

# Part II Principles of Quantum Mechanics

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## 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

Most 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 recommended 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.
- ★ **Observables 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 space  $V$ . Then

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

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:

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

with

$$\begin{aligned} \langle\phi|(\alpha_1|\psi_1\rangle + \alpha_2|\psi_2\rangle) &= \alpha_1\langle\phi|\psi_1\rangle + \alpha_2\langle\phi|\psi_2\rangle, \\ (\beta_1\langle\phi_1| + \beta_2\langle\phi_2|)|\psi\rangle &= \beta_1\langle\phi_1|\psi\rangle + \beta_2\langle\phi_2|\psi\rangle, \end{aligned} \quad (2.1.3)$$

$\alpha, \beta \in \mathbb{C}$ . 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:

$$\begin{aligned} V &\longleftrightarrow V^\dagger \\ \text{with} \quad |\psi\rangle &\longleftrightarrow \langle\psi| = (|\psi\rangle)^\dagger \quad (\text{use same label for corresponding states}) \\ \text{and} \quad \alpha|\psi\rangle + \beta|\phi\rangle &\longleftrightarrow \alpha^*\langle\psi| + \beta^*\langle\phi|. \end{aligned} \quad (2.1.4)$$

The inner product is

$$\begin{aligned} V \times V &\rightarrow \mathbb{C} \\ |\phi\rangle, |\psi\rangle &\mapsto \langle\phi|\psi\rangle = (|\phi\rangle)^\dagger|\psi\rangle, \end{aligned} \quad (2.1.5)$$

and is assumed to obey

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

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  $|\psi\rangle \rightarrow \alpha|\psi\rangle$  ( $\alpha \neq 0$ ). We shall usually normalize states by  $\|\psi\|^2 = 1$  but still have the freedom to change  $|\psi\rangle \rightarrow e^{i\theta}|\psi\rangle$ . 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,  $V \rightarrow V$ :

$$|\psi\rangle \mapsto Q|\psi\rangle, \quad (2.1.7)$$

and, by definition

$$Q(\alpha|\phi\rangle + \beta|\psi\rangle) = \alpha Q|\phi\rangle + \beta Q|\psi\rangle. \quad (2.1.8)$$

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

$$\langle\phi| \mapsto \langle\phi|Q, \quad (2.1.9)$$

$$\begin{aligned} (\langle\phi|Q)|\psi\rangle &= \langle\phi|(Q|\psi\rangle) \quad \forall |\psi\rangle \\ \text{or simply} &= \langle\phi|Q|\psi\rangle. \end{aligned} \quad (2.1.10)$$

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

$$\langle\phi|Q^\dagger = (Q|\phi\rangle)^\dagger, \quad (2.1.11)$$

or, equivalently,

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

Simple consequences are

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

for any  $A, B$ .<sup>1</sup>

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1

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

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  $\lambda$  if

$$Q|\psi\rangle = \lambda|\psi\rangle. \quad (2.1.15)$$

Equivalently (taking  $\dagger$  of this)

$$\langle\psi|Q^\dagger = \lambda^*\langle\psi|. \quad (2.1.16)$$

For general  $Q$ ,  $\lambda$  can be complex.

Of particular importance are commutators of operators

$$[A, B] = AB - BA = -[B, A]. \quad (2.1.17)$$

We have the identities

$$\begin{aligned} [\alpha_1 A_1 + \alpha_2 A_2, B] &= \alpha_1 [A_1, B] + \alpha_2 [A_2, B] \\ [A, \beta_1 B_1 + \beta_2 B_2] &= \beta_1 [A, B_1] + \beta_2 [A, B_2] \end{aligned} \quad \text{linearity} \quad (2.1.18)$$

$$\begin{aligned} [A, B_1 B_2] &= [A, B_1] B_2 + B_1 [A, B_2] \\ [A_1 A_2, B] &= [A_1, B] A_2 + A_1 [A_2, B] \end{aligned} \quad \text{Leibnitz properties} \quad (2.1.19)$$

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

## 2.2 Observables and measurements

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

$$Q^\dagger = Q. \quad (2.2.1)$$

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)

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

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

$$\lambda = \lambda^*. \quad (2.2.3)$$

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

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

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

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

There might be several states with the same eigenvalue  $\lambda$ . 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  $\lambda$  is the number of states in this basis, or  $\dim V_\lambda$ . We say that  $\lambda$  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  $V_\lambda$ :

(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,  $\lambda$ , say.



