Part II Principles of Quantum Mechanics
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Contents

BOOKS

- E. Merzbacher *Quantum Mechanics, 3rd edition.* Wiley 1998 (various prices)

- B.H. Bransden and C.J. Joachain *Quantum Mechanics, 2nd edition.* Pearson 2000 (£50-60 on Amazon)

- J. Binney and D. Skinner *The Physics of Quantum Mechanics, 3rd edition.* Cappella Archive 2013 (£23.71)

- P.A.M. Dirac *The Principles of Quantum Mechanics.* Oxford University Press 1967 reprinted 1999 (£23.99).

- C.J. Isham *Lectures on Quantum Theory: Mathematical and Structural Foundations.* Imperial College Press 1995 (around £18)

- S. Gasiorowicz *Quantum Physics, 3rd edition.* Wiley International 2003 £48.71

Mot of these books are expensive new and there are a lot of pedagogic books on quantum mechanics, so it's good to look at those in the library since many books are good in one area but poor in another. Other books may be recommeneded through the course.

1 Introduction

★ Recall features of elementary (IB) quantum mechanics:

  ⋆ **wave-particle duality.** Waves behaving like particles – e.g., light quanta, photons and vice-versa; interference of electrons passing through crystal grating and electron microscope. To make this more precise need:

  ⋆ **wavefunction** $\psi(x)$ for particle. Probability density $|\psi(x)|^2$; probability is intrinsic to the theory.

  ⋆ **0bservables become (hermitian) operators on wavefunctions**. Lack of commutation limits simultaneous measurement – leads to precise version of uncertainty principle.

  ⋆ **Schrödinger's equation** specifies dynamics (evolution in time) and determines energy levels.

  This is enough to understand e.g., the hydrogen atom and transcends classical physics.

★ Aim of this course:

  ⋆ reformulate QM in a more powerful, abstract, flexible and useful form: **Dirac formalism**. This allows a simpler analysis of known problems such as the harmonic oscillator and is also the clearest way to understand lots of more novel properties, for example:

  ⋆ the spin of particles;

  ⋆ symmetries (e.g., translations and rotations) and conservation laws;

  ⋆ identical particles;

  ⋆ it provides the framework for quantizing other, more general, systems e.g., EM field, and ultimately other forces leading to the 'Standard Model' of elementary particles.

★ Will not dwell on applications in any detail, but will keep track of what the mathematical formalism is for.

★ Assume IB QM and IA Dynamics but no electromagnetism beyond Coulomb's law and intuitive ideas about magnetism.

 Plan:

1. Dirac formalism.
2. Harmonic oscillator.
3. Pictures of quantization.
4. Composite systems and identical particles.
5. Perturbation theory.
6. Angular momentum.
7. Transformations and symmetries.
8. Time-dependent perturbation theory.
9. Quantum basics.

2   Dirac Formalism

2.1   States and Operators

A quantum state is described at each instant by a **state** $|\psi\rangle$ which belongs to a complex vector apace V. Then

$$|\psi\rangle,\ |\phi\rangle\ \in\ V\ \implies\ \alpha|\psi\rangle+\beta|\phi\rangle\ \in\ V\ \ \forall\ \alpha,\beta\ \in\ \mathbb{C}. \tag{2.1.1}$$

Physically this is the superposition principle leading to wave-like behaviour (interference). However, these states are not wavefunctions but we will see that they carry all the quantum information that describes the **state** of the system concerned in a very general way.

There are also **dual** or conjugate states $\langle\phi|$ which belong to the dual space $V^\dagger$. By definition, states and duals can be combined/paired to give a complex number:

$$\underbrace{\langle\phi|}_{\text{`bra'}}\ ,\ \ \underbrace{|\psi\rangle}_{\text{`ket'}}\ \ \mapsto\ \ \underbrace{\langle\phi|\psi\rangle}_{\text{`bra(c)ket'}}\qquad\text{or formally}\quad V^\dagger\times V\ \to\ \mathbb{C}\,, \tag{2.1.2}$$

with

$$\langle\phi|\Big(\alpha_1|\psi_1\rangle\ +\ \alpha_2|\psi_2\rangle\Big)\ =\ \alpha_1\langle\phi|\psi_1\rangle\ +\ \alpha_2\langle\phi|\psi_2\rangle\,,$$

$$\Big(\beta_1\langle\phi_1|\ +\ \beta_2\langle\phi_2|\Big)|\psi\rangle\ =\ \beta_1\langle\phi_1|\psi\rangle\ +\ \beta_2\langle\phi_2|\psi\rangle\,, \tag{2.1.3}$$

$\alpha,\beta\in\mathbb{C}$. This is the definition of the dual as a vector space.

The space of states V and the dual $V^\dagger$ come with an inner-product which can be described as a one-to-one correspondence between states and duals:

$$V\ \longleftrightarrow\ V^\dagger$$

with $\qquad\qquad |\psi\rangle\ \longleftrightarrow\ \langle\psi| = (\ |\psi\rangle)^\dagger$ (use same label for corresponding states)

and $\qquad\alpha|\psi\rangle+\beta|\phi\rangle\ \longleftrightarrow\ \alpha^*\langle\psi|\ +\ \beta^*\langle\phi|\,.$

$$\tag{2.1.4}$$

The inner product is

$$V\times V\ \to\ \mathbb{C}$$
$$|\phi\rangle,|\psi\rangle\ \mapsto\ \langle\phi|\psi\rangle\ =\ (|\phi\rangle)^\dagger|\psi\rangle\,, \tag{2.1.5}$$

and is assumed to obey

$$\begin{aligned}\langle\phi|\psi\rangle\ &=\ \langle\psi|\phi\rangle^* &&\text{hermitian}\\ \||\psi\rangle\|^2\ &=\ \langle\psi|\psi\rangle\ &\geq\ 0\ &\text{(real from above)}\\ \text{with}\quad \||\psi\rangle\|^2\ &=\ 0 &&\text{iffi}\quad |\psi\rangle = 0.\end{aligned} \tag{2.1.6}$$

This means that the inner product is **positive semidefinite**. Note that knowing $\langle\phi|\psi\rangle$ for all $\langle\phi|$ determines $|\psi\rangle$ uniquely and vice-versa.

The physical content of any state is unaltered by changing $|\psi\rangle\to\alpha|\psi\rangle$ ($\alpha\neq 0$). We shall usually normalize states by $\||\psi\rangle\|^2\ =\ 1$ but still have the freedom to change $|\psi\rangle\to e^{i\theta}|\psi\rangle$. The absolute phase of a single state never has any physical significance,

but relative phases in combination such as $\alpha|\phi\rangle + \beta|\psi\rangle$ can be significant; for example, for interference phenomena.

The space V is complete; we assume appropriate sequences or series converge. A complete inner product space of this kind is a **Hilbert space** and this term is often used for the space V in QM. V can be either finite or infinite dimensional and we shall see examples of both.

An operator Q is a linear map on states, $V \to V$:

$$|\psi\rangle \mapsto Q|\psi\rangle, \tag{2.1.7}$$

and, by definition

$$Q\Big(\alpha|\phi\rangle + \beta|\psi\rangle\Big) = \alpha Q|\phi\rangle + \beta Q|\psi\rangle. \tag{2.1.8}$$

The same operator can be regarded as acting 'to the left' on dual states, $V^\dagger \to V^\dagger$:

$$\langle\phi| \mapsto \langle\phi|Q, \tag{2.1.9}$$

$$\Big(\langle\phi|Q\Big)|\psi\rangle = \langle\phi|\Big(Q|\psi\rangle\Big) \quad \forall \quad |\psi\rangle \tag{2.1.10}$$
$$\text{or simply} \qquad = \langle\phi|Q|\psi\rangle.$$

For any Q the **hermitian conjugate** or **adjoint** is an operator $Q^\dagger$ defined by

$$\langle\phi|Q^\dagger = \Big(Q|\phi\rangle\Big)^\dagger, \tag{2.1.11}$$

or, equivalently,

$$\begin{aligned}
\langle\phi|Q^\dagger|\psi\rangle &= \Big(Q|\phi\rangle\Big)^\dagger|\psi\rangle \\
&= \langle\psi|Q|\phi\rangle^* \quad \forall \quad |\psi\rangle, |\phi\rangle.
\end{aligned} \tag{2.1.12}$$

Simple consequences are

$$\begin{aligned}
\Big(\alpha A + \beta B\Big)^\dagger &= \alpha^* A^\dagger + \beta^* B^\dagger, \\
\Big(AB\Big)^\dagger &= B^\dagger A^\dagger,
\end{aligned} \tag{2.1.13}$$

for any A, B.[1]

---

[1]

$$\begin{aligned}
\langle\psi|(AB)^\dagger|\phi\rangle &= \Big((AB)|\psi\rangle\Big)^\dagger|\phi\rangle & \text{defn of } (AB)^\dagger \\
&= \Big(A|\psi'\rangle\Big)^\dagger|\phi\rangle & |\psi'\rangle \equiv B|\psi\rangle \\
&= \langle\psi'|A^\dagger|\phi\rangle & \text{defn of } A^\dagger \\
&= \Big(B|\psi\rangle\Big)^\dagger\Big(A^\dagger|\phi\rangle\Big) \\
&= \langle\psi|B^\dagger A^\dagger|\phi\rangle & \text{defn of } B^\dagger.
\end{aligned} \tag{2.1.14}$$

True for all $|\psi\rangle, |\phi\rangle$ and result follows.

For any operator Q call $|\psi\rangle$ ($\neq 0$) an **eigenstate** of Q with eigenvalue λ if

$$Q|\psi\rangle = \lambda|\psi\rangle. \tag{2.1.15}$$

Equivalently (taking $\dagger$ of this)

$$\langle\psi|Q^\dagger = \lambda^*\langle\psi|. \tag{2.1.16}$$

For general Q, λ can be complex.

Of particular importance are commutators of operators

$$[A, B] = AB - BA = -[B, A]. \tag{2.1.17}$$

We have the identities

$$\begin{array}{ll} [\alpha_1 A_1 + \alpha_2 A_2, B] = \alpha_1[A_1, B] + \alpha_2[A_2, B] \\ [A, \beta_1 B_1 + \beta_2 B_2] = \beta_1[A, B_1] + \beta_2[A, B_2] \end{array} \quad \text{linearity} \tag{2.1.18}$$

$$\begin{array}{ll} [A, B_1 B_2] = [A, B_1]B_2 + B_1[A, B_2] \\ [A_1 A_2, B] = [A_1, B]A_2 + A_1[A_2, B] \end{array} \quad \text{Leibnitz properties} \tag{2.1.19}$$

$$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0 \quad \text{Jacobi identity} \tag{2.1.20}$$

2.2   Observables and measurements

An operator Q is **hermitian** or **self-adjoint** if

$$Q^\dagger = Q. \tag{2.2.1}$$

Such operators are called **observables** because they correspond to physical, measurable, quantities e.g., position, momentum, energy, angular momentum. Key results for any hermitian Q:

(i)   All eigenvalues are real.
(ii) Eigenstates with distinct eigenvalues are orthogonal.
(iii) The eigenstates form a complete basis for V (and their duals for $V^\dagger$). So any state can be expanded in terms of (written as a linear combination of) the eigenstates.

We prove (i) and (ii) and assume (iii).

(i)
$$\begin{array}{lll} & Q|\psi\rangle = \lambda|\psi\rangle \\ \text{and} & \langle\psi|Q^\dagger = \lambda^*\langle\psi| \\ \Rightarrow & \langle\psi|Q = \lambda^*\langle\psi| & \text{since } Q \text{ is hermitian} \\ \Rightarrow & \langle\psi|Q|\psi\rangle = \lambda\langle\psi|\psi\rangle = \lambda^*\langle\psi|\psi\rangle. \end{array} \tag{2.2.2}$$

But $\||\psi\rangle\|^2 = \langle\psi|\psi\rangle \neq 0$ ($|\psi\rangle \neq 0$) and so deduce

$$\lambda = \lambda^*. \tag{2.2.3}$$

(ii) Let $|n\rangle$ be eigenstates of Q with eigenvalues $\lambda = q_n$ real, with n a discrete label possibly of infinite range.

$$
\begin{aligned}
Q|n\rangle &= q_n|n\rangle \\
\text{and} \quad Q|m\rangle &= q_m|m\rangle \\
\text{or} \quad \langle m|Q &= q_m\langle m| \\
\Rightarrow \quad \langle m|Q|n\rangle &= q_n\langle m|n\rangle = q_m\langle m|n\rangle .
\end{aligned}
\tag{2.2.4}
$$

So $q_n \neq q_m \Rightarrow \langle m|n\rangle = 0$.

Combining these three properties we have

★ For any observable Q there is an orthonormal **basis** of eigenstates $\{|n\rangle\}$ for the space of states V with

$$
\begin{aligned}
Q|n\rangle &= q_n|n\rangle , \\
\langle m|n\rangle &= \delta_{mn} .
\end{aligned}
\tag{2.2.5}
$$

We speak of **diagonalizing** Q by choosing the basis to be the eigenstates $|n\rangle$ of Q. This means that a general state $|\psi\rangle$ can be expanded as

$$
|\psi\rangle = \sum_n \alpha_n|n\rangle ,
\tag{2.2.6}
$$

where $\alpha_n = \langle n|\psi\rangle$.

For the state to be properly normalized

$$
\begin{aligned}
\||\psi\rangle\|^2 = \langle\psi|\psi\rangle &= 1 \\
\iff \quad \Big(\sum_m \alpha_m^*\langle m|\Big)\Big(\sum_n \alpha_n|n\rangle\Big) &= \sum_n |\alpha_n|^2 = 1 .
\end{aligned}
\tag{2.2.7}
$$

There might be several states with the same eigenvalue λ. Define the **eigenspace** for a given eigenvalue by

$$
V_\lambda = \{|\psi\rangle : \; Q|\psi\rangle = \lambda|\psi\rangle\} ,
\tag{2.2.8}
$$

which has the basis $\{|n\rangle : \; q_n = \lambda\}$.

The **degeneracy** of λ is the number of states in this basis, or dim V_λ. We say that λ is **non-degenerate** if the degeneracy is 1.

⌈ Note that passing from our three key results to the conclusion (★) is achieved by choosing an orthonormal basis for each V_λ:

(ii) ensures that these spaces are mutually orthogonal;

(iii) implies that the sum of all the eigenspaces is V, the entire space of states. ⌋

Consider a measurement of Q when the system is in state $|\psi\rangle$ immediately before. Then

• The result is an eigenvalue, λ, say.

- This value is obtained with the probability

$$p(\lambda) \;=\; \sum_{n:q_n=\lambda} |\alpha_n|^2. \tag{2.2.9}$$

- Immediately after the measurement the state is

$$|\phi\rangle \;=\; c \sum_{n:q_n=\lambda} \alpha_n |n\rangle \,, \tag{2.2.10}$$

where c is a normalization constant chosen so that $\langle\phi|\phi\rangle = 1$.

So measurement **projects** the system into the eigenspace V_λ.

Example. Consider a system with three orthonormal states: $|1\rangle, |2\rangle, |3\rangle$ on which Q has eigenvalues $q_1 = q_2 = 0$, $q_3 = 1$. Let the state of the system be

$$|\psi\rangle \;=\; \frac{1}{\sqrt{6}}(2|1\rangle + |2\rangle + |3\rangle) \,. \tag{2.2.11}$$

Then

$$\text{Probability of measuring} \begin{cases} 1 & \left|\frac{1}{\sqrt{6}}\right|^2 = \frac{1}{6} & |3\rangle \\[4mm] 0 & \left|\frac{2}{\sqrt{6}}\right|^2 + \left|\frac{1}{\sqrt{6}}\right|^2 = \frac{5}{6} & \frac{1}{\sqrt{5}}(2|1\rangle + |2\rangle) \\[4mm] & & \uparrow \\ & & \text{final states} \end{cases} \tag{2.2.12}$$

In this example we had degeneracy: two states with eigenvalue 0. However, often have the case with λ non-degenerate with eigenstate $|n\rangle$ unique up to a phase. Then

- $p(\lambda) \;=\; |\alpha_n|^2 \;=\; |\langle n|\psi\rangle|^2.$
- $\alpha_n \;=\; \langle n|\psi\rangle$ is called the **amplitude**.
- The state after measurement is $|n\rangle$.

In general,

$$\sum_\lambda p(\lambda) = \sum_n |\alpha_n|^2 = 1 \,, \tag{2.2.13}$$

as required for a probability distribution.

The **expectation value** (mean) of Q in state $|\psi\rangle$ is

$$\langle Q\rangle_\psi \;=\; \langle\psi|Q|\psi\rangle \;=\; \sum_\lambda \lambda p(\lambda) \;=\; \sum_n q_n|\alpha_n|^2 \,, \tag{2.2.14}$$

and the **uncertainty** (spread or variance) is

$$(\Delta Q)^2_\psi \;=\; \langle(Q - \langle Q\rangle_\psi)^2\rangle_\psi \;=\; \langle Q^2\rangle_\psi - \langle Q\rangle^2_\psi \,. \tag{2.2.15}$$

In thinking about many repeated measurements we must be careful to prepare the system in the same state each time.

In the case that $|\psi\rangle$ is an eigenstate of Q with eigenvalue λ, say, then

$$\langle Q \rangle_\psi \;=\; \lambda \,, \quad \text{and} \quad (\Delta Q)_\psi \;=\; 0 \,. \tag{2.2.16}$$

[The process of measurement is still a source of some deep questions about the interpretation of QM].

Quantum mechanical behaviour arises from the fact that observables do not commute in general. In any state $|\psi\rangle$

$$\langle \Delta A \rangle_\psi \langle \Delta B \rangle_\psi \;\geqslant\; \frac{1}{2} |\langle [A, B] \rangle_\psi| \,, \tag{2.2.17}$$

so $[A, B] \neq 0$ means we cannot expect to measure exact values for A and B simultaneously. This generalized **Uncertainty Principle** follows from

$$\|(A + i\lambda B)|\psi\rangle\|^2 \;\geqslant\; 0 \quad \forall \quad \text{real} \quad \lambda \,. \tag{2.2.18}$$

The LHS is a quadratic in λ and the condition implies that the discriminant is $\leqslant 0$; the stated Uncertainty Principle then follows.

Paradigm example: position, $\hat{x}$, and momentum, $\hat{p}$, in one dimension obey

$$\begin{aligned} [\hat{x}, \hat{p}] \;&=\; i\hbar \\ \Rightarrow \quad \Delta x \, \Delta p \;&\geqslant\; \frac{\hbar}{2} \,. \end{aligned} \tag{2.2.19}$$

In $D = 3$, $\hat{x}_i$ and $\hat{p}_i$ obey

$$[\hat{x}_i, \hat{p}_j] \;=\; i\hbar \delta_{ij} \,, \tag{2.2.20}$$

and so the uncertainty principle applies to components of position and momentum which are not orthogonal.

2.3   Time evolution and the Schrödinger Equation

So far our discussion of quantum states has been at a fixed time, even measurement is assumed to be an instantaneous change of state. The evolution of states $|\psi(t)\rangle$ in time is governed by the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle \;=\; H |\psi(t)\rangle \,, \tag{2.3.1}$$

where $H = H^\dagger$ is the Hamiltonian. Equivalently,

$$-i\hbar \frac{\partial}{\partial t} \langle\psi(t)| \;=\; \langle\psi(t)| H \,. \tag{2.3.2}$$

Note that these equations imply

$$\frac{\partial}{\partial t} \Big(\langle\psi(t)|\psi(t)\rangle \Big) \;=\; 0 \,, \tag{2.3.3}$$

so that the normalization of $|\psi(t)\rangle$, and hence the probabilistic interpretation, is preserved in time.

H is an observable: the energy. Consider the eigenstates

$$H|n\rangle = E_n|n\rangle . \tag{2.3.4}$$

Then the states

$$e^{-iE_n t/\hbar}|n\rangle \tag{2.3.5}$$

are **stationary state** solutions of the Schrödinger Equation.

The Schrödinger Equation is first-order in t and linear in $|\psi(t)\rangle$ and so for an initial state at $t = 0$,

$$|\psi(0)\rangle = \sum_n \alpha_n|n\rangle , \tag{2.3.6}$$

we have the unique solution

$$|\psi(t)\rangle = \sum_n \alpha_n e^{-iE_n t/\hbar}|n\rangle . \tag{2.3.7}$$

Example. Consider system with two energy eigenstates $|1\rangle, |2\rangle$ with energy eigenvalues E_1, E_2, respectively. We are interested in measuring Q defined by

$$Q|1\rangle = |2\rangle, \quad Q|2\rangle = |1\rangle \quad \Rightarrow \quad [Q, H] \neq 0 . \tag{2.3.8}$$

The eigenstates of Q are easily found to be

$$|\pm\rangle = \frac{1}{\sqrt{2}}\Big(|1\rangle \pm |2\rangle\Big) \quad \text{with eigenvalues} \quad q_\pm = \pm 1 . \tag{2.3.9}$$

Let the initial state, the state at $t = 0$, be $|\psi(0)\rangle = |+\rangle$. Then have

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\Big(e^{-iE_1 t/\hbar}|1\rangle + e^{-iE_2 t/\hbar}|2\rangle\Big) . \tag{2.3.10}$$

The probability of measuring Q at time t and getting ± 1 is

$$
\begin{aligned}
|\langle\pm|\psi(t)\rangle|^2 &= \left|\frac{1}{2}\Big(\langle 1| \pm \langle 2|\Big)\Big(e^{-iE_1 t/\hbar}|1\rangle + e^{-iE_2 t/\hbar}|2\rangle\Big)\right|^2 \\
&= \left|\frac{1}{2}\Big(e^{-iE_1 t/\hbar} \pm e^{-iE_2 t/\hbar}\Big)\right|^2 \\
&= \begin{cases} \cos^2\left(\frac{(E_1 - E_2)t}{2\hbar}\right) \\[2mm] \sin^2\left(\frac{(E_1 - E_2)t}{2\hbar}\right) \end{cases}
\end{aligned}
\tag{2.3.11}
$$

Note that we are assuming **no** time-dependence in H. This would become a much more complex situation.

2.4   Bases and Representations

Another use of a basis is that we can choose to reduce all states and operators to, possibility infinite, column/row vectors and to matrices as follows

$$|\psi\rangle \;=\; \sum_n \alpha_n |n\rangle \quad\Leftrightarrow\quad \alpha_n \;=\; \langle n|\psi\rangle$$

$$|\phi\rangle \;=\; \sum_n \beta_n |n\rangle \quad\Leftrightarrow\quad \beta_n \;=\; \langle n|\phi\rangle \,. \tag{2.4.1}$$

The inner product is then

$$\langle\phi|\psi\rangle \;=\; \sum_n \beta_n^* \alpha_n \,. \tag{2.4.2}$$

The operation of operator A can be written as

$$A|n\rangle \;=\; \sum_m |m\rangle A_{mn} \,, \tag{2.4.3}$$

where $A_{mn} = \langle m|A|n\rangle$ are the **matrix elements** of the **complex** matrix **representing** the operator A in this basis. Note that the entries in this matrix depend on the basis; a familiar result in linear algebra for any linear map. In contrast, the result of operating with A on any state is **independent** of the basis. Check this result

$$\underbrace{|\phi\rangle \;=\; A|\psi\rangle}_{\text{basis-independent}} \quad\Leftrightarrow\quad \beta_m \;=\; \underbrace{\sum_n A_{mn}\alpha_n}_{\text{basis-dependent}} \,. \tag{2.4.4}$$

Clearly, this representation is multiplication of a vector by a matrix: $\boldsymbol{\beta} = \boldsymbol{A\alpha}$. Also, have that the Hermitian conjugate has the familiar matrix form:

$$(A^\dagger)_{mn} \;=\; A_{nm}^* \,. \tag{2.4.5}$$

If B is another operator with matrix $\boldsymbol{B}$ then

$$(AB)_{mn} \;=\; \sum_p A_{mp} B_{pn} \,. \tag{2.4.6}$$

I.e., as expected the usual rules of matrix multiplication apply.

This, by now familiar, way of representing linear maps on a vector space by the linear algebra of matrices gives the matrix representation of Quantum Mechanics. It is most useful when the number of basis states is finite, but can also be useful for an ∞ dimensional basis as well (does need care).

We are often interested in a function $f(Q)$ of an operator Q. How should this be defined? The answer may be obvious if f is a polynomial or a series:

$$Q \;+\; \frac{Q^3}{3}\,, \quad e^Q\,, \quad \sin(Q) \qquad \text{assuming convergence} \,. \tag{2.4.7}$$

But what about $1/Q$ or $\log(Q)$?

For Q an observable and $|n\rangle$ an eigenbasis for Q:

$$Q|n\rangle \;=\; q_n|n\rangle \qquad \langle n|m\rangle \;=\; \delta_{mn} \,, \tag{2.4.8}$$

setting

$$f(Q)|n\rangle \;=\; f(q_n)|n\rangle \tag{2.4.9}$$

defines $f(Q)$ provided $f(q_n)$ is defined for all n; $f(Q)$ is defined on a basis and so is defined on any state. This is certainly true if f is a polynomial or a power series that converges for all q_n. If $q_n \neq 0 \;\; \forall \;\; n$ then can define

$$Q^{-1}|n\rangle \;=\; \frac{1}{q_n}|n\rangle \,, \tag{2.4.10}$$

and likewise $\log(Q)$ is defined if $0 < q_n < \infty$.

A useful way to express that $\{|n\rangle\}$ is an orthonormal basis is the **completeness relation** or **resolution of the identity**:

$$\sum_n |n\rangle\langle n| \;=\; \mathbb{I}\,, \qquad \text{the identity operator.} \tag{2.4.11}$$

The notation is

$$\Big(\underbrace{|n\rangle\langle m|}_{\text{operator}} \Big) \underbrace{|\psi\rangle}_{\text{state}} \;=\; \underbrace{|n\rangle}_{\text{state}} \Big(\underbrace{\langle m|\psi\rangle}_{\text{number}} \Big) . \tag{2.4.12}$$

This is confirmed by applying each side to an arbitrary state

$$\sum_n |n\rangle\langle n|\psi\rangle \;=\; |\psi\rangle \;=\; \mathbb{I}|\psi\rangle \,. \tag{2.4.13}$$

In the same way can resolve any operator in a similar fashion:

$$Q \;=\; \sum_n q_n |n\rangle\langle n| \,,$$

$$f(Q) \;=\; \sum_n f(q_n)|n\rangle\langle n| \,. \tag{2.4.14}$$

In the case where the eigenvalues are degenerate then we can define a projection operator onto the subspace of eigenstates with eigenvalue λ by

$$P_\lambda \;=\; \sum_{n:\, q_n=\lambda} |n\rangle\langle n| \,. \tag{2.4.15}$$

The bases considered so far may be infinite but have been assumed **discrete** which includes countably infinite bases. However, we can extend the index n to be continuous. This requires some modifications in all relevant formulas:

$$\sum_n \;\to\; \int dn \quad \begin{cases} |\psi\rangle &=& \int dn\, \alpha_n |n\rangle \\ \mathbb{I} &=& \int dn\, |n\rangle\langle n| \\ Q &=& \int dn\, q(n)|n\rangle\langle n| \end{cases}$$

$$\langle n|m\rangle \;=\; \delta_{nm} \;\to\; \delta(n-m) \tag{2.4.16}$$

with $|\alpha_n|^2 \;=\; |\langle n|\psi\rangle|^2$. There is no longer a probability for discrete outcomes but a **probability density** for the continuous range of n. We will see this below for position and momentum operators.

2.5   Position and momentum basis – wavefunctions

Consider particle motion in one dimension. Position and momentum operators $\hat{x}, \hat{p}$ obey

$$[\hat{x}, \hat{p}] \;=\; i\hbar \;. \tag{2.5.1}$$

Let $|x\rangle$ be position eigenstates

$$\hat{x}|x\rangle \;=\; x|x\rangle \;, \tag{2.5.2}$$

with continuous eigenvalue x and normalization

$$\langle x|x'\rangle \;=\; \delta(x - x') \;, \qquad \int dx\, |x\rangle\langle x| \;=\; \mathbb{I} \;. \tag{2.5.3}$$

In this basis, any state can be expanded as

$$|\psi\rangle \;=\; \int dx\, \psi(x)|x\rangle$$
$$\text{with} \quad \psi(x) \;=\; \langle x|\psi\rangle \qquad \text{a complex function} \;. \tag{2.5.4}$$

$\psi(x)$ is just the usual position wavefunction and the standard interpretation is the obvious extension of the measurement postulates in section 2.2 to continuous eigenvalues:

$$|\psi(x)|^2 \quad \text{is the probability density for measuring position.} \tag{2.5.5}$$

The inner product in terms of wavefunctions becomes

$$\langle\phi|\psi\rangle \;=\; \left(\int dx\, \phi(x)^*\langle x|\right)\left(\int dx'\, \psi(x')|x'\rangle\right)$$
$$=\; \int dx \int dx'\, \phi(x)^*\psi(x')\, \underbrace{\langle x|x'\rangle}_{\delta(x - x')}$$
$$=\; \int dx\, \phi(x)^*\psi(x) \;. \tag{2.5.6}$$

So, in particular,

$$\||\psi\rangle\|^2 \;=\; \langle\psi|\psi\rangle \;=\; \int dx\, |\psi(x)|^2 \;=\; 1 \tag{2.5.7}$$

for a normalized state.

