) = 1$.

- All properties are satisfied if $U(\Delta t) = 1 - i\Omega\Delta t + \mathcal{O}((\Delta t)^2)$, with $\Omega^\dagger = \Omega$. We postulate that $\Omega = \frac{H}{\hbar}$, where H is the Hamilton operator.
- From the product property $U(t + \Delta t) = U(\Delta t)U(t)$, with Δt infinitesimal, we obtain the Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|\phi, t\rangle = H|\phi, t\rangle.$$

- For a constant Hamiltonian, $H(t) = H$, the solution is

$$|\phi, t\rangle = e^{-\frac{i}{\hbar}(t - t_0)\cdot H}|\phi, t_0\rangle.$$

- For a self-commuting, time-dependent Hamiltonian with $[H(t_1), H(t_2)] = 0$, $\forall t_1, t_2 \in [t_0, t]$ the solution is:

$$|\phi, t\rangle = e^{-\frac{i}{\hbar}\int_{t_0}^{t} \mathrm{d}t' H(t')}|\phi, t_0\rangle.$$

- If a physical system is in an eigenstate of the Hamiltonian it will always remain in this eigenstate and the expectation value of physical observables does not change. If the state $|\phi\rangle = \sum_m |m\rangle\langle m|\phi\rangle$ is not an eigenstate the expectation value of an observable A oscillates:

$$\langle A\rangle_t = \sum_{n,m} e^{-i(t - t_0)\cdot \overbrace{\omega_{nm}}^{\frac{E_n - E_m}{\hbar}}}\langle m|\phi\rangle^* \langle n|\phi\rangle \langle n| A |m\rangle.$$

- In **Heisenberg's picture of time evolution**, the information is carried by the operators, rather than the state kets:

$$|a\rangle_H = |a, 0\rangle_S, \qquad X_H = U^\dagger X_S U.$$

  The operators change in time according to the Heisenberg equation of motion:

$$\frac{\mathrm{d}X_H}{\mathrm{d}t} = \frac{1}{i\hbar}U^\dagger[X_H, H]U = \frac{1}{i\hbar}[X_S, H].$$

5 Two-State Systems

For a two base state system with a time independent Hamiltonian

$$|1\rangle \coloneqq \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle \coloneqq \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

$$H \coloneqq \begin{pmatrix} H_{11} & H_{12} \\ H_{12}^* & H_{22} \end{pmatrix}, \quad H_{ij} = H_{ji}^* = \langle i| H |j\rangle, \quad H^\dagger = H,$$

the eigenvalues and (normalized) eigenstates are given by

$$E_\pm = \frac{H_{11} + H_{22} \pm \sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2}}{2},$$

$$|E_\pm\rangle = \frac{1}{\sqrt{|H_{12}|^2 + (E_\pm - H_{11})^2}}\begin{pmatrix} H_{12} \\ E_\pm - H_{11} \end{pmatrix}.$$

- The ammonia molecule can spin in two ways and we denote these two states with $|1\rangle$ and $|2\rangle$. The expectation value for the energy in the two states is the same $\langle 1|H|1\rangle = \langle 2|H|2\rangle = E_0$ and we allow for a probability that it can flit its state releasing the energy $\langle 1| H |2\rangle = \langle 2| H |1\rangle = -A$. This gives us the Hamiltonian and its eigenvalues and eigenstates:

$$H = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}, \quad E_\pm = E_0 \pm A,$$

$$|+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}, \quad |-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$

  With the time evolution operator $U(t) = e^{-\frac{iHt}{\hbar}}$ we find that a general state $|\psi, t_0 = 0\rangle = e^{i\phi}\begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix}$ evolves as

$$|\psi, t\rangle = e^{i(\phi - E_0 t/\hbar)}\begin{pmatrix} \cos\theta\cos\left(\frac{At}{\hbar}\right) + i\sin\theta\sin\left(\frac{At}{\hbar}\right) \\ \sin\theta\cos\left(\frac{At}{\hbar}\right) + i\cos\theta\sin\left(\frac{At}{\hbar}\right) \end{pmatrix}.$$

  Let $|\xi, t_0 = 0\rangle = e^{i\phi}\begin{pmatrix} \sin\theta \\ -\cos\theta \end{pmatrix}$ be orthogonal to $|\psi, t_0 = 0\rangle$. We then get the following transition amplitudes:

$$P_1 = |\langle\psi, t_0 = 0|\psi, t\rangle|^2 = 1 - \sin^2\left(\frac{At}{\hbar}\right)\cos^2(2\theta)$$

$$P_2 = |\langle\xi, t_0 = 0|\psi, t\rangle|^2 = \sin^2\left(\frac{At}{\hbar}\right)\cos^2(2\theta)$$

$$P_1 + P_2 = 1$$

- The ammonia molecule has an electric dipole $\mathbf{d}$. If it is in an electric field $\mathbf{E}$ the energy depends on the alignment. The Hamiltonian and its eigenvalues are now given by

$$H = \begin{pmatrix} E_0 + \mathbf{d}\cdot\mathbf{E} & -A \\ -A & E_0 - \mathbf{d}\cdot\mathbf{E} \end{pmatrix}$$

$$E_\pm = E_0 \pm \sqrt{A^2 + \mathbf{d}^2\mathbf{E}^2} \overset{\mathbf{d}\cdot\mathbf{E} \ll E_0}{\approx} E_0 \pm A \pm \frac{\mathbf{d}^2\mathbf{E}^2}{2A}.$$