- This value is obtained with the probability

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

- Immediately after the measurement the state is

$$|\phi\rangle = c \sum_{n:q_n=\lambda} \alpha_n |n\rangle, \quad (2.2.10)$$

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

So measurement **projects** the system into the eigenspace  $V_\lambda$ .

**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

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

Then

$$\text{Probability of measuring } \left\{ \begin{array}{l} 1 \quad \left| \frac{1}{\sqrt{6}} \right|^2 = \frac{1}{6} \quad |3\rangle \\ 0 \quad \left| \frac{2}{\sqrt{6}} \right|^2 + \left| \frac{1}{\sqrt{6}} \right|^2 = \frac{5}{6} \quad \frac{1}{\sqrt{5}}(2|1\rangle + |2\rangle) \end{array} \right. \quad (2.2.12)$$

$\uparrow$   
 final states

In this example we had degeneracy: two states with eigenvalue 0. However, often have the case with  $\lambda$  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,

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

as required for a probability distribution.

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

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

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

$$(\Delta Q)_\psi^2 = \langle (Q - \langle Q \rangle_\psi)^2 \rangle_\psi = \langle Q^2 \rangle_\psi - \langle Q \rangle_\psi^2. \quad (2.2.15)$$

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  $\lambda$ , say, then

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

[ 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  $|\psi\rangle$

$$\langle \Delta A \rangle_\psi \langle \Delta B \rangle_\psi \geq \frac{1}{2} |\langle [A, B] \rangle_\psi|, \quad (2.2.17)$$

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

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

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

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

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

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

$$[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}, \quad (2.2.20)$$

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:

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

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

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

Note that these equations imply

$$\frac{\partial}{\partial t} \left( \langle \psi(t) | \psi(t) \rangle \right) = 0, \quad (2.3.3)$$

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

$$H|n\rangle = E_n|n\rangle. \quad (2.3.4)$$

Then the states

$$e^{-iE_n t/\hbar}|n\rangle \quad (2.3.5)$$

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  $t = 0$ ,

$$|\psi(0)\rangle = \sum_n \alpha_n |n\rangle, \quad (2.3.6)$$

we have the unique solution

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

**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

$$Q|1\rangle = |2\rangle, \quad Q|2\rangle = |1\rangle \quad \Rightarrow \quad [Q, H] \neq 0. \quad (2.3.8)$$

The eigenstates of  $Q$  are easily found to be

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

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

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

The probability of measuring  $Q$  at time  $t$  and getting  $\pm 1$  is

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

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, possibly infinite, column/row vectors and to matrices as follows

$$\begin{aligned} |\psi\rangle &= \sum_n \alpha_n |n\rangle \quad \Leftrightarrow \quad \alpha_n = \langle n|\psi\rangle \\ |\phi\rangle &= \sum_n \beta_n |n\rangle \quad \Leftrightarrow \quad \beta_n = \langle n|\phi\rangle . \end{aligned} \quad (2.4.1)$$

The inner product is then

$$\langle \phi|\psi\rangle = \sum_n \beta_n^* \alpha_n . \quad (2.4.2)$$

The operation of operator  $A$  can be written as

$$A|n\rangle = \sum_m |m\rangle A_{mn} , \quad (2.4.3)$$

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

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

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

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

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

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

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  $\infty$  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:

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

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

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

$$Q|n\rangle = q_n|n\rangle \quad \langle n|m\rangle = \delta_{mn}, \quad (2.4.8)$$

setting

$$f(Q)|n\rangle = f(q_n)|n\rangle \quad (2.4.9)$$

**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  $q_n \neq 0 \quad \forall n$  then can define

$$Q^{-1}|n\rangle = \frac{1}{q_n}|n\rangle, \quad (2.4.10)$$

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**:

$$\sum_n |n\rangle\langle n| = \mathbb{I}, \quad \text{the identity operator.} \quad (2.4.11)$$

The notation is

$$\left( \underbrace{|n\rangle\langle m|}_{\text{operator}} \right) \underbrace{|\psi\rangle}_{\text{state}} = \underbrace{|n\rangle}_{\text{state}} \left( \underbrace{\langle m|\psi\rangle}_{\text{number}} \right). \quad (2.4.12)$$

This is confirmed by applying each side to an arbitrary state

$$\sum_n |n\rangle\langle n|\psi\rangle = |\psi\rangle = \mathbb{I}|\psi\rangle. \quad (2.4.13)$$