Define similarly momentum eigenstates $|p\rangle$ with

$$\hat{p}|p\rangle \;=\; p|p\rangle \;, \tag{2.5.8}$$

and with

$$\langle p|p'\rangle \;=\; \delta(p - p') \;, \qquad \int dp\, |p\rangle\langle p| \;=\; \mathbb{I} \;. \tag{2.5.9}$$

It is very important that the eigenstates of $\hat{x}$ and $\hat{p}$ can be chosen so that they are related by

$$\langle x|p\rangle \;=\; \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar} \;, \tag{2.5.10}$$

$$\Rightarrow \quad \langle p|x\rangle \;=\; \frac{1}{\sqrt{2\pi\hbar}}e^{-ipx/\hbar} \;. \tag{2.5.11}$$

We justify this later after deducing some consequences. First find action of $\hat{x}$ and $\hat{p}$ in terms of position wavefunctions:

$\hat{x}|\psi\rangle$ wavefunction : $\langle x|\hat{x}|\psi\rangle \;=\; x\langle x|\psi\rangle \;=\; x\psi(x)$

$\hat{p}|\psi\rangle$ wavefunction : $\langle x|\hat{p}|\psi\rangle$

$$= \int dp \,\langle x|\hat{p}|p\rangle\langle p|\psi\rangle \quad \text{[resolution of identity using p-states]}$$

$$= \int dp \, p\langle x|p\rangle\langle p|\psi\rangle$$

$$= \int dp \; -i\hbar\frac{\partial}{\partial x}\Big(\langle x|p\rangle\Big)\langle p|\psi\rangle$$

$$= -i\hbar\frac{\partial}{\partial x}\int dp \,\langle x|p\rangle\langle p|\psi\rangle$$

$$= -i\hbar\frac{\partial}{\partial x}\langle x|\psi\rangle \;=\; -i\hbar\frac{\partial}{\partial x}\psi(x) \;, \tag{2.5.12}$$

and so recover familiar results. However, also have new possibility. Can expand states in momentum basis instead:

$$|\psi\rangle \;=\; \int dp \,\tilde{\psi}(p)|p\rangle \;,$$

$$\text{with} \qquad \tilde{\psi}(p) \;=\; \langle p|\psi\rangle \;, \tag{2.5.13}$$

which is the momentum space wavefunction where $|\tilde{\psi}(p)|^2$ is the probability density for measurements of momentum. Then have

$$\||\psi\rangle\|^2 \;=\; \int dp \,\langle\psi|p\rangle\langle p|\psi\rangle \;=\; \int dp \,|\tilde{\psi}(p)|^2 \;=\; 1 \;. \tag{2.5.14}$$

As before, but with $x \;\leftrightarrow\; p$:

$$\left.\begin{array}{ccc} \hat{p}|\psi\rangle & \longrightarrow & p\tilde{\psi}(p) \\[2mm] \hat{x}|\psi\rangle & \longrightarrow & i\hbar\dfrac{\partial}{\partial p}\tilde{\psi}(p) \end{array}\right\} \quad \begin{array}{l}\text{momentum space}\\ \text{wavefunctions}\end{array} \tag{2.5.15}$$

The relationship between the wavefunctions follows from Eq. (2.5.10):

$$\tilde{\psi}(p) \;=\; \langle p|\psi\rangle \;=\; \int dx \,\langle p|x\rangle\langle x|\psi\rangle$$

$$= \frac{1}{\sqrt{2\pi\hbar}}\int dx \, e^{-ipx/\hbar}\,\psi(x) \quad \text{Fourier transform,}$$

$$\text{and} \quad \psi(x) \;=\; \frac{1}{\sqrt{2\pi\hbar}}\int dp \, e^{ipx/\hbar}\,\tilde{\psi}(p) \qquad \text{inverse FT.} \tag{2.5.16}$$

Think of these as two different **representations** of states $|\psi\rangle$ and the operators on them:

$$\begin{array}{cccccc} & \psi(x) & & & \tilde{\psi}(p) & \\[2mm] \hat{x} & \longrightarrow & x & \hat{x} & \longrightarrow & i\hbar\dfrac{\partial}{\partial p} \\[3mm] \hat{p} & \longrightarrow & -i\hbar\dfrac{\partial}{\partial x} & \hat{p} & \longrightarrow & p \end{array} \tag{2.5.17}$$

⌈ The transforms between x and p space are familiar but here we are deriving all the results, including the transform inversion theorem, on the assumption that $\{|x\rangle\}$ and $\{|p\rangle\}$ are bases. ⌋

The corresponding **representations** of the Hamiltonian

$$H(\hat{x}, \hat{p}) \; = \; \frac{\hat{p}^2}{2m} \; + \; V(\hat{x}) \tag{2.5.18}$$

are

$$\text{on} \quad \psi(x): \qquad H \; \longrightarrow \; -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \; + \; V(x) \, ,$$

$$\text{on} \quad \tilde{\psi}(p): \qquad H \; \longrightarrow \; -\frac{p^2}{2m} \; + \; V\left(i\hbar\frac{\partial}{\partial p}\right) \, . \tag{2.5.19}$$

It may be easy to interpret the potential term in momentum space. E.g., $V(x) = \lambda x^n \Rightarrow$

$$V\left(i\hbar\frac{\partial}{\partial p}\right) \; = \; \lambda(i\hbar)^n \frac{\partial^n}{\partial p^n} \, , \tag{2.5.20}$$

but more generally need to use first principles.

$$\begin{aligned}
\langle p|V(\hat{x})|\psi\rangle \; &= \; \int dx \, \langle p|V(\hat{x})|x\rangle\langle x|\psi\rangle \\
&= \; \int dx \, V(x)\langle p|x\rangle \int dp'\langle x|p'\rangle\langle p'|\psi\rangle \\
&= \; \int dp' \left(\frac{1}{2\pi\hbar}\int dx \, V(x) \, e^{-i(p-p')x/\hbar}\right) \tilde{\psi}(p') \\
&= \; \frac{1}{\sqrt{2\pi\hbar}}\int dp' \, \tilde{V}(p-p')\tilde{\psi}(p') \, . \tag{2.5.21}
\end{aligned}$$

Thus $H|\psi\rangle = E|\psi\rangle$ becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\,\psi(x) \; = \; E\,\psi(x) \qquad \text{in position space} \, ,$$

$$\frac{p^2}{2m}\tilde{\psi}(p) + \frac{1}{\sqrt{2\pi\hbar}}\int dp' \, \tilde{V}(p-p') \, \tilde{\psi}(p') \; = \; E\,\tilde{\psi}(p) \qquad \text{in momentum space} \, .$$

$$\tag{2.5.22}$$

⌈ Note that the convolution theorem derived here. ⌋

Now return to the key condition in Eq. (2.5.10) and justify it:

$$\langle x|p\rangle \; = \; \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar} \, . \tag{2.5.23}$$

The point is that eigenstates are only ever unique up to a phase, even if normalized, so we need to show there is a way to choose $|x\rangle$ and $|p\rangle$ which makes this result true. Doing this will involve an approach to translations to which we return later. Claim that

$$|x_0 + a\rangle \; = \; e^{-ia\hat{p}/\hbar}|x_0\rangle \, , \tag{2.5.24}$$

which involves the operator

$$U(a) \equiv e^{-ia\hat{p}/\hbar} = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-ia}{\hbar} \right)^n \hat{p}^n , \qquad (2.5.25)$$

defines position eigenstates $|x\rangle$ $\forall$ x given one with $x = x_0$. To check this first note that

$$[\hat{x}, \hat{p}] = i\hbar \Rightarrow [\hat{x}, \hat{p}^n] = i\hbar n\, \hat{p}^{n-1} . \qquad (2.5.26)$$

[Note that $\hat{x}$ acts like " $i\hbar\, d/d\hat{p}$ " inside a commutator.] Thus find

$$[\hat{x}, U(a)] = \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{-ia}{\hbar} \right)^n n\, \hat{p}^{n-1} = aU(a) . \qquad (2.5.27)$$

So

$$\begin{aligned}
\hat{x}\, U(a)|x_0\rangle &= ([\hat{x}, U(a)] + U(a)\hat{x})|x_0\rangle \\
&= (aU(a) + U(a)x_0)|x_0\rangle \\
&= (x_0 + a)U(a)|x_0\rangle \qquad \text{as required.} \qquad (2.5.28)
\end{aligned}$$

Similarly,

$$|p_0 + b\rangle = e^{ib\hat{x}/\hbar}|p_0\rangle , \qquad (2.5.29)$$

defines momentum eigenstates $|p\rangle$ $\forall$ p given one with $p = p_0$. But then

$$\begin{aligned}
\langle x_0 + a|p_0 + b\rangle &= \langle x_0| e^{ia\hat{p}/\hbar}|p_0 + b\rangle \\
\\
&= e^{ia(p_0+b)/\hbar}\langle x_0|e^{ib\hat{x}/\hbar}|p_0\rangle \\
\\
&= e^{i(ab+ap_0+bx_0)/\hbar}\langle x_0|p_0\rangle . \qquad (2.5.30)
\end{aligned}$$

Choosing $\langle x_0|p_0\rangle = 1/\sqrt{2\pi\hbar}$ for reference values $x_0 = p_0 = 0$, then gives (relabelling a, b as x, p, respectively)

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} . \qquad (2.5.31)$$

Actually, need justification for this last step.

- Since $\{|x\rangle\}$ is a basis we cannot have $\langle x|p_0\rangle = 0$ for every x, and then Eq. (2.5.24) implies $\langle x_0|p_0\rangle \neq 0$, the required result, since

$$\begin{aligned}
|x_0\rangle &= |x + (x_0 - x)\rangle = e^{-i(x_0-x)\hat{p}/\hbar}|x\rangle \\
\Rightarrow \quad \langle x_0|p_0\rangle &= e^{i(x_0-x)p_0/\hbar}\langle x|p_0\rangle \neq 0 . \qquad (2.5.32)
\end{aligned}$$

- Now, the phase of $\langle x_0|p_0\rangle$ is a matter of convention but the modulus must be consistent with

$$\langle p|p'\rangle = \delta(p - p') , \qquad (2.5.33)$$

which is the desired normalization for the $\{|p\rangle\}$ basis. To check:

$$\begin{aligned}
\langle p|p'\rangle &= \int dx\, \langle p|x\rangle\langle x|p'\rangle \\
&= \int dx\, \frac{1}{2\pi\hbar} e^{i(p'-p)x/\hbar} = \delta(p - p') \qquad \text{as required.} \qquad (2.5.34)
\end{aligned}$$

- Similarly,

$$\langle x|x'\rangle = \int dp\, \langle x|p\rangle\langle p|x'\rangle$$

$$= \int dp\, \frac{1}{2\pi\hbar} e^{ip(x-x')/\hbar} = \delta(x-x') \qquad \text{as expected.} \qquad (2.5.35)$$

Note that the operator $U(a)$ implements translation by a on the position states.

2.6   Simultaneous Measurements and Complete Commuting Sets

Return to idea of labelling basis states by eigenvalues of observables. If this cannot uniquely be done with eigenvalues λ of some observable Q because some eigenvalues are degenerate, then need at least one more observable Q' to distinguish the corresponding degenerate states.

Physically, we must be able to measure Q and Q' **simultaneously** or

- first measure Q with result λ,

- then immediately measure Q' with result λ'.

- This second measurement must not change the value for Q and so still get result λ if it is measured again immediately.

Mathematically, this requires a basis of **joint eigenstates** which **simultaneously diagonalize** Q and Q':

$$Q|\lambda,\lambda'\rangle = \lambda|\lambda,\lambda'\rangle$$
$$Q'|\lambda,\lambda'\rangle = \lambda'|\lambda,\lambda'\rangle\,, \qquad (2.6.1)$$

which is only possible iffi

$$[Q,Q'] = 0\,, \qquad (2.6.2)$$

as we now show.

- If there is a basis of joint eigenstates as above then

$$QQ'|\lambda,\lambda'\rangle = Q'Q|\lambda,\lambda'\rangle = \lambda\lambda'|\lambda,\lambda'\rangle\,, \qquad (2.6.3)$$

so $QQ' = Q'Q$ on these basis states and hence on all states since they can be expanded on this basis.

- Conversely, if $[Q,Q'] = 0$ and $|\psi\rangle$ belongs to the eigenspace V_λ of Q then

$$Q\big(Q'|\psi\rangle\big) = Q'\big(Q|\psi\rangle\big) = \lambda\big(Q'|\psi\rangle\big)\,, \qquad (2.6.4)$$

and so $Q'|\psi\rangle$ also belongs to V_λ.

- The definition of a hermitian operator that

$$\langle\phi|Q'|\psi\rangle \;=\; \langle\psi|Q'|\phi\rangle^* \quad \forall \quad |\psi\rangle,\ |\phi\rangle \ \in \ V \tag{2.6.5}$$

holds for the restriction $|\psi\rangle,\ |\phi\rangle \ \in \ V_\lambda$. Hence, $\exists$ a basis for V_λ consisting of eigenstates of Q'. Call these $|\lambda, \lambda'\rangle$.

- Doing this for each V_λ gives a basis of such joint eigenstates for V.

$\lceil$ Note that if dim $V_\lambda = 1$ (no degeneracy) then any state in V_λ is automatically an eigenstate of Q' since Q' maps $V_\lambda \to V_\lambda$. $\rfloor$

Now can extend to any number of hermitian operators. Observables $\{Q_1, Q_2, Q_3. \ldots\}$ are said to be a **complete commuting set** if any pair commute. Then there is a basis of joint eigenstates with members

$$|\lambda_1, \lambda_2, \lambda_3, \ldots\rangle . \tag{2.6.6}$$

An equivalent way to characterize a complete commuting set is as follows. If A is any other observable with $[A, Q_i] = 0 \ \forall \ Q_i$ then

$$A \;=\; f(Q_1, Q_2, Q_3, \ldots) \tag{2.6.7}$$

for some function f. This means that

$$A|\lambda_1, \lambda_2, \lambda_3, \ldots\rangle \;=\; f(\lambda_1, \lambda_2, \lambda_3, \ldots)|\lambda_1, \lambda_2, \lambda_3, \ldots\rangle . \tag{2.6.8}$$

An example is the generalization from one to three dimensions of the position and momentum operators $(\hat{\boldsymbol{x}}, \hat{\boldsymbol{p}})$. These obey the commutation relations defined in terms of their Cartesian component operators in usual notation

$$[\hat{x}_i, \hat{p}_j] \;=\; i\hbar\delta_{ij} . \tag{2.6.9}$$

One complete commuting set is

$$\hat{\boldsymbol{x}} \;=\; (\hat{x}_1, \hat{x}_2, \hat{x}_3) \tag{2.6.10}$$

with joint eigenstates:

$$\hat{x}_i|\boldsymbol{x}\rangle \;=\; x_i|\boldsymbol{x}\rangle$$
orthonormality: $\qquad \langle\boldsymbol{x}|\boldsymbol{x}'\rangle \;=\; \delta^{(3)}(\boldsymbol{x} - \boldsymbol{x}')$
basis: $\qquad\qquad\qquad |\psi\rangle \;=\; \int d^3x\ \psi(\boldsymbol{x})|\boldsymbol{x}\rangle$
position space wavefunction $\qquad \psi(\boldsymbol{x}) \;=\; \langle\boldsymbol{x}|\psi\rangle .$

An alternative complete commuting set is

$$\hat{\boldsymbol{p}} \;=\; (\hat{p}_1, \hat{p}_2, \hat{p}_3) \tag{2.6.11}$$

with joint eigenstates

$$\hat{p}_i|\boldsymbol{p}\rangle \;=\; p_i|\boldsymbol{p}\rangle \tag{2.6.12}$$

and momentum space wavefunction $\tilde{\psi}(\boldsymbol{p}) = \langle\boldsymbol{p}|\psi\rangle$.

The relationship between these eigenstates is

$$\langle \boldsymbol{x}|\boldsymbol{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}}e^{i\boldsymbol{p}\cdot\boldsymbol{x}/\hbar} \quad \Rightarrow$$

$$\tilde{\psi}(\boldsymbol{p}) = \frac{1}{(2\pi\hbar)^{3/2}}\int d^3x \ e^{-i\boldsymbol{p}\cdot\boldsymbol{x}/\hbar}\psi(x)$$

$$\psi(\boldsymbol{x}) = \frac{1}{(2\pi\hbar)^{3/2}}\int d^3p \ e^{i\boldsymbol{p}\cdot\boldsymbol{x}/\hbar}\tilde{\psi}(p) \ . \tag{2.6.13}$$

There are other possibilities such as $\{\hat{x}_1, \hat{x}_2, \hat{p}_3\}$ leading to mixed position and momentum space wavefunctions.

3   The Harmonic Oscillator

A one-dimensional harmonic oscillator of mass m and frequency ω is defined by the Hamiltonian

$$H = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2 \ . \tag{3.1}$$

We will derive the energy levels and construct eigenstates using operator methods and then also see how to find the wavefunctions.

3.1   Analysis using annihilation, creation and number operators

Define

$$a = \left(\frac{m\omega}{2\hbar}\right)^{1/2}\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right) \ ,$$

$$a^\dagger = \left(\frac{m\omega}{2\hbar}\right)^{1/2}\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right) \ . \tag{3.1.1}$$

Note that these are dimensionless. Equivalently,

$$\hat{x} = \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(a + a^\dagger\right) \ ,$$

$$\hat{p} = \left(\frac{\hbar m\omega}{2}\right)^{1/2} i\left(a^\dagger - a\right) \ . \tag{3.1.2}$$

It is easy to check that

$$[\hat{x}, \hat{p}] = i\hbar \quad \Leftrightarrow \quad [a, a^\dagger] = 1 \ . \tag{3.1.3}$$

Also have

$$
\begin{aligned}
aa^\dagger &= \frac{m\omega}{2\hbar}\,\hat{x}^2 + \frac{1}{2m\omega\hbar}\,\hat{p}^2 - \frac{i}{2\hbar}(\hat{x}\hat{p} - \hat{p}\hat{x}) \\
&= \frac{1}{\hbar\omega}H + \frac{1}{2}\,,
\end{aligned}
$$

and similarly

$$
a^\dagger a = \frac{1}{\hbar\omega}H - \frac{1}{2} \qquad \text{(opposite sign for commutator)},
$$

$$(3.1.4)$$

which confirms the commutation relations and also gives

$$
H = \hbar\omega\left(N + \frac{1}{2}\right), \tag{3.1.5}
$$

where $N = a^\dagger a$ is the **number operator**. $N^\dagger = N$ and finding its eigenstates and eigenvalues is equivalent to doing this for H:

$$
N|\lambda\rangle = \lambda|\lambda\rangle \quad \Leftrightarrow \quad H|\lambda\rangle = E|\lambda\rangle \quad \text{with} \quad E = \hbar\omega\left(\lambda + \frac{1}{2}\right). \tag{3.1.6}
$$

Let $|\lambda\rangle$ be **any** such eigenstate normalized s.t. $\||\lambda\rangle\|^2 = 1$. Then

$$
\lambda = \langle\lambda|N|\lambda\rangle = \langle\lambda|a^\dagger a|\lambda\rangle = \|a|\lambda\rangle\|^2 \geqslant 0. \tag{3.1.7}
$$

Thus,

$$
\begin{aligned}
\lambda &\geqslant 0 \qquad \text{all eigenvalues non-negative} \\
&= 0 \qquad \text{iffi} \quad a|\lambda\rangle = 0.
\end{aligned} \tag{3.1.8}
$$

Next consider commutators

$$
\begin{aligned}
[N, a^\dagger] &= [a^\dagger a, a^\dagger] = a^\dagger[a, a^\dagger] = a^\dagger, \\
[N, a] &= [a^\dagger a, a] = [a^\dagger, a]a = -a.
\end{aligned} \tag{3.1.9}
$$

These relations imply that $a^\dagger$ and a act on eigenstates by respectively raising and lowering the eigenvalues by 1, provided the new states are non-zero and so actually are eigenstates.

$$
\begin{aligned}
N(a^\dagger|\lambda\rangle) &= ([N, a^\dagger] + a^\dagger N)|\lambda\rangle \\
&= (a^\dagger + a^\dagger\lambda)|\lambda\rangle \\
&= (\lambda + 1)(a^\dagger|\lambda\rangle),
\end{aligned}
$$

$$
\begin{aligned}
N(a|\lambda\rangle) &= ([N, a] + aN)|\lambda\rangle \\
&= (-a + a\lambda)|\lambda\rangle \\
&= (\lambda - 1)(a|\lambda\rangle).
\end{aligned} \tag{3.1.10}
$$

To find whether the new states are non-zero we compute their norms.

$$
\|a|\lambda\rangle\|^2 = \lambda \qquad \text{(already done above)} \tag{3.1.11}
$$

which is only ever zero if $\lambda = 0$.

$$\begin{aligned}
\|a^\dagger|\lambda\rangle\|^2 &= \langle\lambda|aa^\dagger|\lambda\rangle \\
&= \langle\lambda|a^\dagger a + 1|\lambda\rangle \\
&= \lambda + 1 ,
\end{aligned} \tag{3.1.12}$$

which is never zero since $\lambda \geqslant 0$. Because of these properties $a^\dagger$ and a are called, respectively, **creation** and **annihilation** operators.

Suppose there is an eigenstate $|\lambda\rangle$ with λ not an integer. Then

$$\begin{array}{cccccc}
 & a|\lambda\rangle, & a^2|\lambda\rangle, & \ldots, & a^m|\lambda\rangle, & \ldots & \text{are \textbf{all} non-zero.} \\
\text{eigenvalues:} & \lambda - 1, & \lambda - 2, & \ldots, & \lambda - m & \ldots\,.
\end{array}$$
$$\tag{3.1.13}$$

But for m sufficiently large $\lambda - m < 0$ which is a contradiction since all eigenvalues are non-negative. By contrast if $\lambda = n = 0, 1, 2, \ldots$ then the contradiction is avoided because

$$\begin{array}{cccccc}
 & a|n\rangle, & a^2|n\rangle, & \ldots, & a^n|n\rangle, & \text{are non-zero states} \\
\text{eigenvalues:} & n - 1, & n - 2, & \ldots, & 0 ,
\end{array}$$
$$\tag{3.1.14}$$

but $a^m|n\rangle = 0,\ m > n$ and so the sequence terminates. Furthermore, have additional eigenstates

$$\begin{array}{ccccc}
 & a^\dagger|n\rangle, & (a^\dagger)^2|n\rangle, & \ldots, \\
\text{eigenvalues:} & n + 1, & n + 2, & \ldots &.
\end{array} \tag{3.1.15}$$

The eigenvalues of N are therefore **precisely** the non-negative integers and the oscillator energy levels are

$$E_n = \hbar\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, 3, \ldots. \tag{3.1.16}$$

From calculations of norms above, we can choose normalized eigenstates $|n\rangle$, $\langle n|n\rangle = 1$ which are then related by

$$\left.\begin{array}{ccc}
a^\dagger|n\rangle &=& \sqrt{n+1}\,|n+1\rangle \\
a|n\rangle &=& \sqrt{n}\,|n-1\rangle
\end{array}\right\} \qquad \textbf{ladder operators} \tag{3.1.17}$$

Starting from one state reach others by operating with a and $a^\dagger$. In particular, starting from the **ground state**, $|0\rangle$, characterized by

$$a|0\rangle = 0 , \qquad (3.1.18)$$

have normalized eigenstates

$$|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle . \qquad (3.1.19)$$
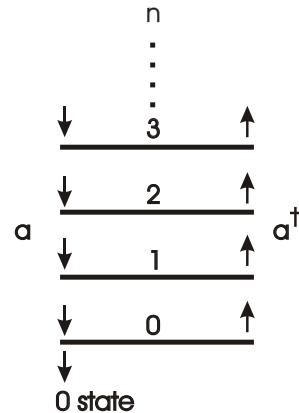
In the absence of any internal structure can take $\{\hat{x}\}$ or $\{\hat{p}\}$ or $\{N\}$ as a complete commuting set. Then the energy levels are non-degenerate (eigenvalues of N label them uniquely) and, in particular, $|0\rangle$ is completely specified by

$$a|0\rangle \;=\; 0 \;. \tag{3.1.20}$$

If there **is** some internal structure then all states can carry an additional label i associated with some observable Q (or its eigenvalues) commuting with $\hat{x}, \hat{p}, a, a^{\dagger}, N$. All energy levels have the same degeneracy with states $|n; i\rangle$ related by $a, a^{\dagger}$ without affecting i.

The analysis above is convenient for finding wavefunctions. In the position representation

$$|0\rangle \qquad \rightsquigarrow \qquad \psi_0(x) \;=\; \langle x|0\rangle$$

$$a \;=\; \left(\frac{m\omega}{2\hbar}\right)^{1/2}\left(\hat{x} + \frac{i}{m\omega}\,\hat{p}\right) \qquad \rightsquigarrow \qquad \left(\frac{m\omega}{2\hbar}\right)^{1/2}\left(x + \frac{\hbar}{m\omega}\,\frac{\partial}{\partial x}\right)$$

$$a|0\rangle \;=\; 0 \qquad \rightsquigarrow \qquad \left(x + \frac{\hbar}{m\omega}\,\frac{\partial}{\partial x}\right)\psi_0(x) \;=\; 0 \tag{3.1.21}$$

$$\Longrightarrow \qquad \psi_0(x) \;=\; N\,e^{-\frac{m\omega x^2}{2\hbar}}$$

with normalization factor $N = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$.

Can also find wavefunctions for higher energy states by using Eq. (3.1.19). E.g.,

$$|1\rangle \;=\; a^{\dagger}|0\rangle \qquad \rightsquigarrow \qquad \psi_1(x) \;=\; \left(\frac{m\omega}{2\hbar}\right)^{1/2}\left(x - \frac{\hbar}{m\omega}\,\frac{\partial}{\partial x}\right)\psi_0(x)$$

$$= \; \left(\frac{2m\omega}{\hbar}\right)^{1/2}\,x\psi_0(x) \;. \tag{3.1.22}$$

The correct normalization is guaranteed.

3.2   Importance of the oscillator – applications in outline

"Physics is that subset of human experience that can be reduced to coupled harmonic oscillators."

<div align="right">

M. Peskin

</div>

- The oscillator is the simplest QM model beyond steps, wells etc. that can be solved exactly; the hydrogen atom with a Coulomb potential is also special in this respect. It is a very useful example to use as test case for new ideas, approaches and techniques.

- More importantly, many physical systems can be described, exactly or approximately, in terms of oscillators.

- Consider a smooth potential $V(x)$ with equilibrium point x_0 ($V'(x_0) = 0$). For displacements x from equilibrium

$$V(x_0 + x) \;=\; V(x_0) + \frac{1}{2}V''(x_0)x^2 + O(x^3) \;, \tag{3.2.1}$$

and so if the displacements are not too large neglecting the $O(x^3)$ contribution may be a good approximation. Indeed, can include the effects of these anharmonic corrections systematically using perturbation theory (see later). The point is that we start with a soluble model. E.g., diatomic molecules where the quantization of vibrational energies is important in understanding the internal energy and hence the heat capacity of the gas – has macroscopic consequences. In other systems this approach can breakdown, though.

- More complicated systems can be analyzed in terms of **normal modes**: each mode is a coherent motion in which all degrees of freedom oscillate with common frequency ω. This is common classically and can now quantize this motion. The general solution for the classical oscillator is

$$x(t) \;=\; A\,e^{-i\omega t} + A^*\,e^{i\omega t} \qquad A \text{ a complex constant.} \tag{3.2.2}$$

Normal modes for a system with variables x_n, $n = 1 \ldots N$ are of the form

$$x_n(t) \;=\; Au_n\,e^{-i\omega t} + A^* u_n^*\,e^{i\omega t} \;, \tag{3.2.3}$$

with u_n, $n = 1 \ldots N$ a complex vector specific to each allowed **normal frequency** ω. The general solution is a superposition of normal modes. To quantize treat normal modes as **independent** oscillators. E.g.,

- Benzene ring with 6 CH units which oscillate around the "clock face" of the ring. They are treated as if joined by identical springs. Actually, analyzed by discrete group theory based on the symmetries of the ring.

- Crystal with # atoms $\mathcal{N} \sim 10^{23}$. The forces between the atoms are approximately elastic and in 3D there are $N = 3\mathcal{N}$ independent coordinates. Each of the $3\mathcal{N}$ modes is a collective motion of the atoms and if the approximation of elastic forces is good then interaction between normal modes is small. If you excite just a single mode then no other mode starts up – no energy transfer between modes; they are effectively independent oscillators.

- Electromagnetic field – normal mode oscillations of electric and magnetic fields at each point in space

$$\boldsymbol{E}(\boldsymbol{x},t) \;=\; A\boldsymbol{u}(\boldsymbol{x})\,e^{-i\omega t} \;+\; A^*\boldsymbol{u}(\boldsymbol{x})^*\,e^{i\omega t} \;. \tag{3.2.4}$$

In fact,

$$\boldsymbol{u}(\boldsymbol{x}) \;=\; \boldsymbol{\epsilon}\,e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \quad \text{with polarization} \quad \boldsymbol{\epsilon} \perp \boldsymbol{k} \quad \text{and} \quad |\boldsymbol{k}| \;=\; \frac{\omega}{c} \;. \tag{3.2.5}$$

This gives a wave solution with behaviour $e^{\pm i(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)}$. General solution is a linear combination of normal modes for various $\omega, \boldsymbol{\epsilon}, \boldsymbol{k}$ – exact for EM field.

- Quantization of normal modes as independent oscillators. For each normal mode have $a(\omega)$ and $a(\omega)^\dagger$ (ω and other labels as necessary). Then

$$\text{Ground state} \quad |0\rangle \quad \text{with} \quad a(\omega)|0\rangle \;=\; 0 \quad \forall \;\text{modes}\,.$$

$$a^\dagger(\omega)|0\rangle \qquad \begin{cases} \text{state carrying energy but also mo-} \\ \text{mentum } \hbar k - \text{like a particle.} \end{cases}$$

$$\left.\begin{array}{ll} a & \text{destroy} \\ a^\dagger & \text{create} \end{array}\right\} \;\text{particles}\; \begin{cases} \textbf{phonons} \text{ in a crystal} \\ \textbf{photons} \text{ in EM field}\,. \end{cases} \qquad (3.2.6)$$

Phonon modes with long wavelength are sound waves (see AQM course in Lent). Macroscopic consequences: heat capacity of crystals, blackbody radiation.

- In summary, the EM field, a relativistically invariant theory, can be understood exactly as a collection of oscillators with quantization producing photons.

  The modern view of **all** elementary particles is that they arise by quantizing some field (though not classically observable like the EM field) but also with interactions between the modes causing energy transfer between them. This give rise to particle decay etc. This is the way to build special relativity into QM and allows particles to be created and destroyed by the action of appropriate combinations of a and $a^\dagger$ on the initial state. This give Quantum Field Theory and the Standard Model of quarks, leptons, gluons, photons, $W^\pm$, Z, ...

4   Pictures and Operators

4.1   Unitary operators

Physical predictions in QM are given by probability amplitudes, eigenvalues, expectation values, etc., and hence by expressions of the form $\langle\phi|\psi\rangle$, $\langle\phi|A|\psi\rangle$, etc.

An operator U is called **unitary** if

$$UU^\dagger \;=\; U^\dagger U \;=\; 1 \quad \text{or} \quad U^\dagger \;=\; U^{-1}\,. \qquad (4.1.1)$$

Given such an operator we can define a map on states

$$\begin{aligned} |\psi\rangle &\;\mapsto\; |\psi'\rangle \;=\; U|\psi\rangle \\ \langle\psi| &\;\mapsto\; \langle\psi'| \;=\; \langle\psi|U^\dagger\,, \end{aligned} \qquad (4.1.2)$$

and on operators

$$A \;\mapsto\; A' \;=\; UAU^\dagger\,, \qquad (4.1.3)$$

under which all physical properties are unchanged:

$$\begin{aligned} \langle\phi|\psi\rangle &\;\mapsto\; \langle\phi'|\psi'\rangle \;=\; \langle\phi|U^\dagger U|\psi\rangle \;=\; \langle\phi|\psi\rangle\,, \\ \langle\phi|A|\psi\rangle &\;\mapsto\; \langle\phi'|A'|\psi'\rangle \;=\; \langle\phi|U^\dagger UAU^\dagger U|\psi\rangle \;=\; \langle\phi|A|\psi\rangle\,. \end{aligned} \qquad (4.1.4)$$

Furthermore

$$
\begin{aligned}
C &= AB &\mapsto\quad C' &= A'B' \\
C &= [A, B] &\mapsto\quad C' &= [A', B'] \quad\text{for any operators.}
\end{aligned}
$$

$$
\begin{aligned}
Q \text{ hermitian} &\Rightarrow\quad Q' = UQU^\dagger \quad\text{also hermitian}, \\
Q|\psi\rangle = \lambda|\psi\rangle &\Rightarrow\quad Q'|\psi'\rangle = \lambda|\psi'\rangle \quad\text{same eigenvalue}.
\end{aligned} \tag{4.1.5}
$$

General results for unitary operators (compare with those for hermitian operators)

(i) Eigenvalues are complex numbers of unit modulus.
(ii) Eigenstates corresponding to distinct eigenvalues are orthogonal.
(iii) Any state can be expanded as a linear combination of eigenstates.