- For a time varying electric field $\mathbf{E}(t) = \mathbf{E}\cos(\omega t)$ the Hamiltonian is given by

$$H(t) = \begin{pmatrix} E_0 + \mathbf{d}\cdot\mathbf{E}\cos(\omega t) & -A \\ -A & E_0 - \mathbf{d}\cdot\mathbf{E}\cos(\omega t) \end{pmatrix}.$$

  By splitting the Hamiltonian into a part without electric field $H_0 = \left(\begin{smallmatrix} E_0 & -A \\ -A & E_0 \end{smallmatrix}\right)$ and one with $H_I(t) = \mathbf{d}\cdot\mathbf{E}\cos(\omega t)\left(\begin{smallmatrix} \cos(\omega_0 t) & i\sin(\omega_0 t) \\ -i\sin(\omega_0 t) & -\cos(\omega_0 t) \end{smallmatrix}\right)$, where $\omega_0 = \frac{2A}{\hbar}$, we can write the Schrödinger equation as

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\rho, t\rangle &= (V^\dagger H_I(t)V)|\rho, t\rangle \\ &= \frac{\mathbf{d}\cdot\mathbf{E}}{2}\begin{pmatrix} 0 & e^{+i(\omega_0 - \omega)t} + e^{+i(\omega_0 + \omega)t} \\ e^{-i(\omega_0 - \omega)t} + e^{-i(\omega_0 + \omega)t} & 0 \end{pmatrix}|\rho, t\rangle, \end{aligned}$$

  where $|\rho, t\rangle$ is a state in the $\{|1\rangle, |2\rangle\}$ basis, and V is the transformation matrix to the energy eigenkets $\{|+\rangle, |-\rangle\}$.
  If the frequency of the electric field is chosen to be $\omega \approx \omega_0$ we get a second order differential equation of a harmonic oscillator with the solution where $\omega_e = \frac{\mathbf{d}\cdot\mathbf{E}}{2\hbar}$:

$$|\rho, t\rangle = \begin{pmatrix} a\cos(\omega_e t) + a\sin(\omega_e t) \\ ib\sin(\omega_e t) - ib\cos(\omega_e t) \end{pmatrix}.$$

  The transition probabilities are then given by

$$P(|-\rangle \to |+\rangle) = \sin^2(\omega_e t), \quad P(|-\rangle \to |-\rangle) = \cos^2(\omega_e t).$$

  For general $\omega \sim \omega_0$ and small t we find the transition probability to be

$$P(|+\rangle \to |-\rangle) = \left(\frac{\mathbf{d}\cdot\mathbf{E}}{\hbar}\right)^2\frac{\sin^2((\omega - \omega_0)t/2)}{(\omega - \omega_0)^2},$$

  which has a peak around $\omega = \omega_0$.

6 Position and Momentum

- For Hermitian operators Ξ with continuous eigenvalues ξ and eigenstates $|\xi\rangle$, we transform the following properties:

$$\begin{aligned} &\text{Kronecker } \delta_{ij} && \to && \text{Dirac } \delta(\xi - \xi') \\ &\langle i|j\rangle = \delta_{ij} && \to && \langle\xi|\xi'\rangle = \delta(\xi - \xi') \\ &|\phi\rangle = \sum_i |i\rangle\langle i|\phi\rangle && \to && |\phi\rangle = \int \mathrm{d}\xi\,|\xi\rangle\langle\xi|\phi\rangle \end{aligned}$$

- The **position operators** $\hat{x}$, $\hat{y}$, $\hat{z}$ commute

$$[\hat{x}, \hat{y}] = [\hat{y}, \hat{z}] = [\hat{z}, \hat{x}] = 0$$

  and have a common set of eigenstates $|x, y, z\rangle = |\mathbf{r}\rangle$

$$\hat{x}|\mathbf{r}\rangle = x|\mathbf{r}\rangle, \quad \hat{y}|\mathbf{r}\rangle = y|\mathbf{r}\rangle, \quad \hat{z}|\mathbf{r}\rangle = z|\mathbf{r}\rangle.$$

- A generic quantum state $|\phi\rangle = \int \mathrm{d}^3\mathbf{r}\,|\mathbf{r}\rangle\langle\mathbf{r}|\phi\rangle$, when measured, collapses to a state $|\mathbf{r}\rangle$ with a probability amplitude

$$\psi_\phi(\mathbf{r}) \equiv \langle\mathbf{r}|\phi\rangle,$$

  which is the so-called **Wave function**. From the normalization of states $1 = \langle\phi|\phi\rangle$ we have

$$1 = \int \mathrm{d}^3\mathbf{r}\,|\psi_\phi(\mathbf{r})|^2.$$

  Scalar products of quantum states are then also given by

$$\langle a|b\rangle = \int \mathrm{d}^3\mathbf{r}\,\langle a|\mathbf{r}\rangle\langle\mathbf{r}|b\rangle = \int \mathrm{d}^3\mathbf{r}\,\psi_a^*(\mathbf{r})\psi_b(\mathbf{r}).$$