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

$$\begin{aligned} Q &= \sum_n q_n |n\rangle\langle n|, \\ f(Q) &= \sum_n f(q_n) |n\rangle\langle n|. \end{aligned} \quad (2.4.14)$$

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

$$P_\lambda = \sum_{n: q_n=\lambda} |n\rangle\langle n|. \quad (2.4.15)$$

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:

$$\begin{aligned} \sum_n &\rightarrow \int dn \quad \begin{cases} |\psi\rangle &= \int dn \alpha_n |n\rangle \\ \mathbb{I} &= \int dn |n\rangle\langle n| \\ Q &= \int dn q(n) |n\rangle\langle n| \end{cases} \\ \langle n|m\rangle &= \delta_{nm} \rightarrow \delta(n-m) \end{aligned} \quad (2.4.16)$$

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

$$[\hat{x}, \hat{p}] = i\hbar . \quad (2.5.1)$$

Let  $|x\rangle$  be position eigenstates

$$\hat{x}|x\rangle = x|x\rangle , \quad (2.5.2)$$

with continuous eigenvalue  $x$  and normalization

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

In this basis, any state can be expanded as

$$|\psi\rangle = \int dx \psi(x)|x\rangle$$

with  $\psi(x) = \langle x|\psi\rangle$  a complex function . (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:

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

The inner product in terms of wavefunctions becomes

$$\begin{aligned} \langle \phi|\psi\rangle &= \left( \int dx \phi(x)^*\langle x| \right) \left( \int dx' \psi(x')|x'\rangle \right) \\ &= \int dx \int dx' \phi(x)^*\psi(x') \underbrace{\langle x|x'\rangle}_{\delta(x - x')} \\ &= \int dx \phi(x)^*\psi(x) . \end{aligned} \quad (2.5.6)$$

So, in particular,

$$\| |\psi\rangle \|^2 = \langle \psi|\psi\rangle = \int dx |\psi(x)|^2 = 1 \quad (2.5.7)$$

for a normalized state.

Define similarly momentum eigenstates  $|p\rangle$  with

$$\hat{p}|p\rangle = p|p\rangle , \quad (2.5.8)$$

and with

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

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

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

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

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

$$\begin{aligned}
\hat{x}|\psi\rangle \quad \text{wavefunction :} \quad & \langle x|\hat{x}|\psi\rangle = x\langle x|\psi\rangle = x\psi(x) \\
\hat{p}|\psi\rangle \quad \text{wavefunction :} \quad & \langle x|\hat{p}|\psi\rangle \\
& = \int dp \langle x|\hat{p}|p\rangle\langle p|\psi\rangle \quad [\text{resolution of identity using p-states}] \\
& = \int dp p\langle x|p\rangle\langle p|\psi\rangle \\
& = \int dp -i\hbar\frac{\partial}{\partial x}\left(\langle x|p\rangle\right)\langle p|\psi\rangle \\
& = -i\hbar\frac{\partial}{\partial x}\int dp \langle x|p\rangle\langle p|\psi\rangle \\
& = -i\hbar\frac{\partial}{\partial x}\langle x|\psi\rangle = -i\hbar\frac{\partial}{\partial x}\psi(x), \tag{2.5.12}
\end{aligned}$$

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

$$\begin{aligned}
|\psi\rangle & = \int dp \tilde{\psi}(p)|p\rangle, \\
\text{with } \tilde{\psi}(p) & = \langle p|\psi\rangle, \tag{2.5.13}
\end{aligned}$$

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  $x \leftrightarrow p$ :

$$\left. \begin{aligned}
\hat{p}|\psi\rangle & \longrightarrow p\tilde{\psi}(p) \\
\hat{x}|\psi\rangle & \longrightarrow i\hbar\frac{\partial}{\partial p}\tilde{\psi}(p)
\end{aligned} \right\} \begin{array}{l} \text{momentum space} \\ \text{wavefunctions} \end{array} \tag{2.5.15}$$

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

$$\begin{aligned}
\tilde{\psi}(p) & = \langle p|\psi\rangle = \int dx \langle p|x\rangle\langle x|\psi\rangle \\
& = \frac{1}{\sqrt{2\pi\hbar}} \int dx e^{-ipx/\hbar} \psi(x) \quad \text{Fourier transform,} \\
\text{and } \psi(x) & = \frac{1}{\sqrt{2\pi\hbar}} \int dp e^{ipx/\hbar} \tilde{\psi}(p) \quad \text{inverse FT.} \tag{2.5.16}
\end{aligned}$$