Summary: given U there is a basis $\{|n\rangle\}$ of orthonormal eigenstates for which

$$
U|n\rangle = e^{i\theta_n}|n\rangle, \qquad \langle n|m\rangle = \delta_{nm}. \tag{4.1.6}
$$

We prove (i) and (ii) and assume (iii).

(i)

$$
\begin{aligned}
&& U|\psi\rangle &= \lambda|\psi\rangle \\
\Rightarrow && \langle\psi|U^\dagger &= \lambda^*\langle\psi| \\
\Rightarrow && \langle\psi|U^\dagger U|\psi\rangle &= \||\psi\rangle\|^2 = |\lambda|^2\||\psi\rangle\|^2, \\
\text{and hence} && |\lambda| &= 1 \qquad (|\psi\rangle \neq 0).
\end{aligned} \tag{4.1.7}
$$

(ii)

$$
\begin{aligned}
&& U|n\rangle &= \lambda_n|n\rangle \\
\text{and} && U|m\rangle &= \lambda_m|m\rangle \\
\text{or} && \langle m|U^\dagger &= \lambda_m^*\langle m| = \lambda_m^{-1}\langle m| \\
\Rightarrow && \langle m|U^\dagger U|n\rangle &= \langle m|n\rangle = \lambda_n\lambda_m^{-1}\langle m|n\rangle.
\end{aligned} \tag{4.1.8}
$$

So $\lambda_n \neq \lambda_m \Rightarrow \langle m|n\rangle = 0$.

4.2   Schrödinger and Heisenberg Pictures

The solution of the Schrödinger equation

$$
i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle \tag{4.2.1}
$$

can be written

$$
|\psi(t)\rangle = U(t)|\psi(0)\rangle, \tag{4.2.2}
$$

where the **time evolution operator** is

$$
U(t) = \exp\left(\frac{-itH}{\hbar}\right) = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{-it}{\hbar}\right)^n H^n. \tag{4.2.3}
$$

This works because

$$i\hbar \frac{\partial}{\partial t} U(t) \;=\; H U(t) \,, \tag{4.2.4}$$

which is shown by differentiating the power series term by term (we assume H is independent of t). Note that

$$U(t)^\dagger \;=\; U(-t) \;=\; U(t)^{-1} \qquad \text{unitary } (H \;=\; H^\dagger)$$
$$\text{and} \qquad U(t_1)U(t_2) \;=\; U(t_1 + t_2) \,. \tag{4.2.5}$$

Thus far we have worked in the **Schrödinger picture** where states depend on time and operators do not. We can use $U(t)$ to pass to the **Heisenberg picture** where the time dependence is shifted from states to operators as follows (subscript denotes the picture)

	Schrödinger	Heisenberg

states $\qquad |\psi(t)\rangle_S \qquad\qquad |\psi\rangle_H \;=\; e^{itH/\hbar}|\psi(t)\rangle_S \qquad =\; |\psi(0)\rangle_S$

operators $\qquad A_S \qquad\qquad A_H(t) \;=\; e^{itH/\hbar} A_S\, e^{-itH/\hbar}, \qquad A_H(0) = A_S$
$$\tag{4.2.6}$$

Because the transformation is unitary,

$$_S\langle \phi(t)|A_S|\psi(t)\rangle_S \;=\; {}_H\langle \phi|A_H(t)|\psi\rangle_H \,, \tag{4.2.7}$$

all physical predictions are the same in either picture. Note that $H_H = H_S = H$.

The Heisenberg picture makes QM look a little more like classical mechanics where position, momentum etc. are the variables that evolve in time. To specify the dynamics in the H-picture we now need an equation to tell us how operators evolve in time. In the S-picture the Schrödinger equation tells us how states evolve. Now

$$\begin{aligned}
\frac{d}{dt} A_H(t) \;&=\; \frac{d}{dt}\left(e^{itH/\hbar} A_S\, e^{-itH/\hbar} \right) \\
&=\; \frac{iH}{\hbar} e^{itH/\hbar} A_S\, e^{-itH/\hbar} \;-\; e^{itH/\hbar} A_S\, e^{-itH/\hbar} \frac{iH}{\hbar} \\
&=\; \frac{i}{\hbar}[H, A_H(t)] \,. \tag{4.2.8}
\end{aligned}$$

or

$$\boxed{i\hbar \frac{d}{dt} A_H(t) \;=\; [A_H(t), H] \qquad \textbf{Heisenberg equation of motion.}}$$

E.g., a particle in one dimension $\hat{x}(t), \hat{p}(t)$ in Heisenberg picture (drop H subscripts). We have that

$$[\hat{x}(t), \hat{p}(t)] \;=\; i\hbar. \tag{4.2.9}$$

I.e., the commutator **at equal times** is unchanged. Consider

$$
\left.
\begin{aligned}
H &= \frac{\hat{p}^2}{2m} + V(\hat{x}) \\[2mm]
\frac{d}{dt}\hat{x}(t) &= \frac{1}{i\hbar}[\hat{x}(t), H] \quad = \quad \frac{1}{m}\hat{p}(t)\,, \\[2mm]
\frac{d}{dt}\hat{p}(t) &= \frac{1}{i\hbar}[\hat{p}(t), H] \quad = \quad -V'(\hat{x}(t))\,.
\end{aligned}
\right\} \quad \text{Heisenberg equations of motion}
$$

$$(4.2.10)$$

Taking expectation values in any state $|\psi\rangle$ (now independent of time in the Heisenberg picture) gives

$$
\left.
\begin{aligned}
\frac{d}{dt}\langle \hat{x}\rangle &= \frac{1}{m}\langle \hat{p}\rangle\,, \\[2mm]
\frac{d}{dt}\langle \hat{p}\rangle &= -\langle V'(\hat{x})\rangle\,.
\end{aligned}
\right\} \quad \text{Ehrenfest's Theorem, true in \textbf{all} pictures} \quad (4.2.11)
$$

Note the similarity to classical equations of motion. For some potentials can solve Heisenberg's equations.

- $V = 0$, the free particle.

$$
\begin{aligned}
\frac{d}{dt}\hat{p}(t) &= 0 \quad \Rightarrow \quad \hat{p}(t) = \hat{p}(0) \quad \text{constant operator} \\[2mm]
\frac{d}{dt}\hat{x}(t) &= \frac{1}{m}\hat{p}(0) \quad \Rightarrow \quad \hat{x}(t) = \hat{x}(0) + \frac{\hat{p}(0)}{m}t\,.
\end{aligned}
$$

$$(4.2.12)$$

A solution just like in classical dynamics but with appearance of constant operators.

- $V(x) = \frac{1}{2}m\omega^2 x^2$, the oscillator.

$$
\left.
\begin{aligned}
\frac{d}{dt}\hat{x}(t) &= \frac{1}{m}\hat{p}(t) \\[2mm]
\frac{d}{dt}\hat{p}(t) &= -m\omega^2 \hat{x}(t)
\end{aligned}
\right\}
\Rightarrow
\begin{aligned}
\frac{d^2}{dt^2}\hat{x} + \omega^2 \hat{x} &= 0 \\[2mm]
\frac{d^2}{dt^2}\hat{p} + \omega^2 \hat{p} &= 0\,.
\end{aligned}
$$

$$(4.2.13)$$

The solution is

$$
\hat{x}(t) = \hat{x}(0)\cos\omega t + \frac{\hat{p}(0)}{m\omega}\sin\omega t
$$

$$
\hat{p}(t) = \hat{p}(0)\cos\omega t - m\omega\,\hat{x}(0)\sin\omega t\,. \qquad (4.2.14)
$$

Can check that the equal-time commutation relation $[\hat{x}(t), \hat{p}(t)] = i\hbar$ holds $\forall\, t$.

Alternatively, can write these as

$$
\hat{x}(t) = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a\,e^{-i\omega t} + a^\dagger\,e^{i\omega t})
$$

$$
\hat{p}(t) = \left(\frac{\hbar m\omega}{2}\right)^{1/2}\frac{1}{i}(a\,e^{-i\omega t} - a^\dagger\,e^{i\omega t})\,, \qquad (4.2.15)
$$

with $a, a^\dagger$ defined from the Schrödinger picture operators $\hat{x}(0), \hat{p}(0)$.

4.3   Canonical Quantization

★ **START OF NON-EXAMINABLE MATERIAL**

The final step in Dirac's systematic approach to QM: have seen how to incorporate position and momentum wavefunctions and S and H pictures in a single logical framework. But how do we pass from general classical system to its quantum version? In particular, what are the fundamental quantum commutation relations between observables ; why $[\hat{x}, \hat{p}] = i\hbar$?

Any classical system can be described by a set of generalized positions $x_i(t)$ and momenta $p_i(t)$ with $1 \leqslant i \leqslant N$ (may include angles, angular momentum etc.) and a Hamiltonian $H(x_i, p_i)$.

In classical dynamics a fundamental idea is that of the Poisson bracket of any two functions $f(x_i, p_i)$ and $g(x_i, p_i)$, say, which is defined to be

$$\{f, g\} \;=\; \sum_i \left(\frac{\partial f}{\partial x_i} \frac{\partial g}{\partial p_i} - \frac{\partial g}{\partial x_i} \frac{\partial f}{\partial p_i} \right) \;, \tag{4.3.1}$$

which is a new function of x_i and p_i. ((x_i, p_i) are coordinates on phase space and PB is a **symplectic structure**.) In particular,

$$\{x_i, p_j\} \;=\; \delta_{ij} \;. \tag{4.3.2}$$

Properties of the PB include antisymmetry, bilinearity and Jacobi identity. In this formulation classical dynamics is given by Hamilton's equation

$$\frac{df}{dt} \;=\; \{f, H\} \;. \tag{4.3.3}$$

Check this for various choices for H and see that you derive Newton's third law in a first order formalism (i.e. first-order in time derivative).

In **canonical quantization** define quantum theory by

- $$\begin{matrix} \text{classical} \\ \text{functions} \end{matrix} \;\; f, g \;\; \longrightarrow \;\; \begin{matrix} \text{quantum} \\ \text{operators} \end{matrix} \;\; \hat{f}, \hat{g} \tag{4.3.4}$$

- Poisson brackets become commutators

  $$[\hat{f}, \hat{g}] \;=\; i\hbar \widehat{\{f, g\}} \;. \tag{4.3.5}$$

  In particular, get

  $$[\hat{x}_i, \hat{p}_j] \;=\; i\hbar \delta_{ij} \tag{4.3.6}$$

 which are the canonical commutation relations.

- Moreover, Hamilton's equations then become Heisenberg's equations

  $$i\hbar \frac{d}{dt} \hat{f} \;=\; [\hat{f}, \hat{H}] \;. \tag{4.3.7}$$

For those taking IIC Classical Dynamics this relationship between classical and quantum mechanics should be mentioned near the end of the course.

All this provides a sound basis for understanding classical mechanics as a limit of quantum mechanics with $\hbar \to 0$. Going the other way, turning $\hbar$ "on" is more problematic and not guaranteed to be either unique or, in some cases, even consistent. For example, if we carry out the procedure above it is correct to $O(\hbar)$ but there may be $O(\hbar^2)$ ambiguities related to how operators are ordered in defining functions like $f(x_i, p_j)$: does x_i multiply p_i on left or right?

Alternative approach to quantization is to use path integrals which are sums of contributions from all possible trajectories or paths between initial and final configurations in phase space.
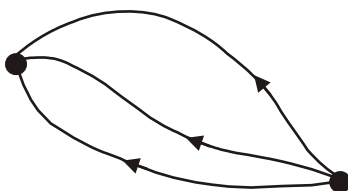
One of these is the classical trajectory, but the quantum amplitude involves contributions from all. This approach has its advantages but, in principle, is equivalent to canonical quantization. In general need both, especially for complicated systems where there are constraints amongst the variables.

⋆ **END OF NON-EXAMINABLE MATERIAL**

5   Composite Systems and Identical Particles

5.1   Tensor products

This is a general way of constructing quantum systems from simpler subsystems. Suppose
$$|\psi\rangle \in V_1 , \quad |\phi\rangle \in V_2 , \tag{5.1.1}$$
i.e., states in the spaces for two systems. The tensor product space
$$V = V_1 \otimes V_2 \tag{5.1.2}$$
consists of all linear combinations of tensor product states $|\psi\rangle \otimes |\phi\rangle$ (duals $\langle\psi| \otimes \langle\phi|$) subject to

$$\left(|\psi\rangle + |\psi'\rangle\right) \otimes |\phi\rangle = |\psi\rangle \otimes |\phi\rangle + |\psi'\rangle \otimes |\phi\rangle$$

$$|\psi\rangle \otimes \left(|\phi\rangle + |\phi'\rangle\right) = |\psi\rangle \otimes |\phi\rangle + |\psi\rangle \otimes |\phi'\rangle$$

$$\left(\alpha|\psi\rangle\right) \otimes |\phi\rangle = \alpha|\psi\rangle \otimes \left(|\phi\rangle\right) = \alpha\left(|\psi\rangle \otimes |\phi\rangle\right) , \tag{5.1.3}$$

and similarly for duals. The inner product is

$$\Big(\langle\psi'|\otimes\langle\phi'|\Big)\Big(|\psi\rangle\otimes|\phi\rangle\Big) \;=\; \langle\psi'|\psi\rangle\,\langle\phi'|\phi\rangle\,, \tag{5.1.4}$$

and extend to all of V by linearity.

If we have bases $\{|n\rangle\}$ for V_1 and $\{|m\rangle\}$ for V_2, then $\{|n\rangle\}\otimes\{|m\rangle\}$ is a basis for V. If the bases are finite, then

$$\dim V \;=\; \dim V_1 \times \dim V_2\,. \tag{5.1.5}$$

Given operators A and B on V_1 and V_2, respectively, define an operator $A\otimes B$ on V by

$$\Big(A\otimes B\Big)\Big(|\psi\rangle\otimes|\phi\rangle\Big) \;=\; \Big(A|\psi\rangle\Big)\otimes\Big(B|\phi\rangle\Big)$$

and extend by linearity. In particular,

$$\begin{aligned}
A &\longleftrightarrow A\otimes\mathbb{I} && \text{acting just on }\ V_1\\
B &\longleftrightarrow \mathbb{I}\otimes B && \text{acting just on }\ V_2\,.
\end{aligned} \tag{5.1.6}$$

Operators of this form commute for any A & B.

Common abuses of notation:

(i) $|\psi\rangle\otimes|\phi\rangle$ written as $|\psi\rangle|\phi\rangle$.
(ii) Leave out $\otimes\mathbb{I}$ or $\mathbb{I}\otimes$ for operators acting on just one subsystem.

Consider a particle in two dimensions with position operators $\hat{x}_1, \hat{x}_2$. Basis of joint eigenstates can be constructed as

$$\begin{aligned}
|x_1, x_2\rangle &= |x_1\rangle\otimes|x_2\rangle\\
\hat{x}_1 &\leftrightarrow \hat{x}_1\otimes\mathbb{I}\\
\hat{x}_2 &\leftrightarrow \mathbb{I}\otimes\hat{x}_2\,.
\end{aligned} \tag{5.1.7}$$

This is the $V = V_1\otimes V_2$ tensor product of states for two one-dimensional particles. The wavefunction for $|\psi\rangle\otimes|\phi\rangle$ is

$$\begin{aligned}
\Big(\langle x_1|\otimes\langle x_2|\Big)\Big(|\psi\rangle\otimes|\phi\rangle\Big) &= \langle x_1|\psi\rangle\langle x_2|\phi\rangle\\
&= \psi(x_1)\phi(x_2)\,.
\end{aligned} \tag{5.1.8}$$

tensor product states	$\longleftrightarrow$	**separable** wavefunctions: product of 1D wavefunctions	
tensor product space	$\longleftrightarrow$	all linear combinations of such wavefunctions	(5.1.9)

Example: two-dimensional oscillator.

$$\begin{aligned}
H &= \frac{1}{2m}(\hat{p}_1^2 + \hat{p}_2^2) + \frac{1}{2}m\omega^2(\hat{x}_1^2 + \hat{x}_2^2)\\
&= H_1 + H_2\,,
\end{aligned} \tag{5.1.10}$$

with

$$H_i \;=\; \frac{1}{2m}\hat{p}_i^2 + \frac{1}{2}m\omega^2\hat{x}_i^2 \;=\; \hbar\omega\left(N_i + \frac{1}{2}\right),$$

$$N_i \;=\; a_i^\dagger a_i, \qquad [a_i, a_j^\dagger] \;=\; \delta_{ij}. \tag{5.1.11}$$

Simultaneous eigenstates of N_1, N_2 constructed by

$$|n_1, n_2\rangle \;=\; |n_1\rangle \otimes |n_2\rangle$$

$$\text{with} \qquad H|n_1, n_2\rangle \;=\; \Big(H_1|n_1\rangle\Big)\otimes|n_2\rangle + |n_1\rangle\otimes\Big(H_2|n_2\rangle\Big)$$

$$\;=\; E_{n_1 n_2}|n_1, n_2\rangle, \tag{5.1.12}$$

where $E_{n_1 n_2} = \hbar\omega(n_1 + n_2 + 1)$.

5.2   Spin

Experiment shows that particles generally carry an internal degree of freedom called **spin** or intrinsic angular momentum. Even if the particle appears 'elementary' or pointlike, its space of states will be of the form $V = V_{\text{space}} \otimes V_{\text{spin}}$ with basis

$$|\boldsymbol{x}, r\rangle \;=\; |\boldsymbol{x}\rangle|r\rangle, \tag{5.2.1}$$

where r takes a finite set of values: the quantum numbers associated with **spin**. The particle is not 'structureless': the position operators, $\hat{\boldsymbol{x}}$, are not a complete commuting set by themselves – there are additional observables Q acting just on V_{spin} with $[\hat{\boldsymbol{x}}_i, Q] = 0$. We will understand these operators later in the study of angular momentum but for now concentrate on the states.

Each kind of particle has a definite total spin S which is a half-integer $0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$; this is a basic characteristic like its mass or charge. For a spin S particle of non-zero mass there are $2S+1$ basis states in V_{spin} labelled by convention $r = S, S-1, \ldots, -S$. E.g.,

$$
\begin{array}{cll}
S & \text{basis states} & \\
0 & |0\rangle & \\[4pt]
\frac{1}{2} & |\tfrac{1}{2}\rangle, \; |-\tfrac{1}{2}\rangle & \text{also written} \quad \underbrace{|\uparrow\rangle}_{\text{up}}, \; \underbrace{|\downarrow\rangle}_{\text{down}} \\[8pt]
1 & |1\rangle, \; |0\rangle, \; |-1\rangle &
\end{array}
\tag{5.2.2}
$$

The existence of spin states is revealed by e.g. the Stern-Gerlach experiment
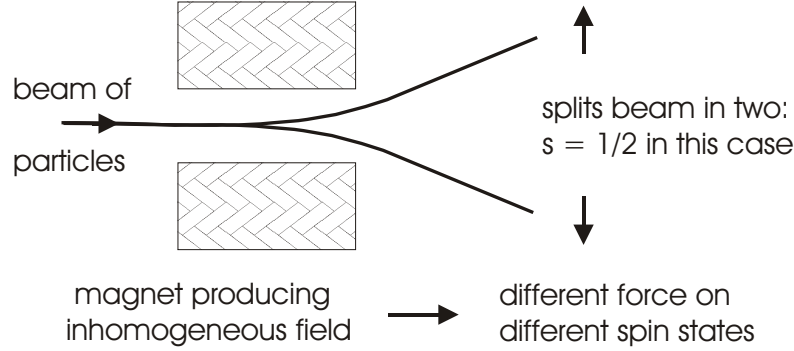
The general state $|\psi\rangle$ in V has a $(2S + 1)$-component wavefunction

$$\psi(\boldsymbol{x}, r) = \langle \boldsymbol{x}, r | \psi \rangle. \tag{5.2.3}$$

It is also useful to write the state in mixed, or hybrid, notation as

$$\sum_r \psi(\boldsymbol{x}, r)|r\rangle. \tag{5.2.4}$$

5.3 Multiparticle states: bosons and fermions

Consider particles labelled by $a = 1, 2, \ldots, N$. Let V_a be the space of states for each particle with basis $\{|\boldsymbol{x}_a, r_a\rangle\}$ - position and spin labels. The general multiparticle states belong to

$$V_1 \otimes V_2 \otimes \ldots \otimes V_N, \tag{5.3.1}$$

with basis states

$$|\boldsymbol{x}_1, r_1; \boldsymbol{x}_2, r_2; \ldots; \boldsymbol{x}_N, r_N\rangle = |\boldsymbol{x}_1, r_1\rangle \otimes |\boldsymbol{x}_2, r_2\rangle \otimes \ldots \otimes |\boldsymbol{x}_N, r_N\rangle$$

constructed from single particle states. If the particles are **identical**, $V_a \cong V$, something interesting can be added.

Consider the simplest case $N = 2$. Define an operator W which exchanges particles by its action on basis states:

$$W|\boldsymbol{x}_1, r_1; \boldsymbol{x}_2, r_2\rangle = |\boldsymbol{x}_2, r_2; \boldsymbol{x}_1, r_1\rangle. \tag{5.3.2}$$

When the two particles are **identical** its action on a general 2-particle state is

$$W|\Psi\rangle = \eta|\Psi\rangle, \tag{5.3.3}$$

because $|\Psi\rangle$ and $W|\Psi\rangle$ must be physically equivalent if the particles are **indistinguishable**. But, given its action on the basis states

$$W^2 = 1 \quad \Rightarrow \quad \eta^2 = 1 \text{ or } \eta = \pm 1. \tag{5.3.4}$$

Thus, 2-particle states do not belong merely to

$$V \otimes V \qquad\qquad \text{spanned by } |\psi\rangle \otimes |\phi\rangle \,,$$

$$\text{but to} \qquad (V \otimes V)_S \qquad \begin{array}{l} \text{spanned by } |\psi\rangle \otimes |\phi\rangle + |\phi\rangle \otimes |\psi\rangle \,, \\ \eta = 1 \quad \text{symm under } W \end{array} \qquad (5.3.5)$$

$$\text{or to} \qquad (V \otimes V)_A \qquad \begin{array}{l} \text{spanned by } |\psi\rangle \otimes |\phi\rangle - |\phi\rangle \otimes |\psi\rangle \,. \\ \eta = -1 \quad \text{antisymm under } W \end{array}$$

Similarly, for multiparticle states with $N \geqslant 2$ we can define $W_{(a,b)}$ which exchanges $(\boldsymbol{x}_a, r_a) \leftrightarrow (\boldsymbol{x}_b, r_b)$ by this action on the basis states. Then for a general N-particle state

$$W_{(a,b)} |\Psi\rangle = \eta_{(a,b)} |\Psi\rangle \qquad\qquad (5.3.6)$$

with, again, $\eta_{(a,b)} = \pm 1$ because $W^2_{(a,b)} = 1$.

For any permutation π of $\{1, 2, \ldots, N\}$ define

$$\begin{aligned} W |\boldsymbol{x}_1, r_1; \boldsymbol{x}_2, r_2; \ldots; \boldsymbol{x}_N, r_N\rangle \\ = |\boldsymbol{x}_{\pi(1)}, r_{\pi(1)}; \boldsymbol{x}_{\pi(2)}, r_{\pi(2)}; \ \ldots \ ; \boldsymbol{x}_{\pi(N)}, r_{\pi(N)}\rangle \end{aligned} \qquad (5.3.7)$$

on the basis states. On a general state

$$W_\pi |\Psi\rangle = \eta_\pi |\Psi\rangle \qquad \text{for some } \eta_\pi \,. \qquad (5.3.8)$$

But algebra of swaps or transpositions implies $\eta_{(a,b)} = \pm 1$ with the same value for all pairs (a, b) since any two swaps are conjugate. This makes physical sense since the particle are identical and the initial choice for the labelling is not unique. Then, since any π can be obtained as a sequence of swaps, we have alternative outcomes

$$\eta_\pi = \begin{cases} 1 \\ \mathrm{sgn}(\pi) = (-1)^{(\# \text{ swaps needed for } \pi)} \,, \end{cases} \qquad (5.3.9)$$

with the same alternative for all π. These correspond to two inequivalent 1-D representations of the permutation group.

Hence, there are two fundamentally different kinds of particles:

- **Bosons** obeying Bose-Einstein statistics:

  (i) interchange of identical bosons leaves the state unchanged: $\eta = 1$;
  (ii) multiparticle states in $(V \otimes V \otimes \ldots \otimes V)_S$.

- **Fermions** obeying Fermi-Dirac statistics:

  (i) interchange of identical fermions changes the state by a sign: $\eta = -1$;
  (ii) multiparticle states in $(V \otimes V \otimes \ldots \otimes V)_A$.

Note that this applies only to identical particles. Indistinguishability has a different character in QM from classical physics. It is the consequence of saying that you cannot attach a label to a given particle and uniquely identify it from any other. You can no longer follow individual particles because of the uncertainly principle.

In addition have the remarkable   ★ **Spin-statistics relation**. ★

5.4   Spin and statistics

> Integral spin particles ($S = 0, 1, 2, \ldots$) are **bosons**.
>
> $\frac{1}{2}$-integral spin particles ($S = \frac{1}{2}, \frac{3}{2}, \ldots$) are **fermions**.

This is confirmed by experiment and can be **derived** in relativistic QM or QFT (quantum field theory) so becomes the spin-statistics theorem; no derivation is know within **non**-relativistic QM. The derivation relies, in particular, on Lorentz symmetry (symmetry under Lorentz transformations and rotations) and causality (no (space-time) event can influence a future event if they are separated by a space-like space-time interval; no light signal can connect them).

- Most common elementary particles are fermions: electrons, protons, neutrons, neutrinos, quarks, muons, τ – all spin $\frac{1}{2}$.

- Particles associated with forces are bosons: photons (EM), $W^{\pm}, Z$ (weak nuclear), gluons (strong nuclear) – all spin 1.

- Other particles such as mesons are bosons e.g., π, K are spin 0, the ρ is spin 1, and many more have been observed with higher spin.

- The recently discovered Higgs boson (LHC experiments) has almost certainly spin 0 although this is still to be confirmed.

- The graviton has spin 2 but is yet to be observed - not likely in the near future (if ever).

- The spin-statistics theorem applies even if the particles are not 'elementary'. Indeed, nucleons (proton etc) and mesons are made of quarks. Atoms obey the theorem, too.

5.5   Two-particle examples

Now know that the states of two identical particles belong to

$$(V \otimes V)_S \quad \text{or} \quad (V \otimes V)_A \quad \text{where} \quad V = V_{\text{space}} \otimes V_{\text{spin}} . \tag{5.5.1}$$

It is convenient to construct these spaces by first taking

$$(V_{\text{space}} \otimes V_{\text{space}})_{S,A} \quad \text{and} \quad (V_{\text{spin}} \otimes V_{\text{spin}})_{S,A} \tag{5.5.2}$$

separately, and then combining to get the correct overall symmetry.

Consider the single particle Hamiltonian $H(\hat{\boldsymbol{x}}, \hat{\boldsymbol{p}})$ independent of spin with non-degenerate energies $E_0 < E_1 < E_2 < \ldots$, and wavefunctions $\psi_0(\boldsymbol{x}), \psi_1(\boldsymbol{x}), \psi_2(\boldsymbol{x}), \ldots$ for states in V_{space}. For two such non-interacting particles the Hamiltonian is

$$H(\hat{\boldsymbol{x}}_1, \hat{\boldsymbol{p}}_1) + H(\hat{\boldsymbol{x}}_2, \hat{\boldsymbol{p}}_2) , \tag{5.5.3}$$

with the wavefunctions for the basis of energy eigenfunctions for $V_{\text{space}} \otimes V_{\text{space}}$

$$\psi_i(\boldsymbol{x}_1)\psi_j(\boldsymbol{x}_2) \qquad E = E_i + E_j . \tag{5.5.4}$$

- Ground state, $E = 2E_0$:

$$\Psi_0^S(\boldsymbol{x}_1, \boldsymbol{x}_2) = \psi_0(\boldsymbol{x}_1)\psi_0(\boldsymbol{x}_2) , \qquad (5.5.5)$$

which is automatically (S)ymmetric.

- 1st excited states, $E = E_0 + E_1$:

$$\psi_0(\boldsymbol{x}_1)\psi_1(\boldsymbol{x}_2) , \quad \psi_1(\boldsymbol{x}_1)\psi_0(\boldsymbol{x}_2) . \qquad (5.5.6)$$

These have no definite symmetry but the following linear combinations do:

$$\Psi_1^S(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{\sqrt{2}}\left(\psi_0(\boldsymbol{x}_1)\psi_1(\boldsymbol{x}_2) + \psi_1(\boldsymbol{x}_1)\psi_0(\boldsymbol{x}_2)\right) , \qquad (5.5.7)$$

$$\Psi_1^A(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{\sqrt{2}}\left(\psi_0(\boldsymbol{x}_1)\psi_1(\boldsymbol{x}_2) - \psi_1(\boldsymbol{x}_1)\psi_0(\boldsymbol{x}_2)\right) , \qquad (5.5.8)$$

which are (S)ymmetric and (A)ntisymmetric, respectively. They are the S and A 1-D representations of the two-particle permutation group S_2.

Spin 0: V_{spin} is just one state so can ignore. Spin-statistics $\Rightarrow$ the particles are **bosons**, and states are in $(V \otimes V)_S$ which in this case is $(V_{\text{space}} \otimes V_{\text{space}})_S$. The allowed states are then

$$\left.\begin{array}{lll}
\text{Ground state} & \Psi_0^S(\boldsymbol{x}_1, \boldsymbol{x}_2) & 2E_0 \\
\text{1st excited state} & \Psi_1^S(\boldsymbol{x}_1, \boldsymbol{x}_2) & E_0 + E_1
\end{array}\right\} \begin{array}{l} \text{both non-} \\ \text{degenerate} \end{array} \qquad (5.5.9)$$

Note that only **one** of the two possible 1st excited states is allowed.

Spin $\frac{1}{2}$: V_{spin} has basis $\{| \uparrow\rangle, | \downarrow\rangle\}$ for each particle. $V_{\text{spin}} \otimes V_{\text{spin}}$ therefore has the basis

$$\{| \uparrow\rangle| \uparrow\rangle, \ | \uparrow\rangle| \downarrow\rangle, \ | \downarrow\rangle| \uparrow\rangle, \ | \downarrow\rangle| \downarrow\rangle\} , \qquad (5.5.10)$$

or normalized combinations with definite symmetry are

$$| \uparrow\rangle| \uparrow\rangle$$

$$\tfrac{1}{\sqrt{2}}\left(| \uparrow\rangle| \downarrow\rangle + | \downarrow\rangle| \uparrow\rangle\right) \qquad\qquad \tfrac{1}{\sqrt{2}}\left(| \uparrow\rangle| \downarrow\rangle - | \downarrow\rangle| \uparrow\rangle\right)$$

$$| \downarrow\rangle| \downarrow\rangle$$

$$\qquad (5.5.11)$$

$$(V_{\text{spin}} \otimes V_{\text{spin}})_S \qquad\qquad (V_{\text{spin}} \otimes V_{\text{spin}})_A$$

We would expect these two kinds of states, S and A, to be associated with a definite spin quantum number. We can see what this is simply by counting since the degeneracy for spin S is $2S + 1$. We see that the S-states have $S = 1$ and the A-state has $S = 0$. Note how state multiplets with a definite spin also have a definite symmetry. This is no accident.