- We define a **transformation operator** P, which transforms a position eigenket $|\mathbf{r}\rangle$ into a new position eigenket $P|\mathbf{r}\rangle = |\mathbf{r} + \Delta\mathbf{r}\rangle$. For a general state $|\phi\rangle$ this is given by

$$P|\phi\rangle = \int \mathrm{d}^3\mathbf{r}\,|\mathbf{r}\rangle\langle\mathbf{r} - \Delta\mathbf{r}|\phi\rangle.$$

  We demand that $P(\Delta\mathbf{r})$ has the following properties:

  i) A translated state must have unit norm, which is satisfied if the translation operator is unitary:

$$P^\dagger(\Delta\mathbf{r})P(\Delta\mathbf{r}) = 1.$$

  ii) Two translations by $\Delta\mathbf{r}_a$ and $\Delta\mathbf{r}_b$ should be equivalent to a single translation by $\Delta\mathbf{r}_a + \Delta\mathbf{r}_b$, which is true if

$$P(\Delta\mathbf{r}_a)P(\Delta\mathbf{r}_b) = P(\Delta\mathbf{r}_a + \Delta\mathbf{r}_b).$$

  iii) The inverse of the translation operator must translate by the opposite amount, which is satisfied if

$$P(\Delta\mathbf{r})^{-1} = P(-\Delta\mathbf{r}).$$

  iv) The limit of infinitesimally small translations is the unit operator:

$$\lim_{\Delta\mathbf{r} \to 0} P(\Delta\mathbf{x}) = 1.$$

- For small translations the translation operator is given by

$$P(\Delta\mathbf{r}) = 1 - i\mathbf{K}\cdot\Delta\mathbf{r} + \mathcal{O}((\Delta\mathbf{r})^2),$$

  where $\mathbf{K} = \mathbf{K}^\dagger$ is a hermitian operator and does not commute with the position operators $\hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z})$:

$$[\hat{\mathbf{r}}, \mathbf{K}\cdot\Delta\mathbf{r}] = i\Delta\mathbf{r} \qquad \left[\hat{l}, K_k\right] = i\delta_{lk}, \quad l, k = x, y, z.$$

- **K** is proportional to the momentum operator **p**, which also does not commute with the position operator:

$$\mathbf{K} = \frac{\mathbf{p}}{\hbar}, \qquad \left[\hat{j}, p_k\right] = i\hbar\delta_{jk}, \quad j,k = x,y,z.$$

- For large translations $|\mathbf{r}_a + \mathbf{r}\rangle = P(\mathbf{r})\,|\mathbf{r}_a\rangle$ the translation operator is given by

$$P(\mathbf{r}) = e^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}.$$

- The **momentum operators** $\hat{p}_x$, $\hat{p}_y$, $\hat{p}_z$ commute

$$[\hat{p}_x, \hat{p}_y] = [\hat{p}_y, \hat{p}_z] = [\hat{p}_z, \hat{p}_x] = 0$$

and have a common set of eigenstates $|p_x, p_y, p_z\rangle = |\mathbf{p}\rangle$

$$\hat{p}_x\,|\mathbf{p}\rangle = p_x\,|\mathbf{p}\rangle\,, \quad \hat{p}_y\,|\mathbf{p}\rangle = p_y\,|\mathbf{p}\rangle\,, \quad \hat{p}_z\,|\mathbf{p}\rangle = p_z\,|\mathbf{p}\rangle\,.$$

- For an arbitrary state $|a\rangle$ we have $\langle\mathbf{r}|\,\hat{\mathbf{p}}\,|a\rangle = [-i\hbar\nabla_{\mathbf{r}}]\,\langle\mathbf{r}|a\rangle$, which gives us the representation of the momentum operator in the position-ket basis:

$$\langle\mathbf{r}|\,\hat{\mathbf{p}}\,|\mathbf{r}'\rangle = [-i\hbar\nabla_{\mathbf{r}}]\delta(\mathbf{r}-\mathbf{r}').$$

- The probability that a particle with momentum **p** is found at position **r**, is given by

$$\langle\mathbf{r}|\mathbf{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}.$$

- The two amplitudes $\langle\mathbf{r}|\phi\rangle$ and $\langle\mathbf{p}|\phi\rangle$ are related by Fourier transform:

$$\langle\mathbf{r}|\phi\rangle = \int_{-\infty}^{+\infty} \frac{\mathrm{d}^3\mathbf{p}}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}\,\langle\mathbf{p}|\phi\rangle$$
$$\langle\mathbf{p}|\phi\rangle = \int_{-\infty}^{+\infty} \frac{\mathrm{d}^3\mathbf{r}}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\mathbf{r}\cdot\mathbf{p}}\,\langle\mathbf{r}|\phi\rangle$$

- A free particle with $H = \frac{\mathbf{p}^2(t)}{2m}$ delocalizes over time:

$$\left\langle(\Delta x(t))^2\right\rangle \left\langle(\Delta x(0))^2\right\rangle \geq \frac{\hbar^2 t^2}{4m^2}.$$

- For a particle in a potential with $H = \frac{\mathbf{p}^2(t)}{2m} + V(\mathbf{x})$ the averages evolve classically:

$$m\frac{\mathrm{d}^2}{\mathrm{d}t^2}\,\langle\mathbf{x}\rangle = -\,\langle\nabla V(\mathbf{x})\rangle\,.$$

7 The Harmonic Oscillator

In this chapter, we have $m = \hbar = \omega = 1$.