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

$$\begin{array}{ccc}
\psi(x) & & \tilde{\psi}(p) \\
\hat{x} \longrightarrow x & & \hat{x} \longrightarrow i\hbar\frac{\partial}{\partial p} \\
\hat{p} \longrightarrow -i\hbar\frac{\partial}{\partial x} & & \hat{p} \longrightarrow p
\end{array} \tag{2.5.17}$$

[ 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

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

are

$$\begin{aligned} \text{on } \psi(x) : \quad H &\longrightarrow -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) , \\ \text{on } \tilde{\psi}(p) : \quad H &\longrightarrow -\frac{p^2}{2m} + V\left(i\hbar \frac{\partial}{\partial p}\right) . \end{aligned} \quad (2.5.19)$$

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

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

but more generally need to use first principles.

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

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

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x) \psi(x) &= E \psi(x) && \text{in position space ,} \\ \frac{p^2}{2m} \tilde{\psi}(p) + \frac{1}{\sqrt{2\pi\hbar}} \int dp' \tilde{V}(p-p') \tilde{\psi}(p') &= E \tilde{\psi}(p) && \text{in momentum space .} \end{aligned} \quad (2.5.22)$$

[ Note that the convolution theorem derived here. ]

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

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} . \quad (2.5.23)$$

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

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



which involves the operator

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

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

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

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

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

So

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

Similarly,

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

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

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

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)

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

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

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

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

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

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

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

- Similarly,

$$\begin{aligned}\langle x|x'\rangle &= \int dp \langle x|p\rangle\langle p|x'\rangle \\ &= \int dp \frac{1}{2\pi\hbar} e^{ip(x-x')/\hbar} = \delta(x-x') \quad \text{as expected.}\end{aligned}\quad (2.5.35)$$

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  $\lambda$  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  $\lambda$ ,
- then immediately measure  $Q'$  with result  $\lambda'$ .
- This second measurement must not change the value for  $Q$  and so still get result  $\lambda$  if it is measured again immediately.

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

$$\begin{aligned}Q|\lambda, \lambda'\rangle &= \lambda|\lambda, \lambda'\rangle \\ Q'|\lambda, \lambda'\rangle &= \lambda'|\lambda, \lambda'\rangle,\end{aligned}\quad (2.6.1)$$

which is only possible iff

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

as we now show.

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

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

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  $V_\lambda$  of  $Q$  then

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

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

- The definition of a hermitian operator that

$$\langle \phi | Q' | \psi \rangle = \langle \psi | Q' | \phi \rangle^* \quad \forall \quad |\psi\rangle, |\phi\rangle \in V \quad (2.6.5)$$

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

- Doing this for each  $V_\lambda$  gives a basis of such joint eigenstates for  $V$ .

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

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

$$|\lambda_1, \lambda_2, \lambda_3, \dots\rangle. \quad (2.6.6)$$

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

$$A = f(Q_1, Q_2, Q_3, \dots) \quad (2.6.7)$$

for some function  $f$ . This means that

$$A|\lambda_1, \lambda_2, \lambda_3, \dots\rangle = f(\lambda_1, \lambda_2, \lambda_3, \dots)|\lambda_1, \lambda_2, \lambda_3, \dots\rangle. \quad (2.6.8)$$

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

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}. \quad (2.6.9)$$

One complete commuting set is

$$\hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3) \quad (2.6.10)$$

with joint eigenstates:

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

An alternative complete commuting set is

$$\hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2, \hat{p}_3) \quad (2.6.11)$$

with joint eigenstates

$$\hat{p}_i|\mathbf{p}\rangle = p_i|\mathbf{p}\rangle \quad (2.6.12)$$

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

The relationship between these eigenstates is

$$\begin{aligned}\langle \mathbf{x} | \mathbf{p} \rangle &= \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{p}\cdot\mathbf{x}/\hbar} \quad \Rightarrow \\ \tilde{\psi}(\mathbf{p}) &= \frac{1}{(2\pi\hbar)^{3/2}} \int d^3x e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar} \psi(x) \\ \psi(\mathbf{x}) &= \frac{1}{(2\pi\hbar)^{3/2}} \int d^3p e^{i\mathbf{p}\cdot\mathbf{x}/\hbar} \tilde{\psi}(p) .\end{aligned}\tag{2.6.13}$$