Spin-statistics $\Rightarrow$ the particles are **fermions**, and the states belong to

$$\begin{aligned}
(V \otimes V)_A &= (V_{\text{space}} \otimes V_{\text{space}})_A \otimes (V_{\text{spin}} \otimes V_{\text{spin}})_S \\
&+ (V_{\text{space}} \otimes V_{\text{space}})_S \otimes (V_{\text{spin}} \otimes V_{\text{spin}})_A
\end{aligned} \qquad (5.5.12)$$

The allowed states are (in hybrid notation, see Eq. (5.2.4))

* Ground state, $E = 2E_0$:

$$\Psi_0^S(\boldsymbol{x}_1, \boldsymbol{x}_2)\frac{1}{\sqrt{2}}\Big(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\Big) \qquad (5.5.13)$$

and there is just one state. (Note that, in general, the ground state of a system is usually non-degenerate.)

* 1st excited states, $E = E_0 + E_1$:

$$\Psi_1^S(\boldsymbol{x}_1, \boldsymbol{x}_2)\frac{1}{\sqrt{2}}\Big(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\Big) \qquad (5.5.14)$$

$$\Psi_1^A(\boldsymbol{x}_1, \boldsymbol{x}_2)\begin{pmatrix} |\uparrow\rangle|\uparrow\rangle \\ \frac{1}{\sqrt{2}}\Big(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle\Big) \\ |\downarrow\rangle|\downarrow\rangle \end{pmatrix} \qquad (5.5.15)$$

There are four states in all made up of $1 + 3 = 4$. The spin quantum numbers associated with these are $S = 0$ and $S = 1$, respectively.

We can see that representations of the two-particle permutation group, S_2, are used extensively in the analysis. The general analysis for N identical particles is based on the representation theory of S_N, the permutation group for N particles.

5.6   Pauli Exclusion Principle and Atomic Structure

A state of N identical fermions can be specified by taking N **distinct** one-particle states (each in V) and antisymmetrizing to ensure Fermi statistics; this produces a state in $(V \otimes \ldots \otimes V)_A$. The condition that the one-particle states must all be different, else the result is zero, is the **Paul Exclusion Principle**. The complete set of such N-particle antisymmetric states from $(V \otimes \ldots \otimes V)_A$ forms a basis for the most general state of N fermions.

The original application was to atomic structure. Consider N electrons bound to a nucleus with Z protons. Ignoring electron-electron interactions, the Hamiltonian is

$$H(\hat{\boldsymbol{x}}_1, \hat{\boldsymbol{p}}_1) + \;\ldots\; + H(\hat{\boldsymbol{x}}_N, \hat{\boldsymbol{p}}_N) , \qquad (5.6.1)$$

where a single electron Hamiltonian is

$$H(\hat{\boldsymbol{x}}, \hat{\boldsymbol{p}}) \;=\; \frac{1}{2m}\hat{\boldsymbol{p}}^2 - \frac{Ze^2}{4\pi\epsilon_0|\hat{\boldsymbol{x}}|} \;. \qquad (5.6.2)$$

Single electron states in V_{space} are similar to hydrogen atom states (for which $Z = 1$)

$$|n, l, m\rangle \quad \text{which are joint eigenstates of} \begin{cases} & \text{evals} \\ H & E_n \\ \boldsymbol{L}^2 & \hbar^2 l(l+1) \\ L_3 & \hbar m \end{cases} \qquad (5.6.3)$$

where

$$E_n = -\frac{m}{2}\left(\frac{Ze^2}{4\pi\epsilon_0\hbar}\right)^2\frac{1}{n^2} = -\alpha^2\frac{Z^2}{2n^2}mc^2 \ ,$$

$$n = 1, 2, \ldots \quad \text{principal quantum number} \ ,$$

$$l = 0, 1, \ldots, n-1 \quad m = \underbrace{0, \pm 1, \pm 2, \ldots, \pm l}_{2l+1 \text{ states}} \ , \quad (5.6.4)$$

where $\alpha = e^2/(4\pi\epsilon_0\hbar c) \approx 1/137$ is the fine-structure constant. So degeneracy (excluding spin!) is

$$1 + 3 + \ldots + (2n-1) = n^2 \quad \text{for level } E_n. \quad (5.6.5)$$

Now, including V_{spin} basis $\{|\uparrow\rangle, |\downarrow\rangle\}$, each electron has $2n^2$ states at energy E_n. Structure of electrically neutral atoms with $N = Z$:

- Fill up energy levels, starting with the lowest, using Pauli Principle.
- This gives a rough picture of the periodic table with some qualitative insights into chemical properties.
- The states that belong to a **given** energy E_n is called a shell. Atoms with completely filled shells are unreactive/stable elements chemically. E.g.

$$E_1 \text{ filled for } Z = 2 \ \rightarrow \ \text{He}$$

$$E_1 \ \& \ E_2 \text{ filled for } Z = 10 \ \rightarrow \ \text{Ne} \quad (5.6.6)$$

- Chemical reactivity is controlled by the **valency** which is given by the number of electrons in an almost empty outer shell (Ca^{2+}) or the number of unoccupied states in a nearly filled outer shell (F^-).
- In real life there are many interactions which perturb the energies of the individual levels and spread the energies within a shell even to the extent that shells can overlap.
- Each electron has a **magnetic moment** because it is a spinning charge – it acts like a bar magnet (indeed an iron magnet is simply the sum of all these small electron magnets). Should include electron-electron interactions, the interactions of the electron magnetic moments with each other and also with magnetic fields due to the orbiting electric charge (see later section 7).

atomic	n	1	2		3			4			
no.	element	s	s	p	s	p	d	s	p	d	f
1	H	1									
2	He	2									
6	C	2	2	2							
9	F	2	2	5							
10	Ne	2	2	6							
11	Na	2	2	6	1						
19	K	2	2	6	2	6		1			
20	Ca	2	2	6	2	6		2			
26	Fe	2	2	6	2	6	6	2			
28	Ni	2	2	6	2	6	8	2			
29	Cu	2	2	6	2	6	10	2			

Table shows some electron configurations. s,p,d,f $\rightarrow$ l = $0, 1, 2, 3$. Above atomic number 18 the states are not always filled in naive order because of interactions between electrons. Can use Aufbau or Madelung rule to get better sequencing. For these see (http://en.wikipedia.org/wiki/Electron_configuration.)

The eigenstate of the fully interaction N-electron Hamiltonian must be expressed as a linear combination of the basis states in $\{V \otimes \dots \otimes V)_A$ constructed here. The most general problem is still a subject of active research.

In the next section we discuss perturbation theory and how we may systematically calculate the effect of adding new interactions to a solved system if they are sufficiently weak.

6   Perturbation Theory

Few quantum mechanical systems can be solved exactly. In perturbation theory we start from a known, soluble, system

$$H|n\rangle \;=\; E_n|n\rangle \,, \tag{6.1}$$

with $\{|n\rangle\}$ an orthonormal basis of energy eigenstates, and calculate the energies and eigenstates for a new **perturbed** Hamiltonian

$$(H + \mu V)|\psi\rangle \;=\; E|\psi\rangle \,, \tag{6.2}$$

order-by-order in parameter μ which is supposed, in some sense, to be small. V is some hermitian operator and we assume that E and $|\psi\rangle$ depend smoothly on μ. The discussion here is for perturbations to H but the technique applies to any observable. [Note that methods of perturbation theory are not just applicable in QM but to the solution of perturbed PDEs in general.]

6.1   The non-degenerate case

Suppose that as $\mu \rightarrow 0$

$$\begin{array}{rcl} |\psi\rangle & \rightarrow & |r\rangle \\ E & \rightarrow & E_r \end{array} \quad \left\{ \begin{array}{l} \text{unique eigenstate with this en-} \\ \text{ergy, i.e., level is non-degenerate.} \end{array} \right. \tag{6.1.1}$$

States $\{|n\rangle\}$ are still a basis when $\mu \neq 0$, and so we can always write

$$\begin{aligned} |\psi\rangle &= \alpha|r\rangle + \sum_{j \neq r} \beta_j|j\rangle \\ &= \alpha(|r\rangle + \sum_{j \neq r} \gamma_j|j\rangle) \,, \end{aligned} \tag{6.1.2}$$

where $\alpha, \beta_j, \gamma_j = \beta_j/\alpha_j$ are power series in μ such that

$$\alpha \rightarrow 1, \quad \beta_j, \gamma_j \rightarrow 0 \;\; \text{as} \;\; \mu \rightarrow 0 \,. \tag{6.1.3}$$

Aim is to calculate the coefficients in these expansions

$$
\begin{array}{rcl}
E & = & E_r \;+\; E_r^{(1)}\mu \;+\; E_r^{(2)}\mu^2 \;+\; \ldots \\
\alpha & = & 1 \;+\; a_1\mu \;+\; a_2\mu^2 \;+\; \ldots \\
\gamma_j & = & \qquad c_{j1}\mu \;+\; c_{j2}\mu^2 \;+\; \ldots
\end{array}
\tag{6.1.4}
$$

First just substitute the expression for $|\psi\rangle$ into Eq. (6.2):

$$
(E_r + \mu V)|r\rangle + \sum_{j\neq r} \gamma_j (E_j + \mu V)|j\rangle \;=\; E\Big(|r\rangle + \sum_{j\neq r} \gamma_j |j\rangle\Big) ,
\tag{6.1.5}
$$

cancelling overall factor of α. Rewrite as

$$
(E - E_r)|r\rangle + \sum_{j\neq r} \gamma_j (E - E_j)|j\rangle \;=\; \mu V|r\rangle + \mu \sum_{j\neq r} \gamma_j V|j\rangle . \qquad (**)
\tag{6.1.6}
$$

Then taking inner product of $\langle r|$ with $(**)$ gives

$$
E - E_r \;=\; \mu\langle r|V|r\rangle \;+\; \mu \sum_{j\neq r} \gamma_j \langle r|V|j\rangle ,
\tag{6.1.7}
$$

and, so far, this is still exact (all orders in μ). Substituting in the series expansions from Eq. (6.1.4) and keeping terms to $O(\mu^2)$ gives

$$
\mu E_r^{(1)} + \mu^2 E_r^{(2)} + \ldots \;=\; \mu\langle r|V|r\rangle + \mu^2 \sum_{j\neq r} c_{j1}\langle r|V|j\rangle + \ldots .
\tag{6.1.8}
$$

Thus, already know first-order energy shift

$$
E_r^{(1)} \;=\; \langle r|V|r\rangle .
\tag{6.1.9}
$$

To find second-order shift we need to know c_{j1}. The inner product of $\langle i|$ with $(**)$ $(i \neq r)$ gives

$$
\gamma_i (E - E_i) \;=\; \mu\langle i|V|r\rangle + \mu \sum_{j\neq r} \gamma_j \langle i|V|j\rangle .
\tag{6.1.10}
$$

Again this is exact but the 2nd term on RHS is $O(\mu^2)$, and so to leading order in μ

$$
\begin{array}{rcl}
\mu\, c_{i1}(E_r - E_i) & = & \mu\langle i|V|r\rangle \\
\Rightarrow \quad c_{i1} & = & \dfrac{\langle i|V|r\rangle}{E_r - E_i} \qquad \text{(note } E_i \neq E_r \text{ since states non-degenerate)}
\end{array}
\tag{6.1.11}
$$

and so substituting in Eq. (6.1.8) we find

$$
E_r^{(2)} \;=\; \sum_{j\neq r} \frac{\langle r|V|j\rangle\langle j|V|r\rangle}{E_r - E_j} \;=\; \sum_{j\neq r} \frac{|\langle j|V|r\rangle|^2}{E_r - E_j} .
\tag{6.1.12}
$$

In summary,

$$
E \;=\; E_r \;+\; \mu\langle r|V|r\rangle \;+\; \mu^2 \sum_{j\neq r} \frac{|\langle j|V|r\rangle|^2}{E_r - E_j} \;+\; \ldots ,
\tag{6.1.13}
$$

$$
|\psi\rangle \;=\; \alpha\left(|r\rangle + \mu \sum_{j\neq r} |j\rangle \frac{\langle j|V|r\rangle}{E_r - E_j} \;+\; \ldots\right) ,
\tag{6.1.14}
$$

where α is chosen so that $|\psi\rangle$ has unit norm. This is second order perturbation theory.

Example:

$$H = \frac{\hat{p}^2}{2m} + \tfrac{1}{2}m\omega^2\hat{x}^2 = \hbar\omega\left(a^\dagger a + \tfrac{1}{2}\right)$$

(6.1.15)

$$\text{states} \ \ |n\rangle, \ \ E_n = \hbar\omega\left(n + \tfrac{1}{2}\right) \ .$$

Perturb with $\ \ V = m\omega^2\hat{x}^2 = \not{m\omega^2}\frac{\hbar}{2\not{m\omega}}(a^2 + a^{\dagger 2} + 2a^\dagger a + 1).$ (6.1.16)

Have

$$
\begin{aligned}
\langle n|V|n\rangle &= \tfrac{1}{2}\hbar\omega(2n+1) \\
\langle n+2|V|n\rangle &= \tfrac{1}{2}\hbar\omega\sqrt{n+1}\sqrt{n+2} \\
\langle n-2|V|n\rangle &= \tfrac{1}{2}\hbar\omega\sqrt{n}\sqrt{n-1} \\
\langle m|V|n\rangle &= 0 \quad \text{all other } m
\end{aligned}
$$

(6.1.17)

Perturbed energy of nth level to $O(\mu^2)$:

$$
\begin{aligned}
E_n \quad &+ \quad \mu\langle n|V|n\rangle \quad + \quad \mu^2 \sum_{m\neq n} \frac{|\langle m|V|n\rangle|^2}{E_n - E_m} \\
= \ \hbar\omega(n+\tfrac{1}{2}) \ &+ \ \mu\hbar\omega(n+\tfrac{1}{2}) \ + \ \mu^2\left(\frac{\hbar\omega}{2}\right)^2 \underbrace{\left(\frac{(n+1)(n+2)}{-2\hbar\omega}}_{m=n+2} + \underbrace{\frac{n(n-1)}{2\hbar\omega}\right)}_{m=n-2} \\
= \ \hbar\omega\left(n+\tfrac{1}{2}\right)&\left(1 + \mu - \tfrac{1}{2}\mu^2\right) \ .
\end{aligned}
$$

(6.1.18)

But this problem can be solved exactly:

$$H \rightarrow H + \mu V \quad \text{equivalent to} \quad \omega \rightarrow \omega' = \omega\sqrt{1 + 2\mu} \ .$$

(6.1.19)

New energies are exactly

$$
\begin{aligned}
\hbar\omega'(n+\tfrac{1}{2}) &= \hbar\omega(n+\tfrac{1}{2})(1+2\mu)^{\frac{1}{2}} \\
&= \hbar\omega(n+\tfrac{1}{2})(1+\mu-\tfrac{1}{2}\mu^2 + O(\mu^3)) \ .
\end{aligned}
$$

(6.1.20)

Validity/usefulness of perturbation theory

If μ dimensionless might expect $\mu \ll 1$ enough to ensure rapid convergence such as in above example. However, this may not be enough since we still require a non-zero radius of convergence. Really have an expansion in

$$\left|\mu\frac{\langle i|V|j\rangle}{E_i - E_j}\right| \quad i \neq j \ ,$$

(6.1.21)

and similar quantities. Condition for accuracy is therefore qualitatively

$$|\text{energy shifts}| \ \ll \ |\text{original energy differences}| \ .$$

(6.1.22)
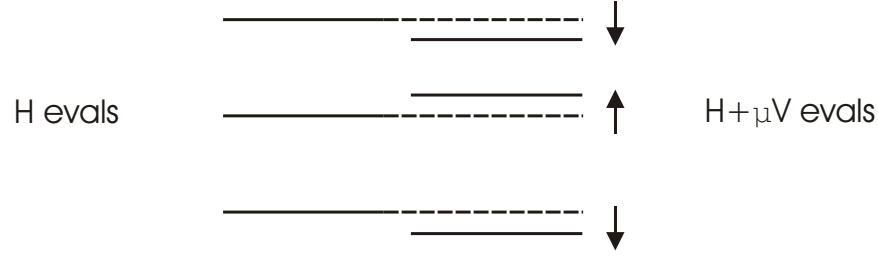
Indeed, it may be that the series is only asymptotic and more sophisticated methods are needed to estimate the energy shifts within a given accuracy.

Example. Ground state energy for Helium.

The unperturbed problem is two non-interacting electrons, charge $-e$ orbiting nucleus with charge $+2e$. The Hamiltonian is

$$H(\hat{\boldsymbol{x}}_1, \hat{\boldsymbol{p}}_1) + H(\hat{\boldsymbol{x}}_2, \hat{\boldsymbol{p}}_2) \quad \text{with} \quad H(\hat{\boldsymbol{x}}, \hat{\boldsymbol{p}}) \;=\; \frac{\hat{\boldsymbol{p}}^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 |\hat{\boldsymbol{x}}|} \;. \tag{6.1.23}$$

Single electron states and energies are

$$\begin{array}{c} |n\,l\,m\rangle \\ \text{wavefn } \psi_{nlm}(\boldsymbol{x}) \end{array} \qquad E_n = -\frac{1}{2}m\left(\frac{2e^2}{4\pi\epsilon_0\hbar}\right)^2 \frac{1}{n^2} \equiv -\frac{2\alpha^2}{n^2}mc^2 \;, \tag{6.1.24}$$

where $\alpha = \dfrac{e^2}{4\pi\epsilon_0\hbar c}$ is the dimensionless fine structure constant: $\alpha \approx 1/137$. The lowest energy eigenstate for two electrons is

$$|\Psi\rangle \;=\; |1\,0\,0\rangle \otimes |1\,0\,0\rangle \otimes |\chi\rangle$$

$$\text{with} \quad |\chi\rangle \;=\; \frac{1}{\sqrt{2}}\Big(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\Big) \quad \text{the spin state .} \tag{6.1.25}$$

This state is totally antisymmetric since constrained by Fermi statistics. The two electron wavefunction is then

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) \;=\; \psi_{100}(\boldsymbol{x}_1)\psi_{100}(\boldsymbol{x}_2)$$

$$\psi_{100}(\boldsymbol{x}) \;=\; \frac{1}{\sqrt{\pi}}\left(\frac{2}{a_2}\right)^{\frac{3}{2}} e^{-|\boldsymbol{x}|/a_2}$$

$$\text{with } (Z=2) \quad a_2 \;=\; \tfrac{1}{2}\left(\frac{1}{\alpha}\frac{\hbar}{mc}\right) \;=\; \tfrac{1}{2} * (\text{Bohr radius}) \tag{6.1.26}$$

The two-electron unperturbed energy is

$$2E_1 \;=\; -4\alpha^2 mc^2 \;\approx\; -108.8\,\text{eV} \;. \tag{6.1.27}$$

Compare with -13.6 eV for the hydrogen atom. (Note: $mc^2 \approx 500\,\text{KeV}$.)

Experimentally, the ground state for He is -79.0 eV. However, have neglected the electron-electron interaction:

$$\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\hat{\boldsymbol{x}}_1 - \hat{\boldsymbol{x}}_2|} \;. \tag{6.1.28}$$

Treat this as a perturbation and write as $\mu V(\hat{\boldsymbol{x}}_1, \hat{\boldsymbol{x}}_2)$ with

$$\mu = \alpha, \quad V(\hat{\boldsymbol{x}}_1, \hat{\boldsymbol{x}}_2) = \frac{\hbar c}{|\hat{\boldsymbol{x}}_1 - \hat{\boldsymbol{x}}_2|} . \tag{6.1.29}$$

Then μ is dimensionless and V has energy dimensions. The first-order correction to the energy is then

$$
\begin{aligned}
\alpha \langle \Psi | V | \Psi \rangle &= \alpha \int d^3 x_1 \int d^3 x_2 \ \Psi^*(\boldsymbol{x}_1, \boldsymbol{x}_2) V(\boldsymbol{x}_1, \boldsymbol{x}_2) \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) \\
&= \alpha \int d^3 x_1 \int d^3 x_2 \ |\psi_{100}(\boldsymbol{x}_1)|^2 |\psi_{100}(\boldsymbol{x}_2)|^2 \frac{\hbar c}{|\boldsymbol{x}_1 - \boldsymbol{x}_2|} \\
&= \frac{5}{4} \alpha^2 m c^2 \ \approx \ 34.0 \, \text{eV} . \tag{6.1.30}
\end{aligned}
$$

The corrected ground state energy is then $-108.8 \, \text{eV} + 34.0 \, \text{eV} \approx -74.8 \, \text{eV}$; in much better agreement with experiment. Note that the variational principle is more efficient (see AQM) at this level but does not help with higher-order corrections.

We might naively expect that the perturbation series is an expansion in α but we see that E_1 and the first-order correction $E_1^{(1)}$ are **both** $\propto \alpha^2$. In fact, all corrections are $\propto \alpha^2$, so what is the expansion parameter? Including the 2nd-order correction the energy can be written

$$E = -Z^2 \alpha^2 m c^2 \left(1 - \frac{5}{8} \frac{1}{Z} + \frac{25}{256} \frac{1}{Z^2} + \dots \right) \Big|_{Z=2} . \tag{6.1.31}$$

So the expansion is in $1/Z$ for $Z = 2$. The series "looks" convergent and gives an answer close to experiment but to my knowledge it is not known if it actually converges. However, treated as an asymptotic series it does give a believable answer. This is typical of many problems in bound state systems.

In scattering theory (Quantum Electrodynamics) the expansion parameter **is** α but convergence is still not provable.

6.2   Degenerate case

Consider the perturbed Hamiltonian in Eq. (6.2) but now with the possibility that H has degenerate eigenstates. Let the degeneracy of states in V_λ be N with common eigenvalue λ. Then use notation

$$
\begin{array}{llllll}
E_1 = \dots = E_r = E_s = \dots = E_N = \lambda & \text{degenerate states} \\
|1\rangle, \quad \dots \quad |r\rangle, \quad |s\rangle, \quad \dots \quad |N\rangle & \text{reserve } r, s \text{ to label these only}
\end{array} \tag{6.2.1}
$$

and suppose that as $\mu \to 0$

$$E \to \lambda, \quad |\psi\rangle \to \sum_r a_r |r\rangle . \tag{6.2.2}$$

Denote other states, not in this degenerate set, by $|j\rangle$ and reserve j to label these only. Then, for general μ, expand the eigenfunction of the perturbed Hamiltonian as

$$
\begin{aligned}
E &= \lambda + \mu E^{(1)} + \mu^2 E^{(2)} + \dots, \\
|\psi\rangle &= \sum_r \alpha_r |r\rangle + \sum_j \beta_j |j\rangle .
\end{aligned}
$$

$$\text{with} \quad \alpha_r = a_r + O(\mu), \quad \beta_j = O(\mu) . \tag{6.2.3}$$

Note that for $\mu \to 0$, $|\psi\rangle \to |\psi_0\rangle \in V_\lambda$ but we do not yet know the values of the a_r which determine it uniquely in this limit. We shall see that the possible choices for the a_r are determined by the perturbation itself. Substitute into Eq. (6.2) and find

$$\sum_r \alpha_r (E_r + \mu V)|r\rangle + \sum_j \beta_j (E_j + \mu V)|j\rangle \;=\; E\left(\sum_r \alpha_r |r\rangle \;+\; \sum_j \beta_j |j\rangle\right) . \quad (6.2.4)$$

Rearranging gives

$$\underbrace{\sum_r \alpha_r (E - E_r)|r\rangle + \sum_j \beta_j (E - E_j)|j\rangle}_{\text{terms containing energy shifts}} \;=\; \underbrace{\mu \sum_r \alpha_r V|r\rangle + \mu \sum_j \beta_j V|j\rangle}_{\text{terms containing } V} . \quad (**)$$

$$(6.2.5)$$

Look for energy shift $E = \lambda + \mu E^{(1)} + O(\mu^2)$ and note that the correction is no longer associated with a single state of the unperturbed problem but with all N states in V_λ. Take the inner product of $\langle s|$ with $(**)$ to get (remember $E_r = \ldots = E_s \ldots = E_N = \lambda$)

$$(E - E_s)\alpha_s \;=\; \mu \sum_r \alpha_r \langle s|V|r\rangle + \mu \sum_j \beta_j \langle s|V|r\rangle , \quad (6.2.6)$$

but the second term on RHS is $O(\mu^2)$ and $\alpha_r = a_r + O(\mu)$, and so hence to leading order

$$\sum_r \langle s|V|r\rangle a_r \;=\; E^{(1)} a_s . \quad (6.2.7)$$

Thus, $E^{(1)}$ is an eigenvalue of the matrix $\langle s|V|r\rangle$ and the a_r are the components of the corresponding eigenvector. Since there are N degenerate states this is an $N \times N$ matrix and so have N solutions for $E^{(1)}$ with associated eigenvectors giving the a_r in each case.

We should expect something like this:

- We started with N degenerate states and we end up with N perturbed states.

- The degeneracy of H is a reflection of some symmetry (e.g., rotational symmetry $\Rightarrow$ $\boldsymbol{L}^2, L_3$ are good quantum numbers) and the perturbed Hamiltonian $H + \mu V$ generally has less symmetry and so the full degeneracy is broken, although some degeneracy amongst a subset of states can remain. The effect is to spilt apart some, or all, levels.
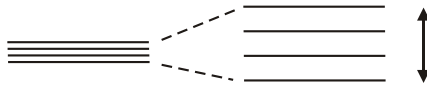
- Raising the degeneracy in this way is important in many physical phenomena. For example, band structure for the electron levels in a crystal giving rise to delocalization of electrons originally bound in each atom and so leading to electrical conduction (see AQM).

Example. Particle in a box in two dimensions, $0 \leqslant x, y \leqslant a$. The unperturbed problem is the free particle with states $|p, q\rangle$ and

$$\text{wavefns} \qquad \psi_{pq}(x, y) = \frac{2}{a} \sin \frac{p\pi x}{a} \sin \frac{q\pi y}{a}$$

$$\text{energies} \qquad E_{pq} = \frac{\hbar^2 \pi^2}{2ma^2}(p^2 + q^2) \quad p, q = 1, 2, \ldots \ . \tag{6.2.8}$$

- Lowest level, $E_{11} = \frac{\hbar^2 \pi^2}{ma^2}$, is non-degenerate.

- Next level has $E_{12} = E_{21} = \frac{5\hbar^2 \pi^2}{2ma^2}$ and so has degeneracy 2.

Consider the perturbation $V(x, y) = \frac{xy}{a^2}$, and then μ has dimensions of energy.

- The shift in the lowest energy level is given by

$$\begin{aligned}
\langle 11|V|11 \rangle &= \int_0^a dx \int_0^a dy \, \frac{xy}{a^2} \, |\psi_{11}(x, y)|^2 \\
&= \left(\frac{2}{a}\right)^2 \frac{1}{a^2} \int_0^a dx \, x \left(\sin \frac{\pi x}{a}\right)^2 \int_0^a dy \, y \left(\sin \frac{\pi y}{a}\right)^2 \\
&= \frac{1}{4} \ .
\end{aligned} \tag{6.2.9}$$

$$\tag{6.2.10}$$

$$\left[\int_0^a dx \, x \left(\sin \frac{\pi x}{a}\right)^2 = \frac{a^2}{4} \right]$$

- Shifts in next level given by eigenvalues of

$$\begin{pmatrix} \langle 12|V|12 \rangle & \langle 12|V|21 \rangle \\ \langle 21|V|12 \rangle & \langle 21|V|21 \rangle \end{pmatrix} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}, \tag{6.2.11}$$

with

$$\begin{aligned}
\alpha &= \int_0^a dx \int_0^a dy \, \frac{xy}{a^2} \, |\psi_{12}(x, y)|^2 \\
&= \left(\frac{2}{a}\right)^2 \frac{1}{a^2} \int_0^a dx \, x \left(\sin \frac{\pi x}{a}\right)^2 \int_0^a dy \, y \left(\sin \frac{2\pi y}{a}\right)^2 \\
&= \frac{1}{4} \ .
\end{aligned} \tag{6.2.12}$$

$$\begin{aligned}
\beta &= \int_0^a dx \int_0^a dy \, \frac{xy}{a^2} \psi_{12}^*(x, y)\psi_{21}(x, y) \\
&= \left(\frac{2}{a}\right)^2 \frac{1}{a^2} \left(\int_0^a dx \, x \sin \frac{\pi x}{a} \sin \frac{2\pi x}{a}\right)^2 \\
&= \left(\frac{16}{9\pi^2}\right)^2 \ .
\end{aligned} \tag{6.2.13}$$

$$\tag{6.2.14}$$

$$\left[\int_0^a dx \, x \sin \frac{\pi x}{a} \sin \frac{2\pi x}{a} = \int_0^a dx \, x \frac{1}{2}\left(\cos \frac{\pi x}{a} - \cos \frac{3\pi x}{a}\right) = -\frac{8a^2}{9\pi^2} \right] .$$

The eigenvalues of the matrix are $\alpha \pm \beta$ with respective eigenvectors

$$\boldsymbol{a} \equiv (a_{12}, a_{21}) = \frac{1}{\sqrt{2}}(1, 1), \quad \frac{1}{\sqrt{2}}(1, -1) \tag{6.2.15}$$

Collecting results:

- New ground state energy $\frac{\hbar^2 \pi^2}{ma^2} + \frac{\mu}{4}$.

- Next two levels

$$\text{energies} \qquad \frac{5\hbar^2 \pi^2}{2ma^2} + \frac{\mu}{4} \pm \mu \frac{256}{81\pi^4}$$

$$\text{states} \qquad |\psi\rangle = \frac{1}{\sqrt{2}}\Big(|12\rangle \pm |21\rangle\Big) . \tag{6.2.16}$$

Note that the state is unperturbed at first order in μ but the perturbation **does** determine the **choice** of basis in V_λ in order that the perturbation can be carried out systematically. This basis is the eigenstates of the matrix with elements $\langle s|V|r\rangle$.