- The Hamiltonian is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 \overset{\cdots=1}{=} \frac{\hat{p}}{2} + \frac{1}{2}\hat{x}^2$$
$$\overset{[x,p]=i}{=} \underbrace{\frac{(x-ip)}{\sqrt{2}}}_{:=a^\dagger} \cdot \underbrace{\frac{(x+ip)}{\sqrt{2}}}_{:=a} \underbrace{-i\frac{xp-px}{2}}_{=+1/2}$$
$$= \underbrace{a^\dagger a}_{:=N} + \frac{1}{2} = N + \frac{1}{2},$$

with the **annihilation operator** a, **creation operator** $a^\dagger$ and the **number operator** N. They commute as follows:

$$\left[a, a^\dagger\right] = 1, \qquad \left[N, a^\dagger\right] = a^\dagger, \qquad [N, a] = -a.$$

- As the Hamiltonian and the number operator commute $[H, N] = 0$, they have common eigenstates $|n\rangle$.
- Let $N\,|n\rangle = n\,|n\rangle$ and require $|\langle n|n\rangle|^2 = 1$. We then get

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

The energy eigenvalues are then $E_n = n + \frac{1}{2}$.

- The eigenstates $|n\rangle$ are therefore generated from the ground state $|0\rangle$ by repeated application of $a^\dagger$:

$$|n\rangle = \frac{a^{\dagger n}}{\sqrt{n!}}\,|0\rangle\,.$$

- By rearranging we get $\hat{x} = \frac{a+a^\dagger}{\sqrt{2}}$ and $\hat{p} = \frac{a-a^\dagger}{\sqrt{2}}$, which satisfy the Heisenberg uncertainty principle

$$\left\langle(\Delta\hat{x})^2\right\rangle_n \left\langle(\Delta\hat{p})^2\right\rangle_n = \left(n + \frac{1}{2}\right)^2 \overset{n=0}{=} \frac{1}{4}.$$

- The wavefunction $\psi_0(x) = \langle x|0\rangle$, where $\hat{x}\,|x\rangle = x\,|x\rangle$ and $a\,|0\rangle = 0$ is given by the following differential equation:

$$\left(\hat{x} + \frac{\mathrm{d}}{\mathrm{d}x}\right)\psi_0(x) = 0 \quad \overset{\langle 0|0\rangle=1}{\rightsquigarrow} \quad \psi_0(x) = \frac{1}{\pi^{1/4}} e^{-\frac{x^2}{2}}.$$

The wavefunction for any energystate is given by

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\hat{x} - \frac{\mathrm{d}}{\mathrm{d}x}\right)^n \psi_0(x).$$

- From the Heisenberg equation of motion we get the following equations for the time evolution of the operators:

$$\frac{\partial\hat{x}(t)}{\partial t} = \hat{p}(t), \qquad \frac{\partial\hat{p}(t)}{\partial t} = -\hat{x}(t),$$

with the solutions

$$\hat{x}(t) = \hat{x}(0)\cos t + \hat{p}(0)\sin t, \quad \hat{p}(t) = -\hat{x}(0)\sin t + \hat{p}(0)\cos t.$$

As $\langle n|\,a^\dagger\,|n\rangle = \langle n|\,a\,|n\rangle = 0$, the expectation values for the position and momentum of an energy eigenstate vanishes.

- States in which the expectation values oscillate classically are called **coherent states** and are eigenstates of the annihilation operator:

$$a\,|\lambda\rangle = \lambda\,|\lambda\rangle\,.$$

The normalized coherent state written as a superposition of energy eigenstates is given by

$$|\lambda\rangle = e^{|\lambda|^2/2}\sum_{n=0}^{\infty}\frac{\lambda^n}{\sqrt{n!}}\,|n\rangle\,.$$

- The probability that a particle in a coherent state $|\lambda\rangle$ is measured to have energy $E_n = n + \frac{1}{2}$ is given by a Poisson distribution with a mean value $\langle n\rangle = |\lambda|^2$:

$$P(|\lambda\rangle \to |n\rangle) = |\langle n|\lambda\rangle|^2 = e^{-|\lambda|^2}\frac{\left(|\lambda|^2\right)^n}{n!}.$$

- The expectation values for the energy, position and momentum of a coherent state are

$$\langle\lambda|\,\hat{H}\,|\lambda\rangle = |\lambda|^2 + \frac{1}{2},$$
$$\langle\lambda|\,\hat{x}\,|\lambda\rangle = \sqrt{2}|\lambda|\cos(t-\theta),$$
$$\langle\lambda|\,\hat{p}\,|\lambda\rangle = -\sqrt{2}|\lambda|\sin(t-\theta).$$

8 Schrödinger's Wave Equation

- Schrödinger's equation is given by

$$i\hbar\frac{\partial}{\partial t}\,|\psi,t\rangle = H\,|\psi,t\rangle\,, \qquad H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}).$$

- For the wave function $\psi(\mathbf{r},t) = \langle\mathbf{r}|\psi,t\rangle$ **Schrödinger's wave equation** is given by

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r},t).$$

And for time-independent Hamiltonians $H\,|\psi_E, t_0\rangle = E\,|\psi_E, t_0\rangle$, **Schrödinger's time independent wave equation** is given by

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi_E = E\psi_E(\mathbf{r}),$$

with the time evolution $\psi_E(\mathbf{r},t) = e^{-iEt/\hbar}\psi_E(\mathbf{r})$.