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  $\omega$  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

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

Note that these are dimensionless. Equivalently,

$$\begin{aligned}\hat{x} &= \left(\frac{\hbar}{2m\omega}\right)^{1/2} (a + a^\dagger) , \\ \hat{p} &= \left(\frac{\hbar m\omega}{2}\right)^{1/2} i (a^\dagger - a) .\end{aligned}\tag{3.1.2}$$

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

$$a^\dagger a = \frac{1}{\hbar\omega} H - \frac{1}{2} \quad (\text{opposite sign for commutator}), \quad (3.1.4)$$

which confirms the commutation relations and also gives

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

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

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

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

$$\lambda = \langle \lambda | N | \lambda \rangle = \langle \lambda | a^\dagger a | \lambda \rangle = \| a | \lambda \rangle \|^2 \geq 0. \quad (3.1.7)$$

Thus,

$$\begin{aligned} \lambda &\geq 0 && \text{all eigenvalues non-negative} \\ &= 0 && \text{iff } a|\lambda\rangle = 0. \end{aligned} \quad (3.1.8)$$

Next consider commutators

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

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.

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

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

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

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  $\lambda \geq 0$ . Because of these properties  $a^\dagger$  and  $a$  are called, respectively, **creation** and **annihilation** operators.

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

$$\begin{array}{l} a|\lambda\rangle, \quad a^2|\lambda\rangle, \quad \dots, \quad a^m|\lambda\rangle, \quad \dots \quad \text{are **all** non-zero.} \\ \text{eigenvalues:} \quad \lambda - 1, \quad \lambda - 2, \quad \dots, \quad \lambda - m \quad \dots \end{array} \tag{3.1.13}$$

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

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

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

$$\begin{array}{l} a^\dagger|n\rangle, \quad (a^\dagger)^2|n\rangle, \quad \dots, \\ \text{eigenvalues:} \quad n + 1, \quad n + 2, \quad \dots \end{array} \tag{3.1.15}$$

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

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

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

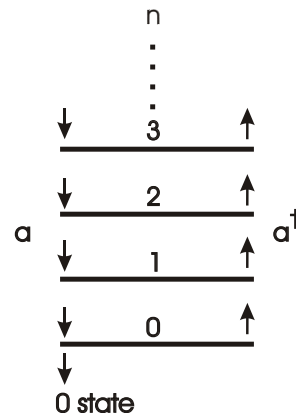
$$\left. \begin{array}{l} a^\dagger|n\rangle = \sqrt{n+1} |n+1\rangle \\ a|n\rangle = \sqrt{n} |n-1\rangle \end{array} \right\} \quad \text{ladder operators} \tag{3.1.17}$$

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

$$a|0\rangle = 0, \tag{3.1.18}$$

have normalized eigenstates

$$|n\rangle = \frac{1}{\sqrt{n!}} (a^\dagger)^n |0\rangle. \tag{3.1.19}$$



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

$$a|0\rangle = 0. \quad (3.1.20)$$

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

$$\begin{aligned} |0\rangle &\rightsquigarrow \psi_0(x) = \langle x|0\rangle \\ a = \left(\frac{m\omega}{2\hbar}\right)^{1/2} \left(\hat{x} + \frac{i}{m\omega} \hat{p}\right) &\rightsquigarrow \left(\frac{m\omega}{2\hbar}\right)^{1/2} \left(x + \frac{\hbar}{m\omega} \frac{\partial}{\partial x}\right) \\ a|0\rangle = 0 &\rightsquigarrow \left(x + \frac{\hbar}{m\omega} \frac{\partial}{\partial x}\right) \psi_0(x) = 0 \\ &\implies \psi_0(x) = N e^{-\frac{m\omega x^2}{2\hbar}} \end{aligned} \quad (3.1.21)$$

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.,

$$\begin{aligned} |1\rangle = a^\dagger|0\rangle &\rightsquigarrow \psi_1(x) = \left(\frac{m\omega}{2\hbar}\right)^{1/2} \left(x - \frac{\hbar}{m\omega} \frac{\partial}{\partial x}\right) \psi_0(x) \\ &= \left(\frac{2m\omega}{\hbar}\right)^{1/2} x \psi_0(x). \end{aligned} \quad (3.1.22)$$

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.”*

*M. Peskin*

- 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

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

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  $\omega$ . This is common classically and can now quantize this motion. The general solution for the classical oscillator is