7   Angular Momentum

7.1   Recap of orbital angular momentum

Mainly to set the analysis to follow in some sort of context but also a few points of special importance.

$$\boldsymbol{L} = \hat{\boldsymbol{x}} \wedge \hat{\boldsymbol{p}} \quad \text{or} \quad L_i = \varepsilon_{ijk}\, \hat{x}_j\, \hat{p}_k \quad \boldsymbol{L}^2 = L_i L_i. \tag{7.1.1}$$

Then

$$[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij} \quad \Rightarrow \quad [L_i, L_j] = i\hbar\, \varepsilon_{ijk}\, L_k, \quad [\boldsymbol{L}^2, L_i] = 0 . \tag{7.1.2}$$

In addition to these fundamental commutation relations we have

$$[L_i, \hat{x}_j] = i\hbar\, \varepsilon_{ijk}\, \hat{x}_k, \quad [L_i, \hat{p}_j] = i\hbar\, \varepsilon_{ijk}\, \hat{p}_k . \tag{7.1.3}$$

Consider the action of all these operators on wavefunctions. Using spherical polar coordinates (r, θ, ϕ), the operators L_i only involve angular derivatives and

$$\nabla^2 = \underbrace{\frac{1}{r}\frac{\partial^2}{\partial r^2}\, r}_{\text{radial}} - \underbrace{\frac{1}{r^2 \hbar^2}\boldsymbol{L}^2}_{\text{angular}} . \tag{7.1.4}$$

The joint eigenstates of $\boldsymbol{L}^2$ and L_3 are the spherical harmonics $Y_{lm}(\theta, \phi)$:

$$\begin{aligned}
\boldsymbol{L}^2 Y_{lm} &= \hbar^2 l(l+1)\, Y_{lm} \\
L_3 Y_{lm} &= \hbar m\, Y_{lm} \\
\text{with} \quad Y_{lm} &= c_{lm} e^{im\phi} P_l^{|m|}(\cos\theta) \\
\text{where} \quad P_l^m(u) &= (1 - u^2)^{m/2}\frac{d^m}{du^m} P_l(u), \quad m \geqslant 0 .
\end{aligned} \tag{7.1.5}$$

$$P_l(u) \qquad \text{is a Legendre polynomial}$$
$$P_l^m(u) \qquad \text{is an associated Legendre function .}$$

Only well-behaved solutions of eigenvalue problems for solving differential equations arise for

$$l = 0, 1, 2, 3, \ldots \quad \text{and} \quad m = 0, \pm 1, \pm 2, \ldots, \pm l \ . \tag{7.1.6}$$

If the Schrödinger equation has a spherically symmetric potential, $V(\boldsymbol{x}) = V(r)$ then we can look for separable solutions

$$\psi_{lm}(\boldsymbol{x}) \;=\; R_l(r) Y_{lm}(\theta, \phi) \ , \tag{7.1.7}$$

where

$$-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2}(r R_l) + \left(\frac{\hbar^2}{2mr^2} l(l+1) + V(r) \right) R_l \;=\; E R_l \ . \tag{7.1.8}$$

Of particular importance is the behaviour of such solutions under parity: $\boldsymbol{x} \mapsto -\boldsymbol{x}$. This is equivalent to

$$r \mapsto r, \quad \theta \mapsto \pi - \theta, \quad \phi \mapsto \phi + \pi \ . \tag{7.1.9}$$

Then, under parity map have

$$Y_{lm}(\pi - \theta, \phi + \pi) \;=\; (-1)^l Y_{lm}(\theta, \phi)$$
$$\Rightarrow \quad \psi_{lm}(-\boldsymbol{x}) \;=\; (-1)^l \psi_{lm}(\boldsymbol{x}) \ . \tag{7.1.10}$$

A very important example of everything above is a system of two particles interacting through a potential which depends only on their relative separation

$$\begin{aligned}
H \;&=\; \frac{\hat{\boldsymbol{p}}_1^2}{2m_1} + \frac{\hat{\boldsymbol{p}}_2^2}{2m_2} + V(|\hat{\boldsymbol{x}}_1 - \hat{\boldsymbol{x}}_2|) \\
&=\; \frac{\hat{\boldsymbol{P}}^2}{2M} + \frac{\hat{\boldsymbol{p}}^2}{2m} + V(|\hat{\boldsymbol{x}}|) \ ,
\end{aligned} \tag{7.1.11}$$

where

$$\begin{aligned}
\hat{\boldsymbol{X}} \;&=\; \frac{m_1 \hat{\boldsymbol{x}}_1 + m_2 \hat{\boldsymbol{x}}_2}{M} & \hat{\boldsymbol{x}} \;&=\; \hat{\boldsymbol{x}}_1 - \hat{\boldsymbol{x}}_2 \\[2mm]
\hat{\boldsymbol{P}} \;&=\; \hat{\boldsymbol{p}}_1 + \hat{\boldsymbol{p}}_2 & \hat{\boldsymbol{p}} \;&=\; \frac{m_2 \hat{\boldsymbol{p}}_1 - m_1 \hat{\boldsymbol{p}}_2}{M} \\[2mm]
M \;&=\; m_1 + m_2 & m \;&=\; \frac{m_1 m_2}{M} \quad \text{reduced mass}
\end{aligned} \tag{7.1.12}$$

$$\text{CoM degrees of freedom} \qquad\qquad \text{relative degrees of freedom}$$

CoM dynamics essentially trivial and relative motion is governed by a spherically symmetric potential. The total wavefunction is then

$$\Psi(\boldsymbol{X}, \boldsymbol{x}) \;=\; e^{i\boldsymbol{k}\cdot\boldsymbol{X}} \psi_{lm}(\boldsymbol{x}) \quad \text{w.r.t} \quad \boldsymbol{L} = \hat{\boldsymbol{x}} \wedge \hat{\boldsymbol{p}} \ . \tag{7.1.13}$$

I.e., plane wave solution in the CoM variables and effective single particle dynamics in potential $V(|\hat{\boldsymbol{x}}|)$ with reduced mass m.

Under $\boldsymbol{x} \mapsto -\boldsymbol{x}$ have $\Psi \mapsto (-1)^l \Psi$. This is particularly important if the two particles are identical.

7.2   General analysis of angular momentum eigenstates

$$
\begin{aligned}
\text{Consider} && \boldsymbol{J} &= (J_1, J_2, J_3) & J_i^\dagger &= J_i \\
\text{obeying} && [J_i, J_j] &= i\hbar\varepsilon_{ijk}J_k \\
\text{Define} && \boldsymbol{J}^2 &= J_i J_i & \text{hermitian} \\
\text{then} && [\boldsymbol{J}^2, J_i] &= 0
\end{aligned}
\tag{7.2.1}
$$

We want to find all possible eigenstates of $\boldsymbol{J}^2$ and J_3 (say) assuming just the commutation relations above. Use $\boldsymbol{J}$ rather than $\boldsymbol{L}$ because there will turn out to be additional possibilities beyond those allowed for orbital angular momentum. First observe that

$$
\begin{aligned}
\boldsymbol{J}^2|\psi\rangle &= \lambda|\psi\rangle \quad\Rightarrow \\
\lambda &= \langle\psi|\boldsymbol{J}^2|\psi\rangle = \|J_1|\psi\rangle\|^2 + \|J_2|\psi\rangle\|^2 + \|J_3|\psi\rangle\|^2 \geqslant 0 .
\end{aligned}
\tag{7.2.2}
$$

It is convenient to set $\lambda = \hbar^2 j(j+1)$ with $j \geqslant 0$ without loss of generality (note: λ unchanged if $j \to -(j+1)$). So label the states $|j, m\rangle$ where

$$
\boldsymbol{J}^2|j, m\rangle = \hbar^2 j(j+1)|j, m\rangle \qquad J_3|j, m\rangle = \hbar m|j, m\rangle .
\tag{7.2.3}
$$

So far all we know is that m and $j \geqslant 0$ are real numbers. To analyze the allowed eigenvalues we define

$$
J_\pm = J_1 \pm iJ_2 , \qquad J_\pm^\dagger = J_\mp ,
\tag{7.2.4}
$$

and work with these new combinations. It is easy to check that

$$
\begin{aligned}
[J_3, J_\pm] &= \pm\hbar J_\pm \\
[J_+, J_-] &= 2\hbar J_3 \\
[\boldsymbol{J}^2, J_\pm] &= 0 .
\end{aligned}
\tag{7.2.5}
$$

Furthermore, we find

$$
\begin{aligned}
J_+ J_- &= \boldsymbol{J}^2 - J_3^2 + \hbar J_3 \\
J_- J_+ &= \boldsymbol{J}^2 - J_3^2 - \hbar J_3
\end{aligned}
\tag{7.2.6}
$$

and also find that

$$
J_\pm|j, m\rangle \;\; \text{is an eigenstate of} \;\;
\begin{cases}
\boldsymbol{J}^2 & \text{with } j \text{ unchanged} \\
J_3 & \text{with } m \to m \pm 1
\end{cases}
\tag{7.2.7}
$$

and, strictly, provided that the new states do not vanish. These statements follow from the commutation relations because

$$
\begin{aligned}
J_3\Big(J_\pm|j, m\rangle\Big) &= \Big([J_3, J_\pm] + J_\pm J_3\Big)|j, m\rangle \\
&= \Big(\pm\hbar J_\pm + J_\pm\hbar m\Big)|j, m\rangle \\
&= \hbar(m \pm 1)J_\pm|j, m\rangle .
\end{aligned}
\tag{7.2.8}
$$

Compare with the harmonic oscillator where

$$
[N, a^\dagger] = a^\dagger \;\; \text{and} \;\; [N, a] = -a \quad\Rightarrow\quad a^\dagger|n\rangle, \; a|n\rangle \;\; \text{have eigenvalues } n \pm 1 .
\tag{7.2.9}
$$

To find out whether the new states vanish we compute

$$
\begin{aligned}
\|J_+|j,m\rangle\|^2 &= \langle j,m|J_-J_+|j,m\rangle \\
&= \langle j,m|\boldsymbol{J}^2 - J_3^2 - \hbar J_3|j,m\rangle \\
&= \hbar^2\big(j(j+1) - m(m+1)\big) \\
&= \hbar^2(j-m)(j+m+1) \\
&\geqslant 0 ,
\end{aligned}
\tag{7.2.10}
$$

and

$$
\begin{aligned}
\|J_-|j,m\rangle\|^2 &= \langle j,m|J_+J_-|j,m\rangle \\
&= \langle j,m|\boldsymbol{J}^2 - J_3^2 + \hbar J_3|j,m\rangle \\
&= \hbar^2\big(j(j+1) - m(m-1)\big) \\
&= \hbar^2(j+m)(j-m+1) \\
&\geqslant 0 .
\end{aligned}
\tag{7.2.11}
$$

These inequalities, which follow just because the inner-product is positive-semidefinite, imply (remember $j \geqslant 0$)

$$
\begin{aligned}
j &\geqslant m \geqslant -(j+1) \\
j+1 &\geqslant m \geqslant -j
\end{aligned}
\tag{7.2.12}
$$

and the states vanish only when equality occurs. Hence, from these bounds, we deduce

$$
\begin{aligned}
j &\geqslant m \geqslant -j \\
J_+|j,m\rangle &= 0 \quad \text{iffi} \quad m = j , \\
J_-|j,m\rangle &= 0 \quad \text{iffi} \quad m = -j .
\end{aligned}
\tag{7.2.13}
$$

These results tell us all we need to know about the possible values of both j and m. Remember, so far only know that m and $j \geqslant 0$ are real. Start from any given state $|j,m\rangle$.

- If the states $J_+^n|j,m\rangle$ are non-vanishing, they have J_3 eigenvalues $\hbar(m+n)$ but subject to the bound $j \geqslant m + n$ from above.

- To avoid a contradiction there must be an integer k with $j = m + k$ and hence

$$
J_+^n|j,m\rangle = 0 \quad \forall \; n > k. \tag{7.2.14}
$$

  Only then will the sequence terminate at $m = j$.

- Similarly, if the states $J_-^n|j,m\rangle$ are non-vanishing, they have J_3 eigenvalues $\hbar(m-n)$ but subject to the bound $m - n \geqslant -j$.

- In this case must have an integer k' with $-j = m - k'$ so that

$$
J_-^n|j,m\rangle = 0 \quad \forall \; n > k'. \tag{7.2.15}
$$
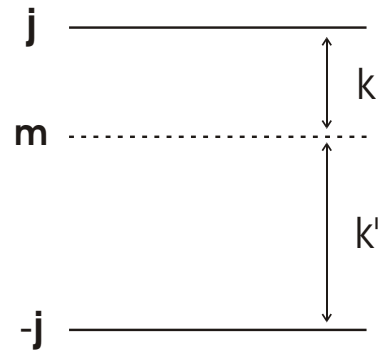
Thus,

$$j = m + k \quad \text{and} \quad j = -m + k' , \quad k, k' \text{ integer}$$
$$\Rightarrow \quad 2j = k + k' , \quad \text{an integer.} \tag{7.2.16}$$

Furthermore, for a given value of j we have states

$$|j, m\rangle \text{ with } m = j, j - 1, \ldots, -j + 1, -j , \quad \text{a total of } 2j + 1 \text{ states.} \tag{7.2.17}$$

This general analysis has revealed two possibilities:

$$
\begin{array}{lll}
j \text{ \bf integral} & m = 0, \pm 1, \pm 2, \ldots, \pm j & \text{odd \# states,} \\
j \text{ \bf half-integral} & m = \pm \frac{1}{2}, \pm \frac{3}{2}, \ldots, \pm j & \text{even \# states.}
\end{array}
\tag{7.2.18}
$$

j **integral.** This possibility is realized in orbital angular momentum. The states $|j, m\rangle$ correspond to wavefunctions $\psi_{jm}(\boldsymbol{x})$ or $Y_{jm}(\theta, \phi)$.

j **half-integral.** This possibility cannot arise for orbital angular momentum since there are no solutions of the differential equations which are well-behaved in this case. Such states must correspond to **intrinsic** angular momentum or **spin** as introduced earlier.

We usually write $\boldsymbol{J} = \boldsymbol{S}$ for spin. Our analysis shows that we must have $j = S$ integral or half-integral for spin. Previously, we wrote $|r\rangle$ with $S \geqslant r \geqslant -S$ for spin-states. Now we see that by this was meant

$$|r\rangle \equiv |j, m\rangle \quad \text{with} \quad j = S, \ m = r. \tag{7.2.19}$$

Analysis reveals mathematically that spin is possible with these quantum numbers but still need to give (very brief) indication of experimental verification.

The set of states $\{|j, m\rangle\}$ for fixed j is often called an angular momentum multiplet or representation. From the analysis above (Eqns. (7.2.10, 7.2.11)) it is clear we can choose normalized states $|j, m\rangle$ with

$$J_+ |j, m\rangle = \hbar \sqrt{(j - m)(j + m + 1)} |j, m + 1\rangle , \tag{7.2.20}$$
$$J_- |j, m\rangle = \hbar \sqrt{(j + m)(j - m + 1)} |j, m - 1\rangle , \tag{7.2.21}$$

which are key relations between the states. The whole multiplet can be defined by

- taking the **top state**, the one with maximum J_3 eigenvalue: $J_+ |j, j\rangle = 0$,
- and applying J_-^n:
$$|j, j - n\rangle = C_{jn} J_-^n |j, j\rangle , \tag{7.2.22}$$
  where C_{jn} is a constant computable using Eq. (7.2.21).
- Alternatively, can start with the **bottom state**, $|j, -j\rangle$ and determine the others by applying J_+^n.

Note that the choice of J_3 as the member of the commuting set along with $\boldsymbol{J}^2$ is a convention. We could have chosen $\boldsymbol{n} \cdot \boldsymbol{J}$ instead. $\boldsymbol{n} \cdot \boldsymbol{J}$ has the same possible eigenvalues as J_3 but the eigenstates are linear combinations of the basis states $\{|j, m\rangle\}$. This will be relevant when we discuss rotations.

7.3   Matrix representations

Recall from section 2.4 that given an orthonormal basis $\{|n\rangle\}$ we can regard states as column vectors $|\psi\rangle \leadsto \alpha_n = \langle n|\psi\rangle$, and operators as matrices $A \leadsto A_{mn} = \langle m|A|n\rangle$ with the action of operators on states to be that of matrix multiplication. This is particularly useful when the space of states is finite-dimensional, as with angular momentum states $\{|j, m\rangle\}$ with fixed j.

For example, with $j = 1$ (3-dim state space)

$$|1, 1\rangle \leadsto \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad |1, 0\rangle \leadsto \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad |1, -1\rangle \leadsto \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad (7.3.1)$$

$$J_3 \leadsto \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad J_+ \leadsto \hbar\sqrt{2} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \quad J_- \leadsto \hbar\sqrt{2} \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad (7.3.2)$$

These follow from the formulas

$$\begin{aligned} J_3|1, 1\rangle &= \hbar|1, 1\rangle & J_\pm|1, \mp 1\rangle &= \hbar\sqrt{2}|1, 0\rangle \\ J_3|1, -1\rangle &= -\hbar|1, -1\rangle & J_\pm|1, 0\rangle &= \hbar\sqrt{2}|1, \pm 1\rangle \end{aligned} \qquad (7.3.3)$$

as the only non-zero results.

This is used very widely for the case of spin-$\frac{1}{2}$ (now use $\boldsymbol{S}$ rather than $\boldsymbol{J}$) with just two states.

$$|\tfrac{1}{2}, \tfrac{1}{2}\rangle \leadsto \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |\tfrac{1}{2}, -\tfrac{1}{2}\rangle \leadsto \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad (7.3.4)$$

previously: $|\uparrow\rangle$ $|\downarrow\rangle$

$$S_3 \leadsto \tfrac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad S_+ \leadsto \tfrac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad S_- \leadsto \tfrac{1}{2}\hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (7.3.5)$$

Moreover, we also write $s_i \leadsto \tfrac{1}{2}\hbar\sigma_i$ where

$$\sigma_1 \leadsto \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 \leadsto \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 \leadsto \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad (7.3.6)$$

are called the **Pauli matrices**. Other combinations are

$$\sigma_+ = \sigma_1 + i\sigma_2 = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}, \quad \sigma_- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}. \qquad (7.3.7)$$

The Pauli matrices are hermitian, traceless matrices obeying

$$\sigma_1^2 = \sigma_2^2 = \sigma_3^2 = \mathbb{I}, \qquad (7.3.8)$$

$$\sigma_1\sigma_2 = -\sigma_2\sigma_1 = i\sigma_3 \quad \text{and cyclic.} \qquad (7.3.9)$$

These properties are conveniently summarized by

$$\sigma_i\sigma_j = \delta_{ij} + i\varepsilon_{ijk}\sigma_k. \qquad (7.3.10)$$

Note that the antisymmetric part (in i, j) of this equation is

$$[\sigma_i, \sigma_j] \;=\; 2i\varepsilon_{ijk}\sigma_k \,, \tag{7.3.11}$$

and corresponds to the fundamental commutation relation

$$[S_i, S_j] \;=\; i\hbar\varepsilon_{ijk}S_k \,, \tag{7.3.12}$$

but the remaining, symmetric part, is special to spin-$\frac{1}{2}$.

The Pauli matrices are components of a vector

$$\boldsymbol{S} \;\rightsquigarrow\; \tfrac{1}{2}\hbar\boldsymbol{\sigma} \,, \quad \boldsymbol{\sigma} \;=\; (\sigma_1, \sigma_2, \sigma_3) \,. \tag{7.3.13}$$

If $\boldsymbol{a}$ and $\boldsymbol{b}$ are constant vectors (or at most operators which commute with $\boldsymbol{S}$) then we can contract a_i and b_j with both sides of Eqn. (7.3.10) to obtain

$$(\boldsymbol{a} \cdot \boldsymbol{\sigma})(\boldsymbol{b} \cdot \boldsymbol{\sigma}) \;=\; (\boldsymbol{a} \cdot \boldsymbol{b})\mathbb{I} + i(\boldsymbol{a} \wedge \boldsymbol{b}) \cdot \boldsymbol{\sigma} \,. \tag{7.3.14}$$

As a special case

$$(\boldsymbol{n} \cdot \boldsymbol{\sigma})^2 \;=\; \mathbb{I} \,, \tag{7.3.15}$$

where $\boldsymbol{n}$ is any unit vector. Note that this is equivalent to $(\boldsymbol{n} \cdot \boldsymbol{S})^2 \;=\; \frac{1}{4}\hbar^2\mathbb{I}$, which agrees with the fact that the eigenstates of $\boldsymbol{n} \cdot \boldsymbol{S}$ are $\pm\frac{1}{2}\hbar$; these are the only possible results for measurement of spin along some direction $\boldsymbol{n}$.

One last example of matrix properties corresponding to known properties of operators:

$$\boldsymbol{\sigma}^2 \;=\; \sigma_1^2 + \sigma_2^2 + \sigma_3^2 \;=\; 3\,\mathbb{I} \,, \tag{7.3.16}$$

to be compared with

$$\boldsymbol{S}^2 \;=\; \hbar^2 \left(\tfrac{1}{2}\right)\left(\tfrac{1}{2}+1\right)\mathbb{I} \;=\; 3\frac{\hbar^2}{4}\mathbb{I} \tag{7.3.17}$$

which has eigenvalue $3\dfrac{\hbar^2}{4}$ on any state.

7.4   Some physical aspects of angular momentum and spin

Our analysis of angular momentum states in section 7.2 has revealed the mathematical possibility of half-integral spin. As asserted earlier, this **is** realized in nature as previously stated that each particle carries an internal space of states $|r\rangle$ with $-S \leqslant r \leqslant S$. Now identify these with $|j = S, m = r\rangle$ angular momentum states. The spin operators obey

$$[S_i, \hat{x}_j] = [S_i, \hat{p}_j] = 0 \,, \tag{7.4.1}$$

which should be contrasted with the commutators for $\boldsymbol{L}$ given in section 7.1. This is consistent with our earlier use of basis states $|\boldsymbol{x}\rangle \otimes |r\rangle$ (fixed S) because $\hat{\boldsymbol{x}}, \boldsymbol{S}, S_3$ are a commuting set.

In general, then, a given particle will have both orbital angular momentum $\boldsymbol{L}$ and spin angular momentum $\boldsymbol{S}$, giving a total angular momentum

$$\boldsymbol{J} \;=\; \boldsymbol{L} + \boldsymbol{S} \,. \tag{7.4.2}$$

Note that $[S_i, L_j] = 0$ and hence

$$[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k \quad [S_i, S_j] = i\hbar\varepsilon_{ijk}S_k \tag{7.4.3}$$

together imply

$$[J_i, J_j] = i\hbar\varepsilon_{ijk}J_k . \tag{7.4.4}$$

How do we know the world works this way? Results of many experiments confirm it. Here just mention the theoretical ideas underlying a few of them. The key idea is how spin and angular momentum degrees of freedom enter into the Hamiltonian.

Main example for us is interaction with a background magnetic field. From classical EM (no previous knowledge required) a moving distribution of electric charge interacts with magnetic field $\boldsymbol{B}(\boldsymbol{x})$ to produce energy

$$-\boldsymbol{\mu} \cdot \boldsymbol{B} , \tag{7.4.5}$$

where $\boldsymbol{\mu}$ is the magnetic dipole moment of the distribution. Think of $\boldsymbol{\mu}$ as being a small magnet which does not disturb $\boldsymbol{B}$. For instance, a single charge q in an orbit with angular momentum $\boldsymbol{L}$ can be shown to have

$$\boldsymbol{\mu} = \frac{q}{2m}\boldsymbol{L} . \tag{7.4.6}$$

Hence, the interaction energy is of the form

$$-\gamma\,\boldsymbol{L} \cdot \boldsymbol{B} , \quad \gamma \text{ some constant.} \tag{7.4.7}$$

This final result is all that is important for us. Now pass to quantum theory and consider the effect of including such a term in the Hamiltonian for the electron in the hydrogen atom (works for any spherically symmetric potential).

(i) Before we turn on any magnetic field have $\psi_{nlm}(\boldsymbol{x})$ joint eigenstates of $H, \boldsymbol{L}^2, L_3$ with degenerate energies E independent of m (as discussed in section 7.1).

Add a weak magnetic field along the 3-direction, $\boldsymbol{B} = (0, 0, B)$ and so

$$H \rightarrow H - \gamma B L_3 , \tag{7.4.8}$$

but $\psi_{nlm}(\boldsymbol{x})$ are still eigenstates and energies now split

$$E \rightarrow E - \gamma B\hbar m \quad \underbrace{-l \leqslant m \leqslant l}_{2l + 1 \text{ levels}} . \tag{7.4.9}$$

This **is** observed: spectral lines split into distinct lines. This is the **Zeeman effect**.

(ii) Replacing $\boldsymbol{L}$ by $\boldsymbol{S}$ we have an interaction energy of the form

$$-\gamma'\,\boldsymbol{S} \cdot \boldsymbol{B} , \quad \gamma' \text{ constant} \neq \gamma \text{ in general.} \tag{7.4.10}$$

For a spin-$\frac{1}{2}$ particle originally in eigenstate of a spin-independent Hamiltonian, adding this term splits the energy states by

$$\pm\gamma'B\frac{\hbar}{2} \quad B \text{ weak and constant.} \tag{7.4.11}$$

Also observed and also called the Zeeman effect. Get appearance of **two** distinct levels – direct experimental evidence for spin-$\frac{1}{2}$.

(iii) An electron in the atom has both an orbital magnetic moment $\boldsymbol{\mu}_L \propto \boldsymbol{L}$ and a spin magnetic moment $\boldsymbol{\mu}_S \propto \boldsymbol{S}$. Like two bar magnets near each other there is an interaction energy

$$\boldsymbol{\mu}_L \cdot \boldsymbol{\mu}_S \propto \boldsymbol{L} \cdot \boldsymbol{S} \,. \tag{7.4.12}$$

This is called **spin-orbit coupling** and when included in the atomic Hamiltonian it leads to splitting of spectral lines into doublets because of the spin-$\frac{1}{2}$ of the electron. The two yellow sodium D lines are a famous outcome. This is called atomic **fine structure**.

(iv) Unlike orbital angular momentum, it is sometimes appropriate to consider spin totally divorced from any space degrees of freedom. E.g., electron somehow confined to one atomic site in a crystal. Then

$$H \;=\; -\gamma \boldsymbol{S} \cdot \boldsymbol{B} \tag{7.4.13}$$

can be the complete Hamiltonian. If allow $\boldsymbol{B}(z) = (0, 0, B(z))$ to vary in space rather than just separating energies can instead physically separate atoms according to whether their spin states are ↑ or ↓. This is due to

$$\text{force in } z\text{-dirn} \;=\; -\frac{d}{dz}(-\gamma \boldsymbol{S} \cdot \boldsymbol{B}(z)) \;=\; -\gamma S_3 \frac{dB}{dz} \;=\; \mp \gamma \frac{\hbar}{2} \frac{dB}{dz} \tag{7.4.14}$$

This is the Stern-Gerlach experiment.
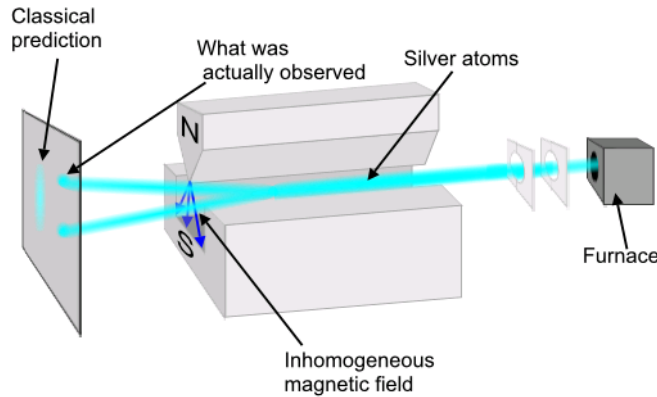
(Source: en.wikipedia.org (Theresa Knott))

(v) The proton is spin-$\frac{1}{2}$ and has a magnetic moment. Even if $l = 0$ for the electron in the H atom and no external field there is a weak interaction between the proton spin $\boldsymbol{I}$ and electron spin $\boldsymbol{S} \propto \boldsymbol{I} \cdot \boldsymbol{S}$. There are two narrowly spaced levels and transitions give radiation with wavelength $\approx 21\text{cm}$ which is observed from interstellar hydrogen.

(vi) In water the proton magnetic moments of the hydrogen nuclei interact with an external B-field, $\propto -\boldsymbol{I} \cdot \boldsymbol{B}$ to produce two levels where the transition absorbs or radiates microwaves. This forms the basis of MRI scanners.

Essential idea is that spin or angular momentum behaves like a magnet/dipole. Actually, an iron bar magnet **is** magnetized because of the sum of the microscopic electron spin magnetic dipoles in the atoms which, below the Curie temperature (T_C), prefer to align and produce the macroscopic magnetic dipole. (For $T > T_C$ the magnetization vanishes; at $T = T_C$ there is a second-order phase transition.)

The existence of an atomic magnetic moment in iron and also the preference for them to align and produce a **macroscopic** magnetization are due to the Pauli Exclusion Principle (spin-statistics theorem) – a quantum effect. Look up Hund's rule.

7.5   Addition of angular momentum

Set $\hbar = 1$ in this section. Standard relations are

$$
\begin{aligned}
\boldsymbol{J}^2|j, m\rangle &= j(j + 1)|j, m\rangle \\
J_3|j, m\rangle &= m|j, m\rangle \\
J_\pm|j, m\rangle &= \sqrt{(j \mp m)(j \pm m + 1)}|j, m \pm 1\rangle \, .
\end{aligned}
\tag{7.5.1}
$$

Consider two independent systems with angular momentum operators $\boldsymbol{J}^{(1)}$, $\boldsymbol{J}^{(2)}$ acting on spaces of states $V^{(1)}$, $V^{(2)}$ each with standard basis $\{|j_i, m_i\rangle\}$ consisting of joint eigenstates of $(\boldsymbol{J}^{(i)})^2, J_3^{(i)}$ for $i = 1, 2$.

Construct space of states for the combined system as $V = V^{(1)} \otimes V^{(2)}$ with basis (shorthand)

$$
|m_1; m_2\rangle \equiv |j_1, m_1\rangle \otimes |j_2, m_2\rangle \equiv |m_1\rangle|m_2\rangle \qquad j_1, j_2 \text{ fixed.}
\tag{7.5.2}
$$

Sum of angular momentum operators is the **total** angular momentum operator

$$
\begin{aligned}
\boldsymbol{J} &= \boldsymbol{J}^{(1)} \otimes \mathbb{I} + \mathbb{I} \otimes \boldsymbol{J}^{(2)} \\
\text{or simply} \qquad &= \boldsymbol{J}^{(1)} + \boldsymbol{J}^{(2)} \, .
\end{aligned}
\tag{7.5.3}
$$

Recall $j_i \geqslant m_i \geqslant -j_i$ for $i = 1, 2$ and so have total of $(2j_1 + 1)(2j_2 + 1)$ basis states for V.

Our aim is to find a new basis for V which consists of joint eigenstates $|J, M\rangle$ of $\boldsymbol{J}^2$ and J_3. Since

$$
J_3 = J_3^{(1)} + J_3^{(2)} \, ,
\tag{7.5.4}
$$

we have

$$
\begin{aligned}
J_3|m_1; m_2\rangle &= \left(J_3^{(1)}|m_1\rangle\right)|m_2\rangle + |m_1\rangle\left(J_3^{(2)}|m_2\rangle\right) \\
&= M|m_1; m_2\rangle \quad \text{with} \quad M = m_1 + m_2 \, .
\end{aligned}
\tag{7.5.5}
$$

So the product states are eigenstates of J_3 already and its eigenvalues have range

$$
j_1 + j_2 \geqslant M \geqslant -(j_1 + j_2) \, .
\tag{7.5.6}
$$

Note that this means that $J \leqslant j_1 + j_2$ since the maximum value of M available must be the largest value J allowed. We shall see how this works now.

It is less obvious how to find eigenstates of $\boldsymbol{J}^2$. Since $\{|m_1; m_2\rangle\}$ is a basis, we must have

$$|J, M\rangle \;=\; \sum_{m_1 + m_2 = M} C^J_{m_1 m_2} |m_1; m_2\rangle . \tag{7.5.7}$$

(Remember j_1, j_2 fixed.) We want to find

(i) which values of J are allowed;

(ii) what are the **Clebsch-Gordan** (CG) coefficients for addition of j_1, j_2:

$$C^J_{m_1 m_2} \;=\; \langle m_1; m_2 | J, M \rangle . \tag{7.5.8}$$

So we are seeking a **change of basis** for V from states with definite m_1, m_2 to states with definite $J, M \,(= m_1 + m_2)$. Of course, either basis will do since they are both complete, and it is usually the physics application that determines which basis is the most appropriate to use. These bases correspond to classification by the alternative complete commuting sets:

$$\underbrace{\boldsymbol{J}^{(1)}, J_3^{(1)}, \boldsymbol{J}^{(2)}, J_3^{(2)}}_{\substack{|j_1, m_1, j_2, m_2\rangle \\ \equiv\; |j_1, m_1\rangle |j_2, m_2\rangle}} \qquad \text{or} \qquad \underbrace{\boldsymbol{J}, J_3, \boldsymbol{J}^{(1)}, \boldsymbol{J}^{(2)}}_{|J, M, j_1, j_2\rangle} . \tag{7.5.9}$$

We now suppress the j_1, j_2 labels as they are common to all states.