- The **probability density** ρ and **probability current j** are given by

$$\rho(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2, \qquad \mathbf{j}(\mathbf{r},t) = \frac{\hbar}{2mi}\left[\psi^*\nabla\psi - \psi\nabla\psi^*\right],$$

which fulfill the **continuity equation**

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{j} = 0$$

- We can rewrite $\psi(\mathbf{r},t) = \sqrt{\rho(\mathbf{r},t)}\cdot e^{iF(\mathbf{r},t)/\hbar}$ with the real function $F(\mathbf{r},t)$. We then have

$$\mathbf{j}(\mathbf{r},t) = \rho(\mathbf{r},t)\underbrace{\frac{\nabla F(\mathbf{r},t)}{m}}_{\text{"velocity"}}.$$

- The integral of the probability current over all space is

$$\int \mathrm{d}^3\mathbf{r}\,\mathbf{j}(\mathbf{r},t) = \frac{1}{m}\,\langle\psi,t|\,\mathbf{p}\,|\psi,t\rangle\,.$$

- If $V(x) > E$, $\psi(x)$ is concave *away* from the x-axis.
- If $V(x) < E$, $\psi(x)$ is concave *towards* the x-axis.
- We can approximate the wave function of a particle in a static system ($\frac{\partial\rho}{\partial t} = 0$, $\nabla\cdot\mathbf{j} = 0$) with the **semiclassical approximation**:

$$\psi_{V(x)>E} \approx \frac{\text{const}}{[2m\,(V(x)-E)]^{\frac{1}{4}}}\exp\left(\pm\int_{x_0}^{x}\mathrm{d}y\,\frac{\sqrt{2m\,(V(y)-E)}}{\hbar}\right)$$
$$\psi_{V(x)<E} \approx \frac{\text{const}}{[2m\,(E-V(x))]^{\frac{1}{4}}}\exp\left(\pm i\int_{x_0}^{x}\mathrm{d}y\,\frac{\sqrt{2m\,(E-V(y))}}{\hbar}\right)$$

For $V(x_{\text{sp}}) = E$, solve: $\left[\frac{\hat{p}^2}{2m} + (\hat{x} - x_{\text{sp}})V'(x_m sp)\right]|\psi_E\rangle = 0.$

- The exact solution for a linear potential

$$\left[\frac{\hat{p}^2}{2m} + a\hat{x} + b\right]|\psi\rangle = 0$$

is given by

$$\langle p|\psi\rangle = N\exp\left(\frac{\frac{p^3}{6m} + pb}{i\hbar a}\right),$$
$$\langle x|\psi\rangle = N\int_{-\infty}^{\infty}\frac{\mathrm{d}p}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}\exp\left(\frac{\frac{p^3}{6m} + pb}{i\hbar a}\right).$$

9 Particle in a constant electromagnetic field

- The Hamiltonian for a charged particle in a time-independent electromagnetic field is

$$H = \frac{(\mathbf{p} - q\mathbf{A})^2}{2m} + q\Phi$$

- The **kinetic momentum Π** is given by

$$\mathbf{\Pi} = m\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \mathbf{p} - q\mathbf{A},$$

with the following commutation relations:

$$[\Pi_i, \Pi_j] = i\hbar q\varepsilon_{ijk}B_k,$$
$$[\Pi_i, H] = i\hbar q\left(-\partial_i\Phi + \varepsilon_{ijk}\frac{1}{2m}\left[\Pi_j B_k - B_j\Pi_k\right]\right).$$

- The quantum operator corresponding to the classical force is given by

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = q\left[-\nabla\Phi + \frac{1}{2}\left(\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t}\times\mathbf{B} - \mathbf{B}\times\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t}\right)\right].$$

- Schrödinger's equation for the state and wavefunction of a particle in a constant electromagnetic field is given by

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,|\phi,t\rangle = \left(\frac{\Pi^2}{2m} + q\Phi\right)|\phi,t\rangle\,,$$
$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\left(\nabla - \frac{i}{\hbar}qA\right)\left(\nabla - \frac{i}{\hbar}qA\right) + q\Phi\right]\psi(\mathbf{r},t).$$

- As the Maxwell equations are invariant under a gauge transformation, a gauge transformation simply results in the wavefunction being multiplied with an overall phase

$$\psi_\Lambda(\mathbf{r},t) = e^{\frac{iq}{\hbar}\Lambda(\mathbf{r})}\psi(\mathbf{r},t).$$

- The **Aharonov-Bohm effect** describes the fact that the interference pattern of a double-slit experiment, where there is a magnetic field in the center wall, depends on that magnetic field, even though none of the paths go through it.

10 Symmetries in Quantum Mechanics

- In quantum mechanics symmetry transformations alter quantum states, without changing the probabilities:

$$|\psi\rangle \overset{T}{\to} |\psi'\rangle\,, \quad |\phi\rangle \overset{T}{\to} |\phi'\rangle \qquad \Rightarrow \qquad |\langle\phi'|\psi'\rangle|^2 = |\langle\phi|\psi\rangle|^2$$

- With the states represented as vectors in a Hilbert space with base kets $\{|a_i\rangle\}$, symmetry transformations T are given by a matrix $U(T)$:

$$|\psi'\rangle = U(T)\,|\psi\rangle\,.$$

- To preserve the probabilities we have two options (**Wigner's theorem**):

  i) $U(T)$ is linear and unitary,
  ii) $U(T)$ is anti-linear and anti-unitary.