The key idea is to find the top state for a given total angular momentum with

$$J_+ |J, M\rangle \;=\; 0 \quad \Leftrightarrow \quad J = M . \tag{7.5.10}$$

Given M, which is easy to determine, we therefore know J for this state. Then the others with the **same** J are found by applying J_-.

- To begin the process consider the largest value of M: $M = j_1 + j_2$. There is a unique state $|j_1\rangle |j_2\rangle$ with this eigenvalue, and so it must be a top state (can check by applying J_+). Hence,

$$| \overset{J}{j_1 + j_2}, \overset{M}{j_1 + j_2} \rangle \;=\; |j_1\rangle |j_2\rangle , \tag{7.5.11}$$

This is called the **highest weight** state since it is the state with the largest value of M possible for given J. (This terminology arises in the group theory approach.) The phase of the state on RHS $(\in V^{(1)} \otimes V^{(2)})$ is chosen by convention to be $+1$.

- Apply $J_- = J_-^{(1)} + J_-^{(2)}$ to this state on LHS and RHS, respectively. We get

$$\overset{J_-}{\sqrt{2(j_1 + j_2)}} \,|j_1 + j_2, j_1 + j_2 - 1\rangle \;=\; \overset{J_-^{(1)} + J_-^{(2)}}{\sqrt{2j_1}\, |j_1 - 1\rangle |j_2\rangle} + \sqrt{2j_2}\, |j_1\rangle |j_2 - 1\rangle \tag{7.5.12}$$

using standard formulas for V on LHS and for $V^{(1)}$, $V^{(2)}$ on RHS. The normalized state is then

$$|j_1 + j_2, j_1 + j_2 - 1\rangle \;=\; \sqrt{\frac{j_1}{j_1 + j_2}} \,|j_1 - 1\rangle |j_2\rangle + \sqrt{\frac{j_2}{j_1 + j_2}} \,|j_1\rangle |j_2 - 1\rangle . \tag{7.5.13}$$

- Continuing to apply J_- generates an entire multiplet of states $|j_1 + j_2, M\rangle$ with $j_1 + j_2 \geqslant M \geqslant -(j_1 + j_2)$. From these expressions we read off the CG coefficients. E.g.,

$$C^{j_1+j_2}_{j_1,j_2} = 1, \quad C^{j_1+j_2}_{j_1-1,j_2} = \sqrt{\frac{j_1}{j_1 + j_2}}, \quad C^{j_1+j_2}_{j_1,j_2-1} = \sqrt{\frac{j_2}{j_1 + j_2}}, \quad \ldots \quad (7.5.14)$$

- But we have not yet found all $|J, M\rangle$ states. We started from a unique state with $M = j_1 + j_2$. At the next level down, with $M = j_1 + j_2 - 1$, there are two states:

$$|j_1 - 1\rangle|j_2\rangle \quad \text{and} \quad |j_1\rangle|j_2 - 1\rangle. \quad (7.5.15)$$

One combination is identified above as $|j_1 + j_2, j_1 + j_2 - 1\rangle$. The **other**, orthogonal, combination (unique up to a phase) must be a new top state

$$| \overset{J}{j_1 + j_2 - 1}, \overset{M}{j_1 + j_2 - 1}\rangle = \sqrt{\frac{j_1}{j_1 + j_2}} \, |j_1\rangle|j_2-1\rangle - \sqrt{\frac{j_2}{j_1 + j_2}} \, |j_1-1\rangle|j_2\rangle. \quad (7.5.16)$$

The overall phase on the RHS is chosen by convention.

- Now proceed as before:

  (i) generate the multiplet with $J = j_1 + j_2 - 1$ by applying J_-;
  (ii) look for a possible new top state at level $M = j_1 + j_2 - 2$;
  (iii) repeat until all states exhausted.

The general pattern can be depicted as follows.
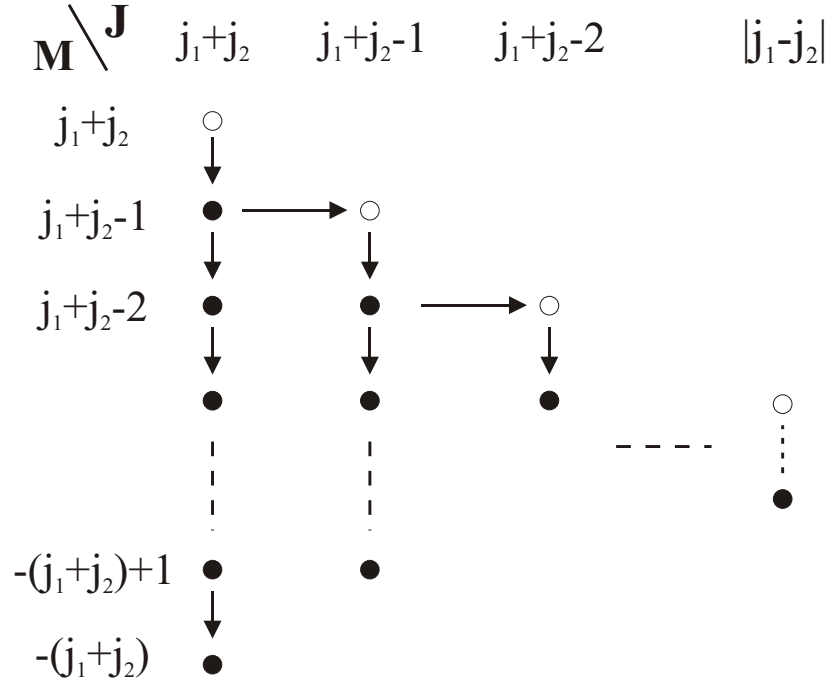
where

$$
\begin{array}{llll}
\circ & \text{top states} & \downarrow & \text{apply } J_- \\
\bullet & \text{other states} & \rightarrow & \text{unique state } \perp \text{ others} \\
& & & \text{with same } M \text{ value}
\end{array} \tag{7.5.17}
$$

Can check that top states $|\psi\rangle$ with J_3 eigenvalue M are annihilated by J_+ directly. This is also guaranteed by

$$
|\psi\rangle \perp J_-|J, M+1\rangle \ \forall \ J > M \quad \text{by our construction.} \tag{7.5.18}
$$

Thus,

$$
\langle J, M+1|J_+|\psi\rangle \ = \ 0 \quad \forall \ J > M \quad \Leftrightarrow \quad J_+|\psi\rangle \ = \ 0 \ . \tag{7.5.19}
$$

The whole process stops with $J = |j_1 - j_2|$ by counting. The number of states in the alternative bases must be the same.

$$
\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) \ = \ (2j_1+1)(2j_2+1) \ . \tag{7.5.20}
$$

We now have the answers to our original questions:

(i) $j_1 + j_2 \geqslant J \geqslant |j_1 - j_2|$ in integer steps. E.g.,

$$
\begin{array}{lll}
j_1=\tfrac{1}{2}, \ j_2=\tfrac{1}{2} & \Rightarrow & J=1, 0 \\
j_1=1, \ j_2=\tfrac{1}{2} & \Rightarrow & J=\tfrac{3}{2}, \tfrac{1}{2} \\
j_1=1, \ j_2=1 & \Rightarrow & J=2, 1, 0
\end{array} \tag{7.5.21}
$$

The range of J values matches bounds for addition of classical vectors $\boldsymbol{J} = \boldsymbol{J}^{(1)} + \boldsymbol{J}^{(2)}$ with lengths of J, j_1, j_2.

(ii) Clebsch-Gordan coefficients are found by explicit calculation of states for given j_1 and j_2.

Simplest example is for

$$
j_1 = j_2 = \tfrac{1}{2} \ , \quad |m_1\rangle|m_2\rangle \ m_i = \pm\tfrac{1}{2} \ , \quad 4 \text{ states.} \tag{7.5.22}
$$

$$
\begin{array}{lll}
|1, 1\rangle & = \ |\tfrac{1}{2}\rangle|\tfrac{1}{2}\rangle & \text{top state with } M = 1 \\
J_- & = \ J_-^{(1)} + J_-^{(2)} & \text{gives} \\
\sqrt{2}|1, 0\rangle & = \ |-\tfrac{1}{2}\rangle|\tfrac{1}{2}\rangle + |\tfrac{1}{2}\rangle|-\tfrac{1}{2}\rangle & \Rightarrow \\
|1, 0\rangle & = \ \frac{1}{\sqrt{2}}\left(|-\tfrac{1}{2}\rangle|\tfrac{1}{2}\rangle + |\tfrac{1}{2}\rangle|-\tfrac{1}{2}\rangle\right) & \\
\sqrt{2}|1, -1\rangle & = \ \frac{1}{\sqrt{2}}\left(|-\tfrac{1}{2}\rangle|-\tfrac{1}{2}\rangle + |-\tfrac{1}{2}\rangle|-\tfrac{1}{2}\rangle\right) & \Rightarrow \\
|1, -1\rangle & = \ |-\tfrac{1}{2}\rangle|-\tfrac{1}{2}\rangle & \text{completes } J = 1 \text{ multiplet}
\end{array} \tag{7.5.23}
$$

Then

$$
|0, 0\rangle \ = \ \frac{1}{\sqrt{2}}\left(|-\tfrac{1}{2}\rangle|\tfrac{1}{2}\rangle - |\tfrac{1}{2}\rangle|-\tfrac{1}{2}\rangle\right) \tag{7.5.24}
$$

with $M = 0$ and $\perp$ $|1, 0\rangle$. Need a phase convention to decide overall sign of top states.

Compare this results with the combination of spin states in Eqns. (5.5.14) and (5.5.15) with $|\frac{1}{2}\rangle = |\uparrow\rangle$, $|-\frac{1}{2}\rangle = |\downarrow\rangle$ which were found previously by demanding definite symmetry; they are precisely the same.

Have

$$
\begin{array}{llll}
3 & \text{(triplet)} & J = 1 & \text{states} & \text{symmetric} \\
1 & \text{(singlet)} & J = 0 & \text{state} & \text{antisymmetric}
\end{array}
\tag{7.5.25}
$$

Indeed, the permutation group and its representations are often central to constructing multiplets in this way.

Tables for CG coefficients can be found in the Particle Data Group (PDG) Tables (http://pdg.lbl.gov/2013/reviews/rpp2012-rev-clebsch-gordan-coefs.pdf). The PDG collate all reviews and tables for properties of elementary particles.

The table for $2 \otimes 1$ giving states with $M = 1$ is

m_1	m_2	J M	3 +1	2 +1	1 +1
2	-1		1/15	1/3	3/5
1	0		8/15	1/6	-3/10
0	1		2/5	-1/2	1/10

Take $\sqrt{}$ but keep the sign. E.g., $-3/10 \rightarrow -\sqrt{3/10}$.

8   Transformations and Symmetries

8.1   Introduction and an Example

Given a unitary operator U define a **transformation** of a quantum system to be **either** a map of states only:

$$
|\psi\rangle \;\mapsto\; U|\psi\rangle \quad \langle\phi| \;\mapsto\; \langle\phi|U^\dagger \,,
\tag{8.1.1}
$$

or a map of operators only:

$$
A \;\mapsto\; U^\dagger A U \,.
\tag{8.1.2}
$$

These are equivalent. Either way, inner products of states $\langle\phi|\psi\rangle$ left unchanged but matrix elements change:

$$
\langle\phi|A|\psi\rangle \;\mapsto\; \langle\phi|U^\dagger A U|\psi\rangle \,.
\tag{8.1.3}
$$

Unlike the change of picture we change states or operators but not both. Such a transformation is a **symmetry** of the quantum system if

$$U^\dagger H U \;=\; H \quad \text{or, equivalently,} \quad [U, H] \;=\; 0 \;. \tag{8.1.4}$$

It then follows that

- in S-picture if $|\psi(t)\rangle$ is a solution of the Schrödinger equation then so is $U|\psi(t)\rangle$;

- in H-picture if $A(t)$ is a solution of the Heisenberg EoM then so is $U^\dagger A(t) U$.

Now consider a group G and transformations of a QM system $U(g)$ for each $g \in G$ with

$$\begin{aligned}
U(g_1)U(g_2) \;&=\; U(g_1 g_2) \\
U(1_G) \;&=\; \mathbb{I} \\
U(g^{-1}) \;&=\; U(g)^{-1} \;=\; U(g)^\dagger \;.
\end{aligned} \tag{8.1.5}$$

In any given case $U(g)$ is a **representation** of G. Our aim is to find the unitary operators $U(g)$ when G is a group of translations, rotations or reflections. In these cases we know how G acts geometrically

$$\boldsymbol{x} \;\mapsto\; g(\boldsymbol{x}) \;, \tag{8.1.6}$$

and similarly for momentum $\boldsymbol{p}$. We infer the action on position eigenstates

$$U(g)|\boldsymbol{x}\rangle \;=\; |g(\boldsymbol{x})\rangle \tag{8.1.7}$$

and on operators

$$U(g)^\dagger \, \hat{\boldsymbol{x}} \, U(g) \;=\; g(\hat{\boldsymbol{x}}) \;. \tag{8.1.8}$$

These statements are equivalent. E.g., assuming the second one

$$\hat{\boldsymbol{x}} \, U(g)|\boldsymbol{x}\rangle = U(g)g(\hat{\boldsymbol{x}})|\boldsymbol{x}\rangle = g(\boldsymbol{x})\left(U(g)|\boldsymbol{x}\rangle\right) \;, \tag{8.1.9}$$

and so confirm the first.

On a general state

$$|\psi\rangle \;\mapsto\; U(g)|\psi\rangle \tag{8.1.10}$$

and the position space wavefunction of the new state is

$$\langle\boldsymbol{x}|U(g)|\psi\rangle = \left(U(g)^\dagger|\boldsymbol{x}\rangle\right)^\dagger|\psi\rangle = \langle g^{-1}(\boldsymbol{x})|\psi\rangle \;. \tag{8.1.11}$$

So the effect of the transformation on the wavefunction is the change

$$\psi(\boldsymbol{x}) \;\mapsto\; \psi(g^{-1}(\boldsymbol{x})) \;. \tag{8.1.12}$$

Simplest example is translation in one dimension

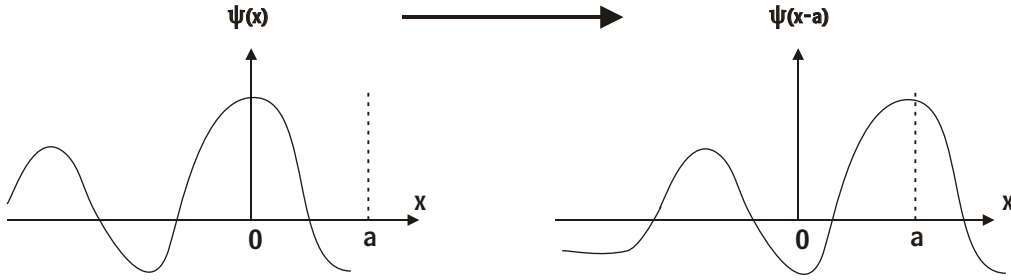$$x \;\mapsto\; g_a(x) \;=\; x + a \tag{8.1.13}$$

and write $U(a) \equiv U(g_a)$ to simplify notation. Then must have

$$
\begin{aligned}
U(a)|x\rangle &= |x + a\rangle \\
U(a)^{\dagger}\, \hat{x}\, U(a) &= \hat{x} + a \,,
\end{aligned}
\tag{8.1.14}
$$

but we showed in section 2 that

$$
U(a) = e^{-ia\hat{p}/\hbar}
\tag{8.1.15}
$$

has precisely these properties. The effect of translation by a on $\psi(x)$ should be $\psi(x-a)$ which is illustrated by the picture below.

Confirmation: on wavefunctions

$$
\hat{p} \;\rightarrow\; -i\hbar\frac{\partial}{\partial x}\,, \quad U(a) \;\rightarrow\; \exp\left(-a\frac{\partial}{\partial x}\right)
\tag{8.1.16}
$$

and so

$$
\begin{aligned}
U(a)\psi(x) &= \exp\left(-a\frac{\partial}{\partial x}\right)\psi(x) \\
&= \psi(x) - a\,\psi'(x) + \frac{1}{2!}a^2\,\psi''(x) - \ldots \\
&= \psi(x - a) \qquad \text{Taylor's theorem,}
\end{aligned}
\tag{8.1.17}
$$

as expected. Because of its special role in $U(a)$ the momentum $\hat{p}$ is called the **generator** of translations.

8.2   Generators and conservation laws

The action of many transformations such as translations, already discussed above, and rotations can be formulated in terms of groups. In the case of rotations the group is $SO(3)$, the group of orthogonal 3×3 real matrices of unit determinant. In many cases the relevant group is non-abelian meaning that successive group operations do not commute; $SO(3)$ is such an example. If $R(\theta, \boldsymbol{n}) \in SO(3)$ is a rotation by θ about the axis $\boldsymbol{n}$ then in general

$$
R(\theta, \boldsymbol{n})R(\phi, \boldsymbol{m}) \neq R(\phi, \boldsymbol{m})R(\theta, \boldsymbol{n}) \,.
\tag{8.2.1}
$$

However, for fixed $\boldsymbol{n}$ the elements $R(\theta, \boldsymbol{n})$ do commute and form a one-parameter, abelian, subgroup:

$$R(\theta, \boldsymbol{n})R(\phi, \boldsymbol{n}) = R(\phi, \boldsymbol{n})R(\theta, \boldsymbol{n}) = R(\theta + \phi, \boldsymbol{n}) \ . \tag{8.2.2}$$

The translation group is another example. It is with general ideas about such abelian subgroups that we begin.

Consider some **continuous** group G, and let g_α (α a real number) be a one parameter family of group elements with

$$g_\alpha g_\beta = g_\beta g_\alpha = g_{\alpha+\beta} \ , \quad g_0 = 1_G \ , \tag{8.2.3}$$

and assume we know

$$g_\alpha(A) = A + \alpha f(A) + O(\alpha^2) \tag{8.2.4}$$

for quantities of interest A (positions, momenta, etc.). Write the corresponding unitary operators as

$$U(\alpha) = U(g_\alpha) \qquad \text{to simplify notation,} \tag{8.2.5}$$

and then have

$$U(\alpha)^\dagger A \, U(\alpha) = g_\alpha(A) \ . \tag{8.2.6}$$

Define

$$Q = i\hbar \left. \frac{\partial U(\alpha)}{\partial \alpha} \right|_{\alpha=0} \tag{8.2.7}$$

so that

$$
\begin{aligned}
U(\delta\alpha) &= \mathbb{I} - \frac{i}{\hbar}\delta\alpha \, Q + O(\delta\alpha^2) \\
U(-\delta\alpha) &= \mathbb{I} + \frac{i}{\hbar}\delta\alpha \, Q + O(\delta\alpha^2) \ .
\end{aligned}
\tag{8.2.8}
$$

Then

$$U(-\delta\alpha) = U(\delta\alpha)^{-1} = U(\delta\alpha)^\dagger \quad \Rightarrow \quad Q = Q^\dagger : \quad Q \text{ is an observable.} \tag{8.2.9}$$

Also have

$$U(\alpha + \delta\alpha) = U(\alpha)U(\delta\alpha) = U(\delta\alpha)U(\alpha) \ , \tag{8.2.10}$$

so deduce

$$[Q, U(\alpha)] = 0 \ . \tag{8.2.11}$$

From above have

$$\frac{\partial U(\alpha)}{\partial \alpha} = -\frac{i}{\hbar}Q \, U(\alpha) \quad \Rightarrow \quad U(\alpha) = \exp\left(-i\frac{\alpha}{\hbar}Q\right) \quad \text{given} \quad U(0) = 1. \tag{8.2.12}$$

Q is the **generator** of this family of transformations, the one-parameter subgroup, within G. To find Q we equate

$$g_\alpha(A) = A + \alpha f(A) + O(\alpha^2) \tag{8.2.13}$$

with

$$U(\alpha)^\dagger A \, U(\alpha) \;=\; \left(\mathbb{I} + \frac{i}{\hbar}\alpha\,Q + \dots\right) A \left(\mathbb{I} - \frac{i}{\hbar}\alpha\,Q + \dots\right)$$

$$=\; A + \frac{i}{\hbar}\alpha[Q, A] + O(\alpha^2) \tag{8.2.14}$$

to obtain

$$[Q, A] = -i\hbar f(A) \,. \tag{8.2.15}$$

Knowing the RHS for any A determines Q. Conversely, the behaviour of any quantity under the transformation is fixed by its commutation relation with the generator.

Now suppose the continuous family g_α corresponds to a symmetry of the quantum system

$$[U(\alpha), H] = 0 \quad \Leftrightarrow \quad [Q, H] = 0 \,. \tag{8.2.16}$$

The second equation says that the **observable** Q is a **conserved quantity**:

- in S-picture can choose joint eigenstates of H and Q

$$Q|\psi(0)\rangle = q|\psi(0)\rangle \quad \Rightarrow \quad Q|\psi(t)\rangle = q|\psi(t)\rangle \,. \tag{8.2.17}$$

- In H-picture expect $Q(t)$ in general but here

$$\frac{dQ}{dt} = -\frac{i}{\hbar}[Q, H] = 0. \tag{8.2.18}$$

Noether's Theorem: for each continous transformation of a quantum system there is an hermitian generator, and if the transformation is a symmetry this generator is conserved; it is called the **Noether charge**.

Example: system of particles labelled by $r, s, \dots$ with positions $\hat{\boldsymbol{x}}^{(r)}$ and momenta $\hat{\boldsymbol{p}}^{(r)}$ which obey

$$[\hat{x}_i^{(r)}, \hat{p}_j^{(s)}] = i\hbar\,\delta_{ij}\delta^{rs} \,. \tag{8.2.19}$$

The transformation is translation along the k-axis.

$$\begin{aligned}
g_a(\hat{x}_i^{(r)}) &= \hat{x}_i^{(r)} + a\delta_{ik} \,, & g_a(\hat{p}_j^{(r)}) &= 0 & \Rightarrow \\
f(\hat{x}_i^{(r)}) &= \delta_{ik} \,, & f(\hat{p}_i^{(r)}) &= 0 &
\end{aligned} \tag{8.2.20}$$

for all r. Then the generators must obey

$$[Q, \hat{x}_i^{(r)}] = -i\hbar\delta_{ik} \,, \quad [Q, \hat{p}_i^{(r)}] = 0 \tag{8.2.21}$$

The solution is $Q = \hat{P}_k = \sum_r \hat{p}_k^{(r)}$, the total momentum in the k-direction.

In general, translations by $\boldsymbol{a}$ are generated by the total momentum $\hat{\boldsymbol{P}}$ with corresponding unitary operator

$$U(\boldsymbol{a}) \;=\; \exp\left(-\frac{i}{\hbar}\boldsymbol{a}\cdot\hat{\boldsymbol{P}}\right) \,. \tag{8.2.22}$$

Noether's Theorem: for particles interacting through potential depending only on $\hat{x}_i^{(r)} - \hat{x}_i^{(s)}$, H is translation invariant and total momentum $\hat{\boldsymbol{P}}$ is conserved.

⌈ Note that there are conserved quantities in classical dynamics such as momentum for translation-invariant systems and angular momentum for rotationaly-invariant systems.
⌋

8.3   Angular Momentum and Rotations

As stated earlier, rotations form a non-abelian group: $[g_1, g_2] \neq 0$, in general. For fixed axis $\boldsymbol{n}$ **do** have an abelian subgroup of rotations g_θ through angle θ so can use approach above.

For A a scalar

$$g_\theta(A) = A \quad \text{unchanged} \quad \Rightarrow \quad f(A) = 0 . \tag{8.3.1}$$

For $\boldsymbol{v} = (v_1, v_2, v_3)$ a vector,

$$g_\theta(\boldsymbol{v}) = \boldsymbol{v} + \theta \boldsymbol{n} \wedge \boldsymbol{v} + O(\theta^2) , \quad \Rightarrow \quad f(\boldsymbol{v}) = \boldsymbol{n} \wedge \boldsymbol{v} . \tag{8.3.2}$$

Write the corresponding unitary operator as

$$U(\theta \boldsymbol{n}) = \mathbb{I} - \frac{i}{\hbar} \theta Q + O(\theta^2) . \tag{8.3.3}$$

We need to determine Q. For a single particle both $\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{p}}$ must transform as vectors:

$$\begin{aligned}
[Q, \hat{\boldsymbol{x}}] &= -i\hbar \, \boldsymbol{n} \wedge \hat{\boldsymbol{x}} \\
[Q, \hat{\boldsymbol{p}}] &= -i\hbar \, \boldsymbol{n} \wedge \hat{\boldsymbol{p}} .
\end{aligned} \tag{8.3.4}$$

Recall the commutators with orbital angular momentum

$$\begin{aligned}
[L_i, \hat{x}_j] &= i\hbar \, \varepsilon_{ijk} \hat{x}_k \\
[L_i, \hat{p}_j] &= i\hbar \, \varepsilon_{ijk} \hat{p}_k
\end{aligned} \tag{8.3.5}$$

These imply that we identify

$$Q = \boldsymbol{n} \cdot \boldsymbol{L} \tag{8.3.6}$$

since it produces the correct commutators. E.g.,

$$\begin{aligned}
[n_i L_i, \hat{x}_j] &= n_i i\hbar \, \varepsilon_{ijk} \hat{x}_k \\
&= -i\hbar \, (\boldsymbol{n} \wedge \hat{\boldsymbol{x}})_j .
\end{aligned} \tag{8.3.7}$$

For a **spinless** particle this is what we seek. Note that $\boldsymbol{L}$ transforms as a vector:

$$[Q, \boldsymbol{L}] = -i\hbar \, \boldsymbol{n} \wedge \boldsymbol{L} . \tag{8.3.8}$$

For a particle **with** spin the generator above needs to be modified to ensure that $\boldsymbol{S}$ also transforms as a vector

$$[Q, \boldsymbol{S}] = -i\hbar \, \boldsymbol{n} \wedge \boldsymbol{S} , \tag{8.3.9}$$

and this is achieved by taking

$$Q = \boldsymbol{n} \cdot \boldsymbol{J} \quad \text{with} \quad \boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \quad \text{the total angular momentum.} \tag{8.3.10}$$

(Recall that $[S_i, \hat{x}_j] = [S_i, \hat{p}_j] = [S_i, L_j] = 0$.)

This analysis can easily be extended to many particles. For a **general** quantum system, the unitary operator for rotation through $\boldsymbol{\theta} = \theta \boldsymbol{n}$ is

$$U(\boldsymbol{\theta}) = \exp\left(-\frac{i}{\hbar} \boldsymbol{\theta} \cdot \boldsymbol{J} \right) , \tag{8.3.11}$$

where $\boldsymbol{J}$ is the **total** angular momentum.

Noether's Theorem: for a rotationally invariant quantum system the total angular momentum $\boldsymbol{J}$ is conserved. E.g., particle with Hamiltonian

$$H = \frac{1}{2m}\hat{\boldsymbol{p}}^2 + V(|\hat{\boldsymbol{x}}|) + U(|\hat{\boldsymbol{x}}|)\,\boldsymbol{L}\cdot\boldsymbol{S}\;. \tag{8.3.12}$$

Note the spin-orbit coupling term in $\boldsymbol{L}\cdot\boldsymbol{S}$. Clearly invariant under rotations so

$$[J_i, H] = 0 \quad \text{or} \quad \boldsymbol{J} \;\; \text{conserved.} \tag{8.3.13}$$

Note that $\boldsymbol{L}$ and $\boldsymbol{S}$ are not separately conserved unless $U = 0$. However, $\boldsymbol{L}^2$ and $\boldsymbol{S}^2$ **are** conserved as is $\boldsymbol{J}^2$. So we can write $(\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S})$

$$\boldsymbol{L}\cdot\boldsymbol{S} = \frac{\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2}{2} = \frac{1}{2}\hbar^2(j(j+1) - l(l+1) - s(s+1)) \tag{8.3.14}$$

for eigenstates of $\boldsymbol{J}^2, \boldsymbol{L}^2, \boldsymbol{S}^2$ with eigenvalues (j, l, s), respectively.

We now have **alternative** definitions of a scalar operator A and a vector operator $\boldsymbol{v}$ in terms of commutation relations:

$$\begin{aligned} \text{scalar:} &\quad [J_i, A] &=& \;\; 0 \\ \text{vector:} &\quad [J_i, v_j] &=& \;\; i\hbar\,\varepsilon_{ijk}v_k\;. \end{aligned} \tag{8.3.15}$$

Have $\hat{\boldsymbol{x}}, \hat{\boldsymbol{p}}, \boldsymbol{L}, \boldsymbol{S}, \boldsymbol{J}$ are vector operators.

Now look at action of rotations on states.

- On angular momentum states $|j, m\rangle$, fixed j, the angular momentum generators J_i can be **represented** as $(2j + 1) \times (2j + 1)$ matrices (see section 7.3).

- Then

$$U(\boldsymbol{\theta}) = \exp\left(-\frac{i}{\hbar}\theta\boldsymbol{n}\cdot\boldsymbol{J}\right) \tag{8.3.16}$$

  can be computed easily in some cases.

- $j = 0$: single state $|0, 0\rangle$ with $\boldsymbol{J}|0, 0\rangle = 0$. Hence

$$U(\boldsymbol{\theta}) = \mathbb{I} \quad \Rightarrow \quad |0, 0\rangle \mapsto |0, 0\rangle \quad \text{scalar} \tag{8.3.17}$$

- $j = 1$: states $|1, m\rangle$ with $m = 0, \pm 1$. Generators are 3×3 matrices. E.g.,

$$J_3 = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{8.3.18}$$

  Consider for simplicity rotations about the 3 (or z) axis – J_3 is diagonal in our representation. Then

$$U(\theta\hat{\boldsymbol{k}}) = \exp(-\frac{i}{\hbar}\theta J_3) = \exp\left[-i\theta\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\right] = \begin{pmatrix} e^{-i\theta} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{i\theta} \end{pmatrix}. \tag{8.3.19}$$

So under this rotation states behave as

$$
\begin{aligned}
|1, \pm 1\rangle &\;\mapsto\; e^{\mp i\theta}|1, \pm 1\rangle \\
|1, 0\rangle &\;\mapsto\; |1, 0\rangle \,.
\end{aligned}
\tag{8.3.20}
$$

Deduce that the states behave as the (spherical) components of a **vector**. More familiar if we compare with same rotation on coordinates in spherical basis (bear in mind for later):

$$
(x \pm iy) \;\mapsto\; (x_\theta \pm iy_\theta) \;=\; e^{\pm i\theta}(x \pm iy) \,, \quad z \;\mapsto\; z \,. \tag{8.3.21}
$$

(Remember, wavefunction transforms with $-\theta$: $\psi(\boldsymbol{x}) \mapsto \psi(\boldsymbol{x}_\theta)$.)

- $j = \frac{1}{2}$: states $|\frac{1}{2}, \pm\frac{1}{2}\rangle$ (or $|\uparrow\rangle$ and $|\downarrow\rangle$) on which

$$
\boldsymbol{J} = \frac{\hbar}{2}\boldsymbol{\sigma} \,. \tag{8.3.22}
$$

The property that $(\boldsymbol{n} \cdot \boldsymbol{\sigma})^2 = \mathbb{I}_2$ allows explicit computation of rotation operator for any $\boldsymbol{\theta}$.

$$
\begin{aligned}
U(\boldsymbol{\theta}) &\;=\; \exp\left(-\frac{i}{\hbar}\theta \boldsymbol{n} \cdot \boldsymbol{J}\right) = \exp\left(-\frac{i\theta}{2}\boldsymbol{n} \cdot \boldsymbol{\sigma}\right) \\
&\;=\; \sum_{p=0}^{\infty} \frac{1}{p!}\left(-\frac{i\theta}{2}\right)^p (\boldsymbol{n} \cdot \boldsymbol{\sigma})^p \\
&\;=\; \cos\frac{\theta}{2} - i\,\boldsymbol{n} \cdot \boldsymbol{\sigma}\,\sin\frac{\theta}{2} \,.
\end{aligned}
\tag{8.3.23}
$$

The effect of a rotation on a general state is

$$
|\chi\rangle \;\mapsto\; U(\boldsymbol{\theta})|\chi\rangle \;=\; \left(\cos\frac{\theta}{2} - i\,\boldsymbol{n} \cdot \boldsymbol{\sigma}\,\sin\frac{\theta}{2}\right)|\chi\rangle \,. \tag{8.3.24}
$$

But note the appearance of $\theta/2$ in final result. Under any rotation by 2π we have

$$
|\chi\rangle \;\mapsto\; U(2\pi\boldsymbol{n})|\chi\rangle \;=\; -\,|\chi\rangle \,. \tag{8.3.25}
$$

We do not get exactly the same state vector after rotation by 2π, which may seem surprising. However, $|\chi\rangle$ and $-|\chi\rangle$ have same physical content. Change in sign can be a real effect if e.g. have two particles and rotate just one; change in sign can make the difference between constructive and destructive interference.

Under rotation by 4π get exactly the same state

$$
|\chi\rangle \;\mapsto\; U(4\pi\boldsymbol{n})|\chi\rangle \;=\; |\chi\rangle \,. \tag{8.3.26}
$$

Similar behaviour under 2π and 4π rotations for any states with half-integral spin.

8.4   Reflections and Parity

Simplest example of a **discrete** transformtion is **parity** or spatial inversion

$$P: \boldsymbol{x} \mapsto -\boldsymbol{x} . \tag{8.4.1}$$

This is not part of a continuous family of isometries connected to the identity (unlike e.g., rotations). Any reflection in a plane can be achieved by composing P with rotations.

The corresponding unitary operator acts on position eigenstates as

$$
\begin{aligned}
U|\boldsymbol{x}\rangle &= |-\boldsymbol{x}\rangle \\
\text{so} \quad U^2 &= 1 \\
\Rightarrow \quad U^\dagger &= U^{-1} = U .
\end{aligned}
\tag{8.4.2}
$$

There is no one-parameter family and so no generator, but U itself is hermitian and thus an observable:

$$U|\psi\rangle = \eta_\psi|\psi\rangle \tag{8.4.3}$$

and

$$U^2 = \mathbb{I} \Rightarrow \eta_\psi = \pm 1, \qquad \text{the parity of the state.} \tag{8.4.4}$$

The corresponding action on operators is

$$
\begin{aligned}
U\,\hat{\boldsymbol{x}}\,U &= -\hat{\boldsymbol{x}} \\
U\,\hat{\boldsymbol{p}}\,U &= -\hat{\boldsymbol{p}} \\
U\,\boldsymbol{L}\,U &= \boldsymbol{L} \qquad (\boldsymbol{L} = \hat{\boldsymbol{x}} \wedge \hat{\boldsymbol{p}}) \\
U\,\boldsymbol{S}\,U &= \boldsymbol{S} \\
U\,\boldsymbol{J}\,U &= \boldsymbol{J} .
\end{aligned}
\tag{8.4.5}
$$

Parity is a symmetry of a quantum system if

$$U\,H\,U = H , \tag{8.4.6}$$

and then we can choose joint eigenstates of H and U. Recall in 1D

$$H = \frac{1}{2m}\hat{p}^2 + V(\hat{x}) \tag{8.4.7}$$

and if $V(\hat{x}) = V(-\hat{x})$ can choose energy eigenstates to have definite parity: even or odd functions. In 3D with

$$H = \frac{1}{2m}\hat{\boldsymbol{p}}^2 + V(|\hat{\boldsymbol{x}}|) \tag{8.4.8}$$

have definite orbital angular momentum states $\psi_{lm}(\boldsymbol{x})$ obeying

$$
\begin{aligned}
\psi_{lm}(-\boldsymbol{x}) &= (-1)^l\psi_{lm}(\boldsymbol{x}) \\
\Rightarrow \quad \eta_\psi &= (-1)^l ,
\end{aligned}
\tag{8.4.9}
$$

which are thus states of definite parity. Note that for two-particle system P **interchanges** the spatial positions and so its eigenvalue determines the spatial symmetry of the state: symmetric $\eta_\psi = 1$, anti-symmetric $\eta_\psi = -1$.

There is also a notion of **intrinsic** parity where a particle state changes as

$$U|a\rangle \;=\; \eta_a|a\rangle, \qquad \eta_a = \pm 1\,. \tag{8.4.10}$$

As with spin this is not attribtable to any internal structure; it is a property of the particle concerned. Values for some particles can be chosen by convention but then others are determined. In general, for a system of particles,

$$\left\{\begin{array}{c} \text{total} \\ \text{parity} \end{array}\right\} \;=\; \left\{\begin{array}{c} \text{spatial} \\ \text{parity} \end{array}\right\} \;\times\; \left\{\begin{array}{c} \text{product of all} \\ \text{intrinsic parities} \end{array}\right\} \tag{8.4.11}$$

E.g., particles a and b with relative position $\hat{\boldsymbol{x}}$
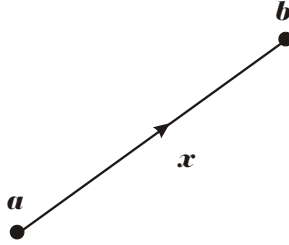
in angular momentum state $\psi_{lm}(\boldsymbol{x})$. The total parity is

$$(-1)^l \eta_a \eta_b\,. \tag{8.4.12}$$

Note that parity gives rise to a **multiplicative** conservation law in contrast to the **additive** conservation of momentum or angular momentum.
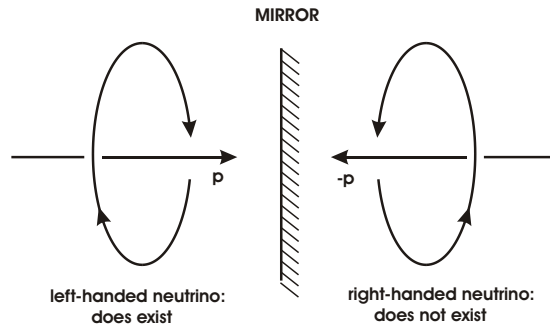
Parity is (famously) not a symmetry of all fundamental interactions; it is conserved for electromagnetic and strong nuclear processes but not for weak nuclear processes responsible for effects like β-decay

$$\begin{array}{ccc} n & \rightarrow & p\; e\; \bar\nu \\ \text{neutron} & & \text{proton, electron, anti-neutrino} \end{array} \tag{8.4.13}$$

If P is a symmetry we cannot tell if we are watching a physical process directly or viewing it in a mirror. Weak processes involve the neutrino, a particle of spin-$\frac{1}{2}$ which is effectively massless and so travels close to the speed of light. A major property is that it has -ve helicity which means that

$$\frac{\boldsymbol{S}\cdot\boldsymbol{p}}{|\boldsymbol{p}|} \;=\; -\tfrac{1}{2}\,. \tag{8.4.14}$$

It is "left-handed"

left-handed neutrino:
does exist

right-handed neutrino:
does not exist

and there is no +ve helicity, "right-handed", neutrino. The anti-neutrino is "right-handed" with no "left-handed" version. But under a P transformation, illustrated by the mirror, "left-handed" $\leftrightarrow$ "right-handed":

$$U \, \boldsymbol{S} \cdot \boldsymbol{p} \, U \;=\; -\, \boldsymbol{S} \cdot \boldsymbol{p} \tag{8.4.15}$$

and so in the looking-glass world Alice only sees "right-handed" neutrinos which are unphysical for us: parity is broken.

Other discrete symmetries (not considered in detail here):

$$T: \qquad \text{time reversal}$$
$$C: \qquad \text{charge conjugation - interchange of particles and anti-particles}$$

If we apply CP to the neutrino then the mirror image above now beomes a right-handed **anti-neutrino** which **does** exist. So CP **is** a symmetry of weak nuclear processes (well almost). The combination CPT is always a symmetry of relativistic quantum mechanics (Quantum Field Theory, QFT).

Example of use of conservation laws and intrinsic parity:

$$\pi \, d \;\to\; n \, n \tag{8.4.16}$$

$$\pi \text{ pion,} \quad d \text{ deuteron } (p\,n \text{ bound state}), \quad n \text{ neutron.}$$
$$S_\pi = 0 \qquad\qquad S_d = 1 \qquad\qquad S_n = \tfrac{1}{2} \tag{8.4.17}$$

- This is a strong interaction process – total angular momentum, $\boldsymbol{J}$, and parity conserved.

- $\pi \, d$ system:

$$\text{Orbital ang. mom.} \quad l = 0 \;\; \text{(given)}, \;\; \text{total spin} \;\; S = 1$$
$$\Rightarrow \quad \text{total ang. mom.} \quad j = 1. \tag{8.4.18}$$

- $n\,n$ system:

    Orbital ang. mom. l unknown to begin with but symmetry of spatial wavefunction $(-1)^l$. Total spin $S = 0$ or 1.

    - $\star$ $S = 0 \Rightarrow$ antisymmetric spin state, so Fermi statistics requires l even. But since $S = 0$ have that $j = l$, and so process forbidden since $j = 1$ from $\boldsymbol{J}$ conservation.

    - $\star$ $S = 1 \Rightarrow$ symmetric spin state, so Fermi statistics requires l odd. But $j = l - 1, l, l + 1$ and have $j = 1$ by $\boldsymbol{J}$ conservation and so deduce

$$j = l = S = 1 \,. \tag{8.4.19}$$

    - $\star$ Concerning parity. The deuteron is predominantly an s-wave bound state ($l = 0$) and so $\eta_d = (-1)^0 \eta_n \eta_p$; but $\eta_n = \eta_p$ (they are from the same nucleon family) and so $\eta_d = 1$.

$$(-1)^0 \eta_\pi \eta_d \;=\; (-1)^1 \eta_n^2$$
$$\eta_d = 1 \;\Rightarrow\; \eta_\pi = -1 \,. \tag{8.4.20}$$

9   Time-dependent Perturbation Theory

Consider a system with Hamiltonian

$$H = H_0 + V(t), \tag{9.1}$$

where H_0 is time-independent with known eigenstates and eigenvalues and $V(t)$ small in some sense (remember perturbation theory earlier). I have suppressed the dependence of $V(t)$ on space coordinates.

★ Our aim: to calculate the effect of $V(t)$ order-by-order (actually stop at first order) and, in particular, calculate probabilities for transitions between eigenstates of H_0 as functions of time. This is a **dynamical** question even if V is time-independent.

9.1   The interaction picture

Start in the Schrödinger picture. States obey

$$i\hbar \frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle = (H_0 + V(t))|\psi(t)\rangle. \tag{9.1.1}$$

The **interaction** picture is defined by moving the 'known' part of the time evolution, which is due to H_0, from states to operators:

$$\begin{aligned}
|\overline{\psi(t)}\rangle &= e^{iH_0 t/\hbar}|\psi(t)\rangle \\
\overline{A(t)} &= e^{iH_0 t/\hbar} A(t) e^{-iH_0 t/\hbar}.
\end{aligned} \tag{9.1.2}$$

The remaining time dependence of the states is then given by

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t}|\overline{\psi(t)}\rangle &= e^{iH_0 t/\hbar}\left(-H_0 + i\hbar\frac{\partial}{\partial t}\right)|\psi(t)\rangle \\
&= e^{iH_0 t/\hbar} V(t)|\psi(t)\rangle \\
&= e^{iH_0 t/\hbar} V(t) e^{-iH_0 t/\hbar} e^{iH_0 t/\hbar}|\psi(t)\rangle
\end{aligned}$$

$$\text{or} \qquad i\hbar \frac{\partial}{\partial t}|\overline{\psi(t)}\rangle = \overline{V(t)}\,|\overline{\psi(t)}\rangle. \tag{9.1.3}$$

This can be rewritten as an integral equation

$$|\overline{\psi(t)}\rangle = |\overline{\psi(0)}\rangle - \frac{i}{\hbar}\int_0^t dt'\, \overline{V(t')}\,|\overline{\psi(t')}\rangle, \tag{9.1.4}$$

which is well suited to solving for $|\overline{\psi(t)}\rangle$ as a power series in V. For instance, we can iterate this equation to deduce

$$|\overline{\psi(t)}\rangle = |\overline{\psi(0)}\rangle - \frac{i}{\hbar}\int_0^t dt'\, \overline{V(t')}\,|\overline{\psi(0)}\rangle + \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt''\, \overline{V(t')}\,\overline{V(t'')}\,|\overline{\psi(t'')}\rangle. \tag{9.1.5}$$

The unknown state still appears on RHS but now in a term of order V^2. We could continue to any desired order in V (see AQM course) but will stop here:

$$|\overline{\psi(t)}\rangle = |\overline{\psi(0)}\rangle - \frac{i}{\hbar} \int_0^t dt' \ \overline{V(t')} \ |\overline{\psi(0)}\rangle + O(V^2) \,. \tag{9.1.6}$$

Let $|i\rangle$ and $|f\rangle$ be eigenstates of H_0, eigenvalues E_i and E_f, and assume $\langle i|f\rangle = 0$. A transition from the state

$$|\psi(0)\rangle = |\overline{\psi(0)}\rangle = |i\rangle \tag{9.1.7}$$

at time $t = 0$ (when S-picture and I-picture coincide) to a state $|f\rangle$ at time t occurs with probability

$$|\langle f|\psi(t)\rangle|^2 = |\langle f|\overline{\psi(t)}\rangle|^2 \tag{9.1.8}$$

since

$$\langle f|\psi(t)\rangle = \langle f| e^{-iH_0 t/\hbar} |\overline{\psi(t)}\rangle = e^{-iE_f t/\hbar} \langle f|\overline{\psi(t)}\rangle \,. \tag{9.1.9}$$

To **order** V, the amplitude we need is therefore

$$
\begin{aligned}
\langle f|\overline{\psi(t)}\rangle &= \cancelto{0}{\langle f|i\rangle} - \frac{i}{\hbar} \int_0^t dt' \langle f| \overline{V(t')} |i\rangle \\[2mm]
&= -\frac{i}{\hbar} \int_0^t dt' \langle f| e^{iH_0 t'/\hbar} V(t') e^{-iH_0 t'/\hbar} |i\rangle \\[2mm]
&= -\frac{i}{\hbar} \int_0^t dt' \ e^{i(E_f - E_i)t'/\hbar} \langle f|V(t')|i\rangle \,,
\end{aligned}
\tag{9.1.10}
$$

and probability for transition to **order** V^2 is

$$\frac{1}{\hbar^2} \left| \int_0^t e^{i\omega t'} \langle f|V(t')|i\rangle \, dt' \right|^2 \,, \qquad \hbar\omega = E_f - E_i \,. \tag{9.1.11}$$

An important special case is when $V(t')$ is constant in time (at least for $0 \leqslant t' \leqslant t$). The amplitude above is then

$$-\frac{i}{\hbar} \int_0^t e^{i\omega t'} \langle f|V|i\rangle \, dt' = \frac{1}{\hbar\omega}(1 - e^{i\omega t}) \langle f|V|i\rangle \,, \tag{9.1.12}$$

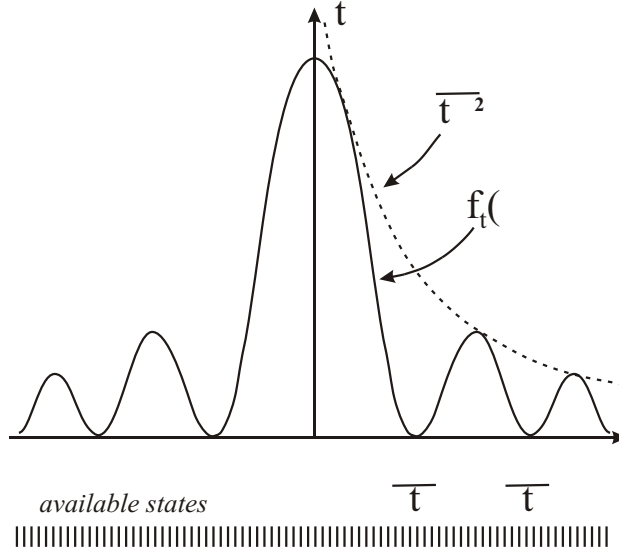and the probability of transition to **order** V^2 is

$$P(t) = \frac{1}{\hbar^2} \left(\frac{\sin \omega t/2}{\omega/2} \right)^2 |\langle f|V|i\rangle|^2 \,. \tag{9.1.13}$$

For fixed $\omega \neq 0$ have a periodic function of t.

9.2 Transition rates and Fermi's Golden Rule

Probability found above for transition $i \to f$ to second order in V (a constant perturbing potential) can be written

$$P(t) = \frac{t}{\hbar^2} f_t(\omega) |\langle f|V|i\rangle|^2$$

$$f_t(\omega) = \frac{1}{t} \left(\frac{\sin \omega t/2}{\omega/2} \right)^2 \,. \tag{9.2.1}$$

available states

Now
$$\lim_{\omega \to 0} f_t(\omega) = t \,, \qquad \int_{-\infty}^{\infty} f_t(\omega)\, d\omega = 2 \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}\, dx = 2\pi \,. \tag{9.2.2}$$
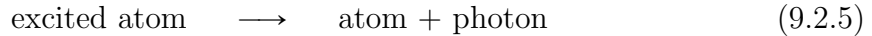
As t increases $f_t(\omega)$ is concentrated more and more around $\omega = 0$ and $P(t)$ will be non-negligible only when
$$-\frac{2\pi}{t} \lesssim \omega \lesssim \frac{2\pi}{t} \,. \tag{9.2.3}$$

So for t large enough we have
$$\omega \approx 0 \quad \text{and} \quad E_f \approx E_i \,. \tag{9.2.4}$$

In many cases we deal with a transition to final states with closely packed energy levels or even a continuum of energies such as in the decay
$$\text{excited atom} \quad \longrightarrow \quad \text{atom + photon} \tag{9.2.5}$$

where the photon has momentum $\boldsymbol{q}$ and energy $E = |\boldsymbol{q}|c$.

Similarly, a free particle of mass m and momentum $\boldsymbol{p}$ has energy $E = \boldsymbol{p}^2/2m$; E is a **continuous** variable and the states $|\boldsymbol{p}\rangle$ form a **continuum**. It is often useful to think of these states in a box of large side L with periodic boundary conditions. The wavefunction is then $(V = L^3)$

$$\psi_{\boldsymbol{p}}(\boldsymbol{x}) = \frac{1}{\sqrt{V}}\, e^{i\boldsymbol{p}\cdot\boldsymbol{x}} \,, \qquad \boldsymbol{p} = \frac{2\pi}{L}(n_1, n_2, n_3) \qquad n_i \in \mathcal{Z} \,, \qquad E = \frac{2\pi^2\hbar^2}{mL^2}(n_1^2 + n_2^2 + n_3^2) \,. \tag{9.2.6}$$

This is a **discrete** set which becomes a **continuum** as $L \to \infty$. In what follows shall **assume** the gap between levels is always much less than $2\pi\hbar/t \implies$ always choose L sufficiently large. See diagram which illustrates this idea.

Suppose the final states have certain parameters fixed (e.g. scattering angle wrt initial state) but with E_f variable. Define the **density of states**, $\rho(E_f)$, by

$$\rho(E_f)\Delta E \;=\; \# \text{ states with specified parameters and energy in range } (E_f,\, E_f + \Delta E).$$

Consider a transition to a number of states **temporarily** represented as a discrete set as described above.

$$P(t) = \sum_f \frac{t}{\hbar^2} f_t(\omega_{fi}) |\langle f|V|i\rangle|^2, \qquad \omega_{fi} = \frac{E_f - E_i}{\hbar} . \tag{9.2.7}$$

Now consider the limit as set of states $|f\rangle$ becomes a continuum ($L \to \infty$) and t is **large enough** that $\rho(E)$ is **slowly varying** over the range $(E_i - 2\pi\hbar/t, \; E_i + 2\pi\hbar/t)$. Probability of transition to some state in a band of energy F can be found from the formula for $P(t)$ by replacing

$$\sum_f \quad \to \quad \int_F dE_f \, \rho(E_f) . \tag{9.2.8}$$

Note, we are assuming that $|\langle f|V|i\rangle|^2$ only depends on E_f and does **not** depend on other unspecified quantum numbers which distinguish the different states with energy E_f. This assumption is easily relaxed by summing over them, too.

For t sufficiently large

$$f_t(\omega) \;\approx\; 2\pi\delta(\omega) \;=\; 2\pi\hbar\,\delta(E_f - E_i) , \tag{9.2.9}$$

and then

$$P(t) \;=\; \frac{t}{\hbar^2} \int_F dE_f \, \rho(E_f) \, 2\pi\hbar \, \delta(E_f - E_i) \, |\langle f|V|i\rangle|^2$$

$$= \begin{cases} 0 & \text{if } E_i \text{ is not in } F \\[2mm] \left. \dfrac{2\pi t}{\hbar} \rho(E_i) |\langle f|V|i\rangle|^2 \right|_{E_f = E_i} & \text{if it is} \end{cases} \tag{9.2.10}$$

For this to be a good approximation we need:

- t not so large that 1st order perturbation theory breaks down: need $P(t) \ll 1$.
- t large enough that the δ-function approximation is valid. This means changes in $\rho(E_f)|\langle f|V|i\rangle|^2$ are small for changes in E_f of order $\hbar/t$ (see diagram above).

Under these conditions have a constant **transition rate**:

$$\boxed{\frac{P(t)}{t} \;=\; \frac{2\pi}{\hbar} \rho(E_i) \, |\langle f|V|i\rangle|^2 \qquad \textbf{Fermi's Golden Rule.}}$$

9.3   Interaction of radiation/EM field with atoms

The Hamiltonian for an electron in the hydrogen atom and interacting with an external EM field is given by the minimal substitution rule (there can, of course, be other terms which do appear when the particle is not 'elementary'):

$$H = \frac{1}{2m}(\hat{\boldsymbol{p}} - e\boldsymbol{A}(\hat{\boldsymbol{x}}, t))^2 + V(\hat{r}) = H_0 - \frac{e}{2m}(\hat{\boldsymbol{p}} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \hat{\boldsymbol{p}}) + \frac{e^2}{2m}\boldsymbol{A}^2 , \tag{9.3.1}$$

where $\boldsymbol{A}(\hat{\boldsymbol{x}}, t)$ is the vector potential of the EM field and H_0 is the hydrogen atom Hamiltonian. We assume that the EM field is weak and so can ignore the last term – it is certainly suppressed by an extra factor of e, anyway. We assume that $\boldsymbol{A}$ has some definite frequency ω_0 and wave-vector $\boldsymbol{q}$. Then we write (using position representation)

$$\boldsymbol{A}(\boldsymbol{x}, t) = \boldsymbol{\varepsilon}\,\cos\left(\boldsymbol{q}\cdot\boldsymbol{x} - \omega_0 t\right), \tag{9.3.2}$$

where $\boldsymbol{\varepsilon}$ is the polarization vector which is transverse to the direction of propagation so that $\boldsymbol{\varepsilon}\cdot\boldsymbol{q} = 0$ (this ensures that the EM wave has two polarizations $\perp \boldsymbol{q}$). In this case $\hat{\boldsymbol{p}}\cdot\boldsymbol{A} = \boldsymbol{A}\cdot\hat{\boldsymbol{p}}$ since

$$-i\hbar\nabla\cdot\boldsymbol{\varepsilon}\,\cos\left(\boldsymbol{q}\cdot\boldsymbol{x} - \omega_0 t\right) = i\hbar\,\boldsymbol{q}\cdot\boldsymbol{\varepsilon}\,\sin\left(\boldsymbol{q}\cdot\boldsymbol{x} - \omega_0 t\right) = 0. \tag{9.3.3}$$

The interesting interaction term is then

$$V_I(\hat{\boldsymbol{x}}, t) = -\frac{e}{m}\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}\,\cos\left(\boldsymbol{q}\cdot\hat{\boldsymbol{x}} - \omega_0 t\right). \tag{9.3.4}$$

There is no significance to $\cos$ rather than $\sin$ here. We are considering the decay of an excited atom $H^* \to H + \gamma$ and the reverse, absorption, process and so the energy of the photon is

$$\hbar\omega_0 = |E_f - E_i| \sim \alpha^2 mc^2 \quad\text{with wavelength}\quad \lambda \sim \frac{1}{\alpha^2}\frac{\hbar}{mc}, \tag{9.3.5}$$

where E_i and E_f are now the energies of initial and final atomic states, respectively. Compare λ with the size of the atom given by the Bohr radius

$$a_0 \sim \frac{1}{\alpha}\frac{\hbar}{mc}. \tag{9.3.6}$$

Have $|\boldsymbol{q}| = 2\pi/\lambda$ and $\boldsymbol{x}$ is confined to the atomic interior so $|\boldsymbol{x}| \lesssim a_0$. Thus,

$$\boldsymbol{q}\cdot\boldsymbol{x} \lesssim \frac{a_0}{\lambda} \sim \alpha \sim \frac{1}{137}. \tag{9.3.7}$$

To lowest order we therefore neglect $\boldsymbol{q}\cdot\boldsymbol{x}$ and consider the interaction to be

$$V_I(t) = -\frac{e}{m}\hat{\boldsymbol{p}}\cdot\boldsymbol{\varepsilon}\,\cos\left(\omega_0 t\right). \tag{9.3.8}$$

We now note that

$$[\hat{\boldsymbol{x}}, H_0] = i\hbar\frac{\hat{\boldsymbol{p}}}{m}, \tag{9.3.9}$$

and so

$$V_I(t) = \frac{ie}{\hbar}\,\cos\left(\omega_0 t\right)[\hat{\boldsymbol{x}}\cdot\boldsymbol{\varepsilon}, H_0] \tag{9.3.10}$$

Now the first-order transition amplitude $i \to f$ is

$$-\frac{i}{\hbar}\int_0^t dt'\,e^{i(E_f - E_i)t'/\hbar}\,\langle f|V_I(t')|i\rangle$$

$$= \frac{e}{\hbar^2}\int_0^t dt'\,e^{i(E_f - E_i)t'/\hbar}\,\cos\left(\omega_0 t'\right)\langle f|[\hat{\boldsymbol{x}}\cdot\boldsymbol{\varepsilon}, H_0])|i\rangle$$

$$= \frac{e}{\hbar^2}(E_i - E_f)\int_0^t dt'\,e^{i(E_f - E_i)t'/\hbar}\,\cos\left(\omega_0 t'\right)\langle f|\hat{\boldsymbol{x}}\cdot\boldsymbol{\varepsilon}|i\rangle. \tag{9.3.11}$$

This is called the **dipole approximation** since the operator appearing in the matrix element has the form $e\hat{\boldsymbol{x}} \cdot \boldsymbol{\varepsilon} \cos(\omega_0 t)$ and may be interpreted as the interaction of the electric dipole operator $\hat{\boldsymbol{d}} = -e\hat{\boldsymbol{x}}$ with a classical electric field given by $\boldsymbol{E} \propto \boldsymbol{\varepsilon} \cos(\omega_0 t)$ of the form $V(t) = -\hat{\boldsymbol{d}} \cdot \boldsymbol{E}$. However, the derivation is from minimal substitution and there are clearly corrections higher-order in $\boldsymbol{q} \cdot \boldsymbol{x}$. Can analyze formula in two parts.

(i) Time dependence. Separate $\cos$ into exponentials and integrate gives two terms

$$\int_0^t dt' \, e^{i(E_f - E_i)t'/\hbar} \, e^{\mp i\omega_0 t'} . \tag{9.3.12}$$

Evaluating and taking $|.|^2$ gives contributions to probability

$$\frac{\sin^2((\omega \mp \omega_0)t/2)}{(\omega \mp \omega_0)^2/4} \qquad \omega = \frac{(E_f - E_i)}{\hbar} . \tag{9.3.13}$$

together with a somewhat messy cross-term. As t becomes sufficiently large these terms are sharply peaked around $\omega \approx \pm\omega_0$, and the cross term is small in comparison. Thus, for t large enough we have two kinds of transitions

$$i \to f \qquad \text{with} \qquad E_f = E_i \pm \hbar\omega_0 \qquad (\omega_0 > 0) \tag{9.3.14}$$

which occur with **equal** probability. These processes are **absorption** and **emission**, respectively. Proceeding as in derivation of the Golden Rule could find precise formula for transition rate. This would require computing the density of states $\rho(E_f)$ (see Statistical Physics for example of this).

(ii) Matrix element (t independent):
$$\boldsymbol{\varepsilon} \cdot \langle f | \hat{\boldsymbol{x}} | i \rangle \tag{9.3.15}$$

which must be non-zero for transition to occur. Probability for transition then proportional to

$$|\boldsymbol{\varepsilon}|^2 \propto \text{intensity} \propto \text{energy density of classical EM radiation.} \tag{9.3.16}$$

Consider H-atom states

$$|i\rangle = |n\,l\,m\rangle, \quad |f\rangle = |n'\,l'\,m'\rangle, \tag{9.3.17}$$

labelled as usual by principal and ang. mom. quantum numbers. Use parity and angular momentum properties of operators and states to determine when $\langle f | \hat{\boldsymbol{x}} | i \rangle \neq 0$.

$\star$ **Parity**.
   Parity operator U satisfies $U^2 = 1$ and have

$$U|n\,l\,m\rangle = (-1)^l |n\,l\,m\rangle \quad \text{and} \quad U\hat{\boldsymbol{x}}U = -\hat{\boldsymbol{x}}$$

$$\Rightarrow \quad \langle n'\,l'\,m'|\hat{x}_i|n\,l\,m\rangle = \langle n'\,l'\,m'|UU\hat{x}_iUU|n\,l\,m\rangle$$

$$= (-1)^{l+l'+1}\langle n'\,l'\,m'|\hat{x}_i|n\,l\,m\rangle \tag{9.3.18}$$

and hence vanishes unless

$$l + l' \quad \text{odd} \qquad \textbf{first selection rule.} \tag{9.3.19}$$

⋆ **Angular momentum**.