- Continuous transformations that are connected to the unity must have a unitary and linear representation. Such transformations (rotations, translations, Lorentz boosts) are described by continuous parameters θ^a:

$$T \equiv T(\theta^a), \quad \theta^a \equiv \begin{cases} \theta, \phi & \text{angles} \\ \beta_x, \beta_y, \beta_z & \text{boosts} \\ \varepsilon_1, \varepsilon_2, \varepsilon_3 & \text{translations} \end{cases}$$

- The product of two transformations is also a transformation and differs at most by a phase:

$$T_3 = T_1 T_2, \qquad U(T_2)U(T_1) = e^{i\phi(T_2,T_1)} U(T_2 T_1).$$

- Continuous symmetry transformations $T(\theta^a)$ parameterized by $\{\theta^a, a = 1, \dots, N\}$ for a **Lie group**:

$$T(\theta_1^a)T(\theta_2^a) = T(f^a(\theta_1^a, \theta_2^a)), \qquad T(\theta^a = 0) = 1.$$

- For small parameters θ^a, we can expand the representation of the transformation, with the matrices $1, t_a, t_{bc} = t_{cb}$:

$$U(T(\theta^a)) = 1 + i\theta^a t_a + \frac{1}{2}\theta^b\theta^c t_{bc} + \dots$$

- The matrices t^a are called **generators** and commute as follows:

$$[t_b, t_c] = iC^a_{bc} t_a,$$

where $C^a_{bc} = f^a_{cb} - f^a_{bc}$ are the **structure constants** of the Lie group, where $t_{bc} = -t_b t_c - i f^a_{bc} t_a$.

- The generators t^a are Hermitian and form a **Lie algebra**. They are represented as

$$U(T(\theta^a)) = \exp(i\theta^a t_a).$$

- Symmetry transformations T change the system irrespective of time. We therefore get the following commutations:

$$\left[U(T), e^{iHt\hbar} = 0\right], \qquad [U(T), H] = 0, \qquad [t_a, H] = 0$$

If $|E\rangle$ is an eigenstate $H|E\rangle = E|E\rangle$, then $U(T)E$ also is.

- Euclidean changes of reference frame preserve the magnitude of space-vectors $|\mathbf{r}| = |\mathbf{r}|$. Transformations $\mathbf{r} \to \mathbf{r}'$ are therefore linear:

$$r_i' = R_{ij} r_j + a_i,$$
$$RR^\top, \qquad R_{ij}^\top = R_{ji}, \qquad (\det R)^2 = 1, \qquad R_{ij}^{-1} = R_{ij}^\top,$$
$$T(R, a)T(\bar{R}, \bar{a}) = T(R\bar{R}, R\bar{a} + a).$$

- For infinitesimal transformations $T(\delta_{ij} + \omega_{ij}, \varepsilon_i)$, we can expand the representation U in the small parameters:

$$U(\omega, \varepsilon) = 1 + \frac{i}{2}\omega_{ij} J^{ij} - i\varepsilon_\rho P^\rho + \dots$$

From this, we identify the **generators of translations** P^ρ as the **operator of momentum** $p^\rho = \hbar P^\rho$, and the **generators of rotations** J^{kl} as the **operators of angular momentum** $\hbar J^{kl}$:

$$\mathbf{p} \equiv \hbar(P^1, P^2, P^3), \qquad \mathbf{J} \equiv \hbar(J^{23}, J^{31}, J^{12}).$$

- They form a Lie algebra with the following commutations:

$$[J_i, J_j] = i\hbar\varepsilon_{ijk} J_k, \qquad [J_i, p_j] = i\hbar\varepsilon_{ijk} p_k, \qquad [p_i, p_j] = 0.$$

11 Representations of Angular Momentum

- The square of the angular momentum vector

$$J^2 = J_k J_k = J_1^2 + J_2^2 + J_3^2$$

commutes with the generators J_i:

$$\left[J^2, J_i\right] = 0.$$

Thus, they have common eigenstates:

$$J^2|j,m\rangle = \hbar^2 j(j+1)|j,m\rangle,$$
$$J_3|j,m\rangle = \hbar m|j,m\rangle,$$

where j and m are quantized:

$$-j < m < j, \qquad j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \dots$$

- We can also construct the **ladder operator** from the first two components of angular momentum.

$$J_\pm = J_1 \pm iJ_2, \qquad [J_3, J_\pm] = \pm\hbar J_\pm,$$
$$J_\pm|j,m\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)}\,|j, m\pm 1\rangle.$$

- In the spin-$\frac{1}{2}$ representation we have a base of two angular momentum base eigenstates:

$$\left|\frac{1}{2}, +\frac{1}{2}\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \left|\frac{1}{2}, -\frac{1}{2}\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$J_1 = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad J_2 = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad J_3 = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$J_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad J_+ = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

- The representations can also be given via the **Pauli matrices** $J_i = \hbar\frac{\sigma_i}{2}$:

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

$$[\sigma_i, \sigma_j] = 2i\varepsilon_{ijk}\sigma_k, \quad \{\sigma_i, \sigma_j\} = 2\delta_{ij}\mathbf{1}_{2\times 2}, \quad \sigma_i, \sigma_j = \delta_{ij}\mathbf{1}_{2\times 2} + \varepsilon_{ijk}\sigma_k.$$

- The representation of a rotation of a small angle θ around the z-axis is given by

$$U(\theta) = \mathbf{1}_{2\times 2} + i\frac{\theta\sigma_3}{2}.$$

For large angles θ and a general rotation axis $\hat{n}$ we have

$$U(\theta) = \lim_{N\to\infty}\left[U\left(\frac{\theta}{N}\right)\right]^N = \exp\left(\frac{i\sigma_3\theta}{2}\right)$$
$$= \begin{pmatrix} \exp\left(i\frac{\theta}{2}\right) & 0 \\ 0 & \exp\left(-i\frac{\theta}{2}\right) \end{pmatrix},$$
$$U(\hat{n}, \theta) = \exp\left(i\frac{\boldsymbol{\sigma}\cdot\hat{n}}{2}\right).$$

- A general state for a two-state system $|\psi\rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$ under a rotation θ around the z-axis transforms as

$$|\psi\rangle \to |\psi'\rangle = U(\theta)|\psi\rangle = \begin{pmatrix} e^{i\theta/2}\psi \\ e^{-i\theta/2}\psi_2 \end{pmatrix}.$$

Notice that a rotation of $\theta = 2\pi$ doesn't bring the system back to the original. A 4π rotation is required.

$$U(2\pi)|\psi\rangle = -|\psi\rangle$$

- We define the **orbital angular momentum** L as

$$L_i = \varepsilon_{ijk} x_j p_k, \qquad \left[\frac{L_i}{\hbar}, \frac{L_j}{\hbar}\right] = i\varepsilon_{ijk}\frac{L_k}{\hbar}, \qquad L^2 = \sum_i L_i^2,$$
$$L^2|l,m\rangle = \hbar^2 l(l+1)|l,m\rangle, \quad L_3|l,m\rangle = \hbar m|l,m\rangle.$$

- The action of a position bra $\langle\mathbf{r}|$ on the action of an angular momentum operator on a general state $|a\rangle$ is given in polar coordinates as

$$\langle\mathbf{r}|L_1|a\rangle = -i\hbar(\cot\theta\sin\phi\partial_\phi - \cos\phi\partial_\theta)\langle\mathbf{r}|a\rangle$$
$$\langle\mathbf{r}|L_2|a\rangle = -i\hbar(\cot\theta\sin\phi\partial_\phi + \cos\phi\partial_\theta)\langle\mathbf{r}|a\rangle$$
$$\langle\mathbf{r}|L_3|a\rangle = i\hbar(+\partial_\phi)\langle\mathbf{r}|a\rangle$$
$$\langle\mathbf{r}|L_\pm|a\rangle = i\hbar(e^{\mp i\phi}[\partial_\theta \mp i\cot\theta\partial_\phi])\langle\mathbf{r}|a\rangle$$
$$\langle\mathbf{r}|L^2|a\rangle = -\hbar^2\underbrace{\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]}_{=(\nabla^2)_{\theta,\phi}}\langle\mathbf{r}|a\rangle$$

- The eigenstates $|l,m\rangle$ of L^2, L_3 satisfy

$$i\hbar\partial_\phi\langle\mathbf{r}|l,m\rangle = \hbar m\langle\mathbf{r}|l,m\rangle.$$

The solution decomposes into a radial and an angular part:

$$\langle\mathbf{r}|l,m\rangle = \psi_{lm}(r)Y_l^m(\theta,\phi),$$

where $Y_l^m(\theta,\phi)$ are the **spherical harmonics**, which can be given in terms of the unitary rotation operator $U(\theta,\phi)$:

$$Y_l^m(\theta,\phi)^* = \langle l,m|U(\theta,\phi)|l,0\rangle\sqrt{\frac{(2l+1)}{4\pi}}$$

- For potentials with spherical symmetry, the Hamiltonian $H = \frac{p^2}{2M} + V(r)$ commutes with the generators of rotations:

$$[H, L_i] = 0$$

- The radial wavefunction $\psi_{E,l}(r) = \frac{R(r)}{r}$ does not depend on the eigenvalue m of L_3 and is given by the following differential equation:

$$0 = R''(r) - \left[\frac{l(l+1)}{r^2} + \frac{2M\,(V(r) - E)}{\hbar^2}\right]R(r)$$

- The Hamiltonian for a simplified model (ignore electron spin) of the **hydrogen atom** is given by

$$H = \frac{p^2}{2m} - \frac{Ze^2}{r}.$$

It has the energy eigenvalues

$$E_n = -Z^2\frac{me^4}{2\hbar}\frac{1}{n^2}, \qquad \text{where } n = 1, 2, \dots$$

- The quantum mechanical analogue of the **Runge-Lenz vector**, a conserved quantity in classical mechanics for the Coulomb potential, is given by

$$\mathbf{R} = -\frac{Ze^2\mathbf{r}}{r} + \frac{1}{2m}(\mathbf{p}\times\mathbf{L} - \mathbf{L}\times\mathbf{p}), \quad \text{where } \mathbf{L} = \mathbf{r}\times\mathbf{p},$$
$$R_i = -\frac{Ze^2 r_i}{r} + \frac{\left[L^2, p_i\right]}{2mi}, \qquad R^2 = Z^2e^4 + \frac{2H}{2m}\left(\hbar^2 + L^2\right),$$
$$R_i^\dagger = R_i, \qquad [H, R_i] = 0, \qquad \mathbf{L}\cdot\mathbf{R} = 0,$$
$$[R_i, R_j] = \frac{-2H}{m}i\hbar\varepsilon_{ijk}L_k, \quad [L_i, R_j] = i\hbar\varepsilon_{ijk}R_k, \quad [L_i, L_j] = i\hbar\varepsilon_{ijk}L_k.$$