First show that $\hat{x}_i|n\,l\,m\rangle$ are like product states for addition of ang. mom. 1 to l. Intuitively, $\hat{x}_i$ is a vector and we know that $l = 1$ states also behave like a vector under rotations. Now

$$[L_i, \hat{x}_j] = i\hbar\varepsilon_{ijk}\,\hat{x}_k \quad \text{means } \hat{\boldsymbol{x}} \text{ behaves as a vector operator,} \quad (9.3.20)$$

and define

$$
\begin{aligned}
X_1 &= -\frac{1}{\sqrt{2}}(\hat{x}_1 + i\hat{x}_2) \\
X_0 &= \hat{x}_3 \\
X_{-1} &= \frac{1}{\sqrt{2}}(\hat{x}_1 - i\hat{x}_2)\,.
\end{aligned}
\quad (9.3.21)
$$

It is easy to check

$$
\begin{aligned}
[L_3, X_q] &= \hbar q X_q \\[2mm]
[L_\pm, X_q] &= \hbar\sqrt{(1\mp q)(1\pm q+1)}X_{q\pm 1}\,,
\end{aligned}
\quad (9.3.22)
$$

look back at (8.3.21). Compare with standard formulas in section 7.5 and Eqs. (7.5.1) for action of $L_3, L_\pm$ on ang. mom. states $|1,q\rangle$. These formulas match exactly implying that with respect to angular momentum

$$X_q|n\,l\,m\rangle \quad \text{behave just like product states} \quad |1,q\rangle|l,m\rangle\,. \quad (9.3.23)$$

Another indication that this is an exact parallel is that in the position representation using spherical polars coordinates

$$X_{\pm 1} = \mp\frac{1}{\sqrt{2}}r\sin\theta\,e^{\pm i\phi} = \sqrt{\frac{4\pi}{3}}r\,Y_{1\,\pm 1}(\theta,\phi)\,, \quad X_0 = r\cos\theta = \sqrt{\frac{4\pi}{3}}r\,Y_{1\,0}(\theta,\phi)\,,$$
$$(9.3.24)$$

which are angular momentum wavefunctions for $l = 1$:

$$Y_{lm}(\theta,\phi) = \langle\theta,\phi|l,m\rangle\,. \quad (9.3.25)$$

What this means is that

$$\boldsymbol{L}\Big(X_q|n\,l\,m\rangle\Big) = [\boldsymbol{L}, X_q]|n\,l\,m\rangle + X_q\Big(\boldsymbol{L}|n\,l\,m\rangle\Big) \quad (9.3.26)$$

corresponds exactly to

$$\boldsymbol{L}\Big(|1,q\rangle|l,m\rangle\Big) = \Big(\boldsymbol{L}|1,q\rangle\Big)|l,m\rangle + |1,q\rangle\Big(\boldsymbol{L}|l,m\rangle\Big)\,, \quad (9.3.27)$$

which is the usual action on product states for addition of angular momentum for two subsystems. Use the same strategy as before:

◆ note that

$$L_+ \left(X_1 | n\, l\, l \rangle \right) \;=\; 0$$

$$L_3 \left(X_1 | n\, l\, l \rangle \right) \;=\; \hbar(l+1) \left(X_1 | n\, l\, l \rangle \right). \tag{9.3.28}$$

So, as far as angular momentum is concerned (i.e., ignore r dependence for current purpose)

$$|l+1, l+1\rangle \propto X_1 | n\, l\, l \rangle. \tag{9.3.29}$$

◆ Then

$$|l+1, l\rangle \propto L_- \left(X_1 | n\, l\, l \rangle \right) \quad \text{etc.} \tag{9.3.30}$$

◆ Find orthogonal state to $|l+1, l\rangle$ and take this as the next top state $|l, l\rangle$.
◆ Repeat procedure as before.

Then we find that $X_q | n\, l\, m \rangle$ has angular momentum q. numbers

$$\begin{array}{ll} l+1 \text{ or } l \text{ or } l-1 & \text{for } \boldsymbol{L}^2 \quad \text{and} \\ \qquad m+q & \text{for } L_3 \end{array} \tag{9.3.31}$$

So for $\langle n'\, l'\, m' | X_q | n\, l\, m \rangle$ to be non-zero need

$$\left. \begin{array}{rl} l' & \in \;\; (l+1, l, l-1) \\ m' & = \;\; m+q \;\; (q=0, \pm 1) \end{array} \right\} \qquad \textbf{second set of selection rules.} \tag{9.3.32}$$

But parity already forbids $l' = l$.

Summary: the possible atomic transitions for dipole radiation are given by

$$\begin{array}{rll} l' & = & l \pm 1 \\ m' & = & m \qquad \text{if} \quad \varepsilon_3 \neq 0 \\ m' & = & m \pm 1 \quad \text{if} \quad \varepsilon_1 \;\; \text{or} \;\; \varepsilon_2 \neq 0 \end{array} \tag{9.3.33}$$

In addition we must have

$$E_{n'} \;=\; E_n \pm \hbar \omega_0 \tag{9.3.34}$$

for large enough t, and the transition rate is then proportional to $|\boldsymbol{\varepsilon}|^2$, the strength (intensity or energy density) of the EM field/radiation. This corresponds to absorption ($+$ sign) and emission ($-$ sign). Although there are other operators which can cause radiative transitions with different selection rules it turns out that dipole radiation of the nature discussed here generally has the largest transition rate.

9.4   Emission and absorption of photons

★ START OF NON-EXAMINABLE MATERIAL

Quantization of EM field discussed in outline in section 3.2. By expanding in normal modes we can reduce the EM field equations to a set of oscillators. Here consider just

one mode of frequency ω_0 for simplicity. By comparison with results in section 3 (on the oscillator) and 4 (on Schrödinger and Heisenberg pictures) the electric field has a Heisenberg picture operator for each polarization of the form (c.f. Eqn. (4.2.15))

$$\boldsymbol{\varepsilon} \cdot \boldsymbol{E}(\omega_0) \propto a\, e^{-i\omega_0 t} + a^\dagger\, e^{i\omega_0 t} \tag{9.4.1}$$

where a, $a^\dagger$ are the S-picture operators which destroy/create a photon of frequency ω_0 and the given polarization $\boldsymbol{\varepsilon}$. Use this now to sketch how transitions between atomic energy levels are influenced by **quantum** EM field; before, in section 9.3 we treated the EM field classically in the dipole coupling approximation. The discussion there is modified by including the photon states in the initial and final states for the reaction:

$$\begin{aligned} |i\rangle &= |n\,l\,m\rangle|N\rangle \\ |f\rangle &= |n'\,l'\,m'\rangle|N'\rangle \end{aligned} \tag{9.4.2}$$

where N, N' are the number of photons or the oscillator level in the quantum version for the field intensity which is $N\hbar\omega_0$ (ignoring the oscillator zero-point energy). As before have two possible processes corresponding to time-dependent factors

$$e^{-i\omega_0 t} \qquad\qquad\qquad e^{i\omega_0 t} \tag{9.4.3}$$

and these are now respectively accompanied by factors

$$\langle N'|a|N\rangle = \begin{cases} \sqrt{N} & N' = N - 1 \\ 0 & \text{otherwise} \end{cases} \qquad \langle N|a^\dagger|N'\rangle = \begin{cases} \sqrt{N+1} & N' = N + 1 \\ 0 & \text{otherwise} \end{cases} \tag{9.4.4}$$

while the atomic matrix elements are unmodified. On taking $|.|^2$ to get probabilities find rates for absorption and emission of photon are equal except for the factors N and $N + 1$. Interpretation is as follows.

- **Absorption.** $N' = N - 1$ and N is the **intensity** in photon units $(\hbar\omega_0)$ of the EM radiation from which one photon is absorbed. Classically this is $\propto |\boldsymbol{\varepsilon}|^2$. This is what we expect.

- **Emission.** Look at two cases

  ⋆ $N = 0, N' = 1$. This is **spontaneous emission**. There is no photon in the initial state which then decays spontaneously emitting the photon. A prediction of QM – not a classical phenomenon.

  ⋆ $N > 0$. Rate $\propto N + 1$. We still associate the "1" here with spontaneous emission but now the rate contains a term $\propto N$. I.e., the atom is induced/stimulated to decay at rate proportional to the intensity of the radiation in which it is bathed. In addition, the emitted photon is in the **same state** as those inducing its emission – it is in phase with them and adds to the intensity of the radiation coherently. If N is very large so that the excited atom is bathed in high-intensity coherent radiation then the stimulated emission of a photon is overwhelmingly more likely than spontaneous emission.

Thus for general atomic energy levels $E_i > E_j$ and EM radiation of frequency ω_0 have transitions when $E_i - E_j = \pm\hbar\omega_0$.
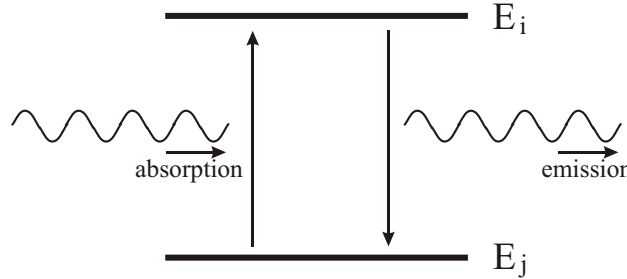
Transition rates are of the form

$$\underbrace{A_{i\to j}}_{\text{spontaneous}} + \underbrace{B_{i\to j} \cdot (\text{intensity})}_{\text{stimulated}} \quad \text{or} \quad \underbrace{B_{j\to i} \cdot (\text{intensity})}_{\text{spontaneous}} \tag{9.4.5}$$

$$\textit{emission rate} \qquad\qquad\qquad \textit{absorption rate}$$

The quantities above are called the Einstein A and B coefficients. (There is a nice original treatment using thermal equilibrium, the Boltzmann distribution for atomic excitations and the Bose-Einstein distribution appropriate for indistinguishable photons.) Always have $B_{i\to j} = B_{j\to i}$. Also, with intensity measured in natural units of photon number then have

$$A_{i\to j} = B_{i\to j} = B_{j\to i}. \tag{9.4.6}$$

Stimulated emission is the basis of operation of the laser.

★ END OF NON-EXAMINABLE MATERIAL

10 Quantum Basics

There are many aspects of QM which still seem rather mysterious, particularly in relation to measurements and how they have been axiomatized. For example,

- QM is inherently probabilistic whereas classical mechanics is deterministic.

- QM gives special status to (macroscopic) observer as distinct from (microscopic) system.

- In QM measurements always interfere with the state of the system.

Obvious question raised by the first point:

Could probabilities in QM arise from ignorance of some hidden, deterministic (i.e. inherently classical) degrees of freedom?

The main aim of this last section is to see how such questions may be addressed, and we will also look briefly at some loosely related topics to do with information in classical and quantum systems.

10.1   Classical and Quantum Data

Consider the simplest possible system: one measurable quantity s with observable values 0 and 1.

- Classically, specifying s is one **bit** of information.

- In QM, s becomes an operator with eigenstates $|0\rangle$ and $|1\rangle$ corresponding to observed values. The general normalized state of the system is

$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle\,, \qquad \||\psi\rangle\|^2 = |\alpha|^2 + |\beta|^2 = 1\,. \tag{10.1.1}$$

So ∞ (uncountable) many complex coefficients α, β (parametrizing S^3). This is called a **quantum bit** or **qubit**.

It would seem that a qubit contains vastly more information than a classical bit, but we must beware: the information is not easily accessed.

- Classically we can inspect s to find 0 or 1 without disturbing the system.

- In QM, measuring s irrevocably changes $|\psi\rangle$ since it is projected onto $|0\rangle$ or $|1\rangle$ in the process. We could recover the values of $|\alpha|^2$ and $|\beta|^2$ to some degree of accuracy if we had a large number of copies of $|\psi\rangle$, by measuring s many times. This raises the question of whether we can faithfully **copy** some given state $|\psi\rangle$ in a quantum system. It turns out that this is forbidden by the

No-cloning Theorem.

We must be careful about what we mean. I **can** prepare an ensemble of systems each of which is in the given state $|\psi\rangle$. For example, use a Stern-Gerlach apparatus to produce a beam (the ensemble) of spin-$\frac{1}{2}$ particles each with eigenvalue of $\sigma_z = 1$: a "spin up" state. Then clearly I have a lot of systems (i.e. the particles) in state

$$|\psi\rangle = |\uparrow\rangle\,, \tag{10.1.2}$$

Now choose the qubit to be an eigenstate of

$$\sigma_\theta = \boldsymbol{n} \cdot \boldsymbol{\sigma} = \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix} \quad \text{with} \quad \boldsymbol{n} = (\sin\theta, 0, \cos\theta)\,. \tag{10.1.3}$$

Then σ_θ has eigenstates

$$
\begin{array}{cccc}
 & & & \text{evals} \\
|\uparrow\theta\rangle & = & \cos\frac{\theta}{2}|\uparrow\rangle + \sin\frac{\theta}{2}|\downarrow\rangle \;\rightsquigarrow\; \begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} \end{pmatrix} & +1 \\
 & & & \tag{10.1.4} \\
|\downarrow\theta\rangle & = & -\sin\frac{\theta}{2}|\uparrow\rangle + \cos\frac{\theta}{2}|\downarrow\rangle \;\rightsquigarrow\; \begin{pmatrix} -\sin\frac{\theta}{2} \\ \cos\frac{\theta}{2} \end{pmatrix} & -1
\end{array}
$$

And so the Stern-Gerlach prepared state can be written

$$|\psi\rangle = |\uparrow\rangle = \cos\frac{\theta}{2}|\uparrow\,\theta\rangle - \sin\frac{\theta}{2}|\downarrow\,\theta\rangle. \qquad (10.1.5)$$

Thus, I can measure σ_θ many times and find $|\alpha|^2$ and $|\beta|^2$ which are the respective probabilities for measuring $\sigma_\theta = \pm 1$. Alternatively, I can measure $\langle\sigma_\theta\rangle$. Here have

$$
\begin{aligned}
|\alpha|^2 &= |\langle\uparrow\,\theta|\uparrow\rangle|^2 = \cos^2\frac{\theta}{2} \\
|\beta|^2 &= |\langle\downarrow\,\theta|\uparrow\rangle|^2 = \sin^2\frac{\theta}{2} \\
\langle\sigma_\theta\rangle &= \cos^2\frac{\theta}{2} - \sin^2\frac{\theta}{2} = \cos\theta.
\end{aligned}
\qquad (10.1.6)
$$

So if I have an ensemble prepared in this way, there is no problem in interrogating the ensemble to find detailed properties of the state $|\psi\rangle$. However, this is the only way I can do it – I need an ensemble over which to average.

Suppose now that have access to just one system prepared in the state $|\psi\rangle$. For example, I have one particle taken from my original ensemble. Can I now clone this state and generate an ensemble like the one we just discussed? Can I take one particle from the Stern-Gerlach apparatus, clone it many times and then deduce properties of $|\psi\rangle$ from the resulting ensemble? The **no-cloning theorem** states that this is not possible.

There are various versions of the theorem depending on assumptions and we will look at the simplest. Suppose we have a quantum copier; a machine that can copy any given state $|\psi\rangle$ onto a 'blank state' $|b\rangle$. We assume all states are normalized and that the copying is implemented by a linear, unitary, operator, U. Note that U must be independent of $|\psi\rangle$ since it must be able to copy **any** state.

$$|\psi\rangle \otimes |b\rangle \xrightarrow{\ U\ } |\psi\rangle \otimes |\psi\rangle. \qquad (10.1.7)$$

Can copy another state $|\phi\rangle$ in the same way:

$$|\phi\rangle \otimes |b\rangle \xrightarrow{\ U\ } |\phi\rangle \otimes |\phi\rangle. \qquad (10.1.8)$$

Since U is unitary inner-products are preserved. So

$$
\begin{aligned}
\langle\phi|\psi\rangle\langle b|b\rangle &= \langle\phi|\psi\rangle\langle\phi|\psi\rangle \\
\Rightarrow \quad \langle\phi|\psi\rangle &= 0 \ \text{ or } \ 1.
\end{aligned}
\qquad (10.1.9)
$$

This shows that copying can never work for general states in a space with dimension > 1. This is a vital result for the success of the quantum encryption algorithm where it is central to the idea that the encryption key for a classical algorithm can be transmitted in such a way that a spy cannot intercept the message and decode it. Interception irrevocably destroys the information and the interception is known to the sender/receiver.

10.2   EPR experiment and Bell's inequality

The EPR (Einstein-Podolsky-Rosen) thought experiment in modern language: two spin-$\frac{1}{2}$ particles are produced in an (entangled) spin-0 state

$$|\psi\rangle \;=\; \frac{1}{\sqrt{2}}\Big(\,|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\,\Big)\,, \tag{10.2.1}$$

and components of spin $\boldsymbol{\sigma}^A$, $\boldsymbol{\sigma}^B$ (leave out $\frac{1}{2}\hbar$ factor) of first and second particle are subsequently measured by experimenters Alice (A) and Bob (B) in some order. However, they carry the particles far apart in space without altering the spin state $|\psi\rangle$ before measuring anything. Until the first measurement is made there is no definite value for e.g. σ_z^A or σ_z^B.

Suppose Alice makes the first measurement of σ_z^A and gets the result $+1$, say (probability $\frac{1}{2}$). This projects $|\psi\rangle$ onto the new state $|\uparrow\rangle|\downarrow\rangle$ and so if Bob now measures σ_z^B he gets result -1 with probability 1. He does not know this (unless Alice has sent him a signal to tell him) but Alice knows with certainty what he will get! Einstein was troubled by these kinds of **non-local** correlations but there is actually no loss of causality here. Alice cannot use the collapse of the wave-packet

$$|\psi\rangle \;\overset{collapse}{\longrightarrow}\; |\uparrow\rangle|\downarrow\rangle \qquad (\text{Alice measured } \sigma_z^A = +1) \tag{10.2.2}$$

to send a message to Bob superluminally. Actually, Bob does not even know whether or not Alice has made a measurement, since if the experiment is repeated many times with an ensemble of pairs, Bob with get $\sigma_z^B = +1$ and -1 with 50:50 probability **whether or not** Alice has made a prior measurement.

One way to explain such correlations and idea of non-locality is to ask whether the spin components could actually take **definite** values, which are correlated, at the instant the particles were created, i.e. at their point of origin. We still need a classical probability distribution to describe how these values arise, but this ultimately might be explained by some deterministic hidden variables. Can such a distribution reproduce the predictions of QM. Or, if not, which possibility is supported by experiment?

A simple example is suppose I make two identical parcels one containing a green ball and the other a red one. I give one to Alice and one to Bob who then travel far apart. When Alice opens her parcel and sees, say, a green ball she knows instantly the Bob has a red ball. This "learning at a distance" is mundane and not controversial; there is no perception of non-locality. Can repeat many times and, indeed, Bob has a 50:50 change of getting red and green. However, in this case each ball had a definite colour before starting out – there is no analogue of "collapse of the wavepacket". Can the spins in an entangled state be thought of as having definite spin components in a like manner?

It is useful to think about measuring **different** components of $\boldsymbol{\sigma}^A$ and $\boldsymbol{\sigma}^B$ and use the results above for eigenstates of σ_θ in Eqns. (10.1.4) and (10.1.6) to consider first what happens to a single particle in conventional QM. Have

$$|\langle\uparrow\theta|\uparrow\rangle|^2 \;=\; |\langle\downarrow\theta|\downarrow\rangle|^2 = \cos^2\frac{\theta}{2}$$

$$|\langle\uparrow\theta|\downarrow\rangle|^2 \;=\; |\langle\downarrow\theta|\uparrow\rangle|^2 = \sin^2\frac{\theta}{2}\,. \tag{10.2.3}$$

These results clearly depend on the angle between $\hat{\boldsymbol{k}}$ and $\boldsymbol{n}$ defined earlier. Also, for a component along a new direction ϕ we have

$$|\langle\uparrow\theta|\uparrow\phi\rangle|^2 \;=\; |\langle\downarrow\theta|\downarrow\phi\rangle|^2 = \cos^2\left(\frac{\theta-\phi}{2}\right)$$

$$|\langle\uparrow\theta|\downarrow\phi\rangle|^2 \;=\; |\langle\downarrow\theta|\uparrow\phi\rangle|^2 = \sin^2\left(\frac{\theta-\phi}{2}\right). \qquad (10.2.4)$$

Now return to the two particle system $|\psi\rangle$ and note that the spin-0 state is

$$|\psi\rangle \;=\; \frac{1}{\sqrt{2}}\Big(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\Big)$$

$$\;=\; \frac{1}{\sqrt{2}}\Big(|\uparrow\theta\rangle|\downarrow\theta\rangle - |\downarrow\theta\rangle|\uparrow\theta\rangle\Big). \qquad (10.2.5)$$

This can be checked directly but also follows because spin-0 is a rotationally invariant state – it cannot depend on the choice of the z-axis.

We want to consider probabilities for various outcomes when

Alice measures one of	**then**	Bob measures one of	(10.2.6)
$\sigma^A_z, \sigma^A_\theta, \sigma^A_\phi$		$\sigma^B_z, \sigma^B_\theta, \sigma^B_\phi$	

E.g.,

$\sigma^A_z = 1$	new state	**then**	$\sigma^B_\theta = -1$	(10.2.7)
$|\psi\rangle$: prob: $\frac{1}{2}$	$|\uparrow\rangle|\downarrow\rangle$		prob: $|\langle\downarrow\theta|\downarrow\rangle|^2 = \cos^2\frac{\theta}{2}$	

Total probabilities for this and some other measurement outcomes are similarly

$$P(\sigma^A_z = +1, \sigma^B_\theta = -1) \;=\; \tfrac{1}{2}\cos^2\frac{\theta}{2}$$

$$P(\sigma^A_z = -1, \sigma^B_\phi = +1) \;=\; \tfrac{1}{2}\cos^2\frac{\phi}{2}$$

$$P(\sigma^A_\theta = +1, \sigma^B_\phi = +1) \;=\; \tfrac{1}{2}\sin^2\left(\frac{\theta-\phi}{2}\right). \qquad (10.2.8)$$

Also, know components along same direction are exactly anticorrelated. So, e.g.

$$P(\sigma^A_z = 1, \sigma^B_z = -1) \;=\; 1 \quad \text{etc.} \qquad (10.2.9)$$

All is standard QM.

Now ask could there exist classical variables

$$s^A_z, s^A_\theta, s^A_\phi \quad \text{and} \quad s^B_z, s^B_\theta, s^B_\phi \qquad (10.2.10)$$

for each particle, all taking values ± 1 according to some probability distribution, with values assigned as the particles are created (c.f. the classical red and green ball discussion), yet still reproducing the QM results?

- To ensure anticorrelation of spins along same direction probability must be zero unless $s_z^B = -s_z^A$ etc. So we can write the distributions as functions of **Alice's** variables $p(s_z^A, s_\theta^A, s_\phi^A)$ alone.

- Then, summing over variables that are not specified, we can write

$$P(s_\theta^A = +1, s_\phi^A = -1)$$

$$= p(1, 1, -1) + p(-1, 1, -1)$$

$$\leqslant \big[p(1, 1, -1) + p(1, 1, 1)\big] + \big[p(-1, 1, -1) + p(-1, -1, -1)\big]$$

$$= P(s_z^A = +1, s_\theta^A = +1) \quad + \quad P(s_z^A = -1, s_\phi^A = -1) \tag{10.2.11}$$

- Specifying outcomes in terms of one measurement for A and one for B instead (using exact anticorrelation) we get

$$P(s_\theta^A = +1, s_\phi^B = +1) \leqslant P(s_z^A = +1, s_\theta^B = -1) + P(s_z^A = -1, s_\phi^B = +1). \tag{10.2.12}$$

This is **Bell's inequality** of which there are many versions.

- Can such a probability distribution reproduce the results of QM? If so, then the expressions derived for the QM probabilities above must satisfy Bell's inequality. This means

$$\sin^2\left(\frac{\theta - \phi}{2}\right) \leqslant \cos^2\frac{\theta}{2} + \cos^2\frac{\phi}{2} \tag{10.2.13}$$

for any θ and ϕ. But this is **false**. E.g., $\theta = 3\pi/4$, $\phi = 3\pi/2$ with this inequality would imply

$$\underbrace{-\left(\cos^2\frac{3\pi}{8} - \sin^2\frac{3\pi}{8}\right)}_{\cos 3\pi/4} \leqslant \cos^2\frac{3\pi}{4}$$

$$\Rightarrow \qquad \frac{1}{\sqrt{2}} \leqslant \frac{1}{2} \qquad \textbf{FALSE!} \tag{10.2.14}$$

The fact that this approach **cannot** reproduce QM means that we can distinguish these alternatives experimentally, and it is QM which is correct. With these assumptions, the indeterminate nature of state (no definite values of observables until measurement is made) seems inescapable. There is a non-locality to the notion of collapse of the wavefunction.

10.3 Density operators and hidden sectors

Next topic is still about conventional QM but raises questions about 'hidden' or unobserved parts of the system.

- Observations usually confined to some subset of physical degrees of freedom, either by choice or necessity. What effect will the rest of the system have on our measurements?

- There is loss of information. Expect some uncertainties and probability distribution to emerge, but not like fundamental probabilities which are part of measurement axioms.

- Need a general formalism to handle this. Useful in e.g., statistical mechanics where 'hidden' degrees of freedom are all the fine details of the system which are not of interest. I.e., we care about pressure, temperature etc. but not the dynamics of individual particles.

- Develop idea of **density** or **state** operator.

Consider a space of states of the form

$$V \;=\; U \,\otimes\, W \tag{10.3.1}$$

where U is observed but W is the hidden/unobserved sector. The general state is then

$$|\Psi\rangle \;=\; \sum_{ia} \alpha_{ia} |\psi_i\rangle \otimes |\phi_a\rangle, \tag{10.3.2}$$

with $\{|\psi_i\rangle\}$ and $\{|\phi_a\rangle\}$ orthonormal bases for U and W, respectively. Assume

$$\||\Psi\rangle\|^2 \;=\; \sum_{ia} |\alpha_{ia}|^2 \;=\; 1. \tag{10.3.3}$$

What we really mean by distinction between U and W is that observables Q act just on U, i.e. Q acts on V as the operator $Q \otimes \mathbb{I}$. Then

$$\begin{aligned}
\langle Q \rangle_\Psi \;&=\; \sum_{ia} \sum_{jb} \alpha_{jb}^* \alpha_{ia} \langle \psi_j | Q | \psi_i \rangle \underbrace{\langle \phi_b | \phi_a \rangle}_{\delta_{ab}} \\
&=\; \sum_{ij} \beta_{ij} \langle \psi_j | Q | \psi_i \rangle.
\end{aligned} \tag{10.3.4}$$

The matrix $\beta_{ij} = \sum_a \alpha_{ia} \alpha_{ja}^*$ is hermitian and positive-definite, and

$$\sum_i \beta_{ii} \;=\; \operatorname{Tr}(\boldsymbol{\beta}) \;=\; \sum_{ia} |\alpha_{ia}|^2 \;=\; 1 : \qquad \text{trace or sum of eigenvalues}. \tag{10.3.5}$$

Hence, $\exists$ a unitary matrix $\boldsymbol{S}$ diagonalizing $\boldsymbol{\beta}$ with

$$\boldsymbol{S}^\dagger \boldsymbol{\beta} \boldsymbol{S} \;=\; \operatorname{diag}(p_i) \quad \text{where evals } \; p_i \geqslant 0 \; \text{ and } \; \sum_i p_i = 1. \tag{10.3.6}$$

Define a new orthonormal basis for U

$$|\chi_i\rangle \;=\; \sum_j |\psi_j\rangle S_{ji}, \tag{10.3.7}$$

and then find

$$\langle Q \rangle_\Psi \;=\; \sum_i p_i \langle Q \rangle_{\chi_i} \quad \text{with} \quad \langle Q \rangle_{\chi_i} \;=\; \langle \chi_i | Q | \chi_i \rangle. \tag{10.3.8}$$

- Working just with U, the effect of the hidden sector W is to produce a probability distribution $\{p_i\}$ for a particular set of states $|\chi_i\rangle$ in the observed sector.

- If there is only one non-zero probability we say we have a **pure** state for U and $|\Psi\rangle$ can then be written as a single tensor product

$$|\Psi\rangle \;=\; |\chi_1\rangle \otimes |\phi_1\rangle \quad \Rightarrow \quad \boldsymbol{\beta} \;=\; \mathrm{diag}(1,0,\ldots,0) \tag{10.3.9}$$

  where I have chosen $p_1 = 1, \; p_i = 0 \; i > 1$.

- If there is more than one non-zero probability we say we have a **mixed state** for U, and $|\Psi\rangle$ **cannot** be written as a single tensor product. In this case we also say that we have an **entangled** state of the subsystems U and W.

Density operators or matrices provide a powerful way of re-expressing results about quantum measurements. Recall first that the **trace** of an operator A on a space V is defined by

$$\mathrm{Tr}_V(A) \;=\; \sum_n \langle n|A|n\rangle, \qquad \{|n\rangle\} \text{ any orthonormal basis for } V. \tag{10.3.10}$$

We can express all aspects of measurements in terms of traces of operators rather than inner-products of states. So, with notation as before,

$$\text{on} \quad V \;=\; U \otimes W$$
$$\text{define} \quad \rho \;=\; |\Psi\rangle\langle\Psi|, \qquad \text{the **density operator** corresponding to } |\Psi\rangle.$$
$$\tag{10.3.11}$$

Then

$$\langle Q\rangle_\Psi = \langle\Psi|Q|\Psi\rangle = \sum_n \langle\Psi|n\rangle\langle n|Q|\Psi\rangle = \sum_n \langle n|\Big(Q|\Psi\rangle\langle\Psi|\Big)|n\rangle = \mathrm{Tr}_V(Q\,\rho) \tag{10.3.12}$$

with $\mathrm{Tr}_V(\rho) = \langle 1\rangle = 1$.

When V has the tensor product structure given above we have a convenient way of restricting the calculation to U by using the **reduced density matrix operator**

$$\bar\rho \;=\; \sum_{ija} \alpha_{ia}\alpha_{ja}^*|\psi_i\rangle\langle\psi_j| \;=\; \sum_{ij} \beta_{ij}|\psi_i\rangle\langle\psi_j| \;=\; \sum_i p_i|\chi_i\rangle\langle\chi_i|. \tag{10.3.13}$$

For an observable Q acting just on U we have

$$\langle Q\rangle \;=\; \mathrm{Tr}_U(Q\,\bar\rho) \tag{10.3.14}$$

so everything is written in terms of the 'observable' sector. Other results:

- Provided the states $|\chi_i\rangle$ obey the time-dependent Schrödinger equation with Hamiltonian H, the EoM for $\rho(t)$ is (see Q4.8(a))

$$i\hbar\frac{d}{dt}\rho \;=\; [H,\rho]. \tag{10.3.15}$$

- For a **pure** state have

$$\bar\rho^2 \;=\; \bar\rho \quad \text{and} \quad \mathrm{Tr}(\bar\rho^2) \;=\; \mathrm{Tr}(\bar\rho). \tag{10.3.16}$$

  I.e., $\bar\rho$ is a projection operator on U (see Q4.8(b)).

- For an **entangled** state

$$\bar\rho^2 \;\neq\; \bar\rho \quad \text{and} \quad \mathrm{Tr}(\bar\rho^2) \;<\; \mathrm{Tr}(\bar\rho). \tag{10.3.17}$$