- The Lie algebra of SO(N) is given by

$$[J_{ab}, J_{cd}] = -i\hbar(\delta_{ab}J_{bc} - \delta_{ac}J_{bd} + \delta_{bc}J_{ad} - \delta_{bd}J_{ac}).$$

The hydrogen atom has an SO(4) symmetry, with

$$L_1 = J_{32}, \quad L_2 = J_{31}, \quad L_3 = J_{12}, \quad R_i = \sqrt{\frac{-2H}{m}}J_{i4}.$$

12 Addition of Angular Momenta

- A system can have multiple types of angular momentum (e.g. spin and orbital angular momentum), which are described by independent generators of angular momenta J_a, J_b with $[J_{ai}, J_{bj}] = 0$, $i,j = 1\dots3$, satisfying the same Lie algebra $[J_{ai,bi}, J_{aj,bj}] = i\hbar\varepsilon_{ijk}J_{ak,bk}$, and common eigenstates of the operators $J_a^2, J_b^2, J_{a3}, J_{b3}$.

- The sum of two angular momenta satisfies the same Lie algebra and the operators J_a^2, J_b^2 commute with the components of the total angular momentum:

$$J_i = J_{ai} + J_{bi}, \qquad [J_i, J_j] = i\hbar\varepsilon_{ijk}J_k, \qquad \left[J_{a,b}^2, J_i\right] = 0.$$

- The operators J^2, J_3, J_a^2, J_b^2 have common eigenstates $|j, m, j_a, j_b\rangle$, which can be written as a linear combination of states $|j_a, m_a, j_b, m_b\rangle$:

$$|j, m, j_a, j_b\rangle = \sum_{m_a, m_b}|j_a, m_a, j_b, m_b\rangle\underbrace{\langle j_a, m_a, j_b, m_b|j, m, j_a, j_b\rangle}_{\textbf{Clebsch-Gordan coefficients}}$$

- Using the rising/lowering operators $J_\pm = J_1 \pm iJ_2 = J_{a\pm} + J_{b\pm}$ we can rise/lower the m, m_a, m_b eigenvalues. Therefore the quantum numbers of the total angular momentum take discrete values

$$j = |j_a - j_b|, \dots, j_a + j_b, \qquad m = -j, \dots, j.$$

- The hydrogen atom has n^2 degeneracy, as the energy levels depend only on n but not on l, m:

$$n^2 = \sum_{l=0}^{l_{\max}}(2l+1) = (l_{\max}+1)^2 \quad \Rightarrow \quad l = 0, \dots, n-1$$

The total angular momentum of the electron is the sum of its spin and the orbital angular momentum $J = L + S$. A hydrogen state is denoted by nl_j, with $l = s, p, d, f, \dots$:

$$1s_{\frac{1}{2}}, 2p_{\frac{3}{2}}, 2p_{\frac{1}{2}}, 2s_{\frac{1}{2}}, 3d_{\frac{5}{2}}, 3d_{\frac{3}{2}}, 3p_{\frac{3}{2}}, 3p_{\frac{1}{2}}, 3s_{\frac{1}{2}}, \dots$$

- The **Wigner-Eckart theorem** states that the matrix-elements of spin-operators satisfy

$$\langle a', j_3, m_3|O_{j_2}^{m_2}|a, j_1, m_1\rangle$$
$$= \langle j_2, m_2, j_1, m_1|j_3, m_3, j_2, j_1\rangle\langle a'|\,\|O\|\,|a\rangle,$$

where the term $\langle a'|\,\|O\|\,|a\rangle$ is independent of the quantum numbers m_1, m_2, m_3 and is known as the reduced matrix-element.

13 Discrete Symmetries

- Under **parity transformations** the position vector changes sign $\mathbf{r} \to -\mathbf{r}$, so should the expectation value $\langle\psi|\hat{\mathbf{r}}|\psi\rangle \to -\langle\psi'|\hat{\mathbf{r}}|\psi'\rangle$, with $|\psi'\rangle = \Pi|\psi\rangle$. We also require the phase change to be zero and that $\Pi^2 = 1$. The representation of the parity operator Π is therefore unitary and hermitian:

$$\Pi^\dagger = \Pi^{-1} = \Pi$$

- For a system which is symmetric, the energy eigenstates are also parity eigenstates. Therefore, the wavefunctions are either even or odd:

$$\Pi|\pi\rangle = \pi|\pi\rangle, \quad \pi = \pm 1 \quad \Rightarrow \quad \psi_\pm(\mathbf{r}) = \pm\psi_\pm(-\mathbf{r})$$

- The **time reversal** operator $|\psi\rangle \to \Theta|\psi\rangle$ is anti-linear and anti-unitary. It operates as follows:

$$\Theta^{-1}\hat{\mathbf{r}}\Theta = \hat{\mathbf{r}}, \qquad \Theta^{-1}\hat{\mathbf{p}}\Theta = -\hat{\mathbf{p}}, \qquad \Theta^{-1}J_i\Theta = -J_i.$$