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

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

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

with  $u_n$ ,  $n = 1 \dots N$  a complex vector specific to each allowed **normal frequency**  $\omega$ . 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

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

In fact,

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

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



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

$$\begin{array}{l} \text{Ground state} \quad |0\rangle \quad \text{with} \quad a(\omega)|0\rangle = 0 \quad \forall \text{ modes .} \\ \\ a^\dagger(\omega)|0\rangle \quad \left\{ \begin{array}{l} \text{state carrying energy but also mo-} \\ \text{mentum } \hbar k - \text{ like a particle.} \end{array} \right. \\ \\ \left. \begin{array}{l} a \quad \text{destroy} \\ a^\dagger \quad \text{create} \end{array} \right\} \text{ particles} \quad \left\{ \begin{array}{l} \mathbf{phonons} \text{ in a crystal} \\ \mathbf{photons} \text{ in EM field .} \end{array} \right. \end{array} \quad (3.2.6)$$

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

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

Given such an operator we can define a map on states

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

and on operators

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

under which all physical properties are unchanged:

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

Furthermore

$$\begin{aligned}
C = AB &\mapsto C' = A'B' \\
C = [A, B] &\mapsto C' = [A', B'] \quad \text{for any operators.} \\
Q \text{ hermitian} &\Rightarrow Q' = UQU^\dagger \text{ also hermitian,} \\
Q|\psi\rangle = \lambda|\psi\rangle &\Rightarrow Q'|\psi'\rangle = \lambda|\psi'\rangle \text{ same eigenvalue.}
\end{aligned} \tag{4.1.5}$$

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

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

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

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

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

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

$$i\hbar \frac{\partial}{\partial t} U(t) = HU(t), \quad (4.2.4)$$

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

$$\begin{aligned} U(t)^\dagger &= U(-t) = U(t)^{-1} && \text{unitary } (H = H^\dagger) \\ \text{and } U(t_1)U(t_2) &= U(t_1 + t_2). \end{aligned} \quad (4.2.5)$$

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	$ \psi(t)\rangle_S$	$ \psi\rangle_H = e^{itH/\hbar} \psi(t)\rangle_S$	$=  \psi(0)\rangle_S$
operators	$A_S$	$A_H(t) = e^{itH/\hbar}A_S e^{-itH/\hbar}$ ,	$A_H(0) = A_S$

(4.2.6)

Because the transformation is unitary,

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

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

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

or

$$i\hbar \frac{d}{dt}A_H(t) = [A_H(t), H] \quad \text{Heisenberg equation of motion.}$$

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

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

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

$$\left. \begin{aligned} H &= \frac{\hat{p}^2}{2m} + V(\hat{x}) \\ \frac{d}{dt}\hat{x}(t) &= \frac{1}{i\hbar}[\hat{x}(t), H] = \frac{1}{m}\hat{p}(t), \\ \frac{d}{dt}\hat{p}(t) &= \frac{1}{i\hbar}[\hat{p}(t), H] = -V'(\hat{x}(t)). \end{aligned} \right\} \text{Heisenberg equations of motion} \quad (4.2.10)$$

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

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

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

- $V = 0$ , the free particle.

$$\left. \begin{aligned} \frac{d}{dt}\hat{p}(t) &= 0 \Rightarrow \hat{p}(t) = \hat{p}(0) \quad \text{constant operator} \\ \frac{d}{dt}\hat{x}(t) &= \frac{1}{m}\hat{p}(0) \Rightarrow \hat{x}(t) = \hat{x}(0) + \frac{\hat{p}(0)}{m}t. \end{aligned} \right\} \quad (4.2.12)$$

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

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

$$\left. \begin{aligned} \frac{d}{dt}\hat{x}(t) &= \frac{1}{m}\hat{p}(t) \\ \frac{d}{dt}\hat{p}(t) &= -m\omega^2\hat{x}(t) \end{aligned} \right\} \Rightarrow \begin{aligned} \frac{d^2}{dt^2}\hat{x} + \omega^2\hat{x} &= 0 \\ \frac{d^2}{dt^2}\hat{p} + \omega^2\hat{p} &= 0. \end{aligned} \quad (4.2.13)$$

The solution is

$$\begin{aligned} \hat{x}(t) &= \hat{x}(0) \cos \omega t + \frac{\hat{p}(0)}{m\omega} \sin \omega t \\ \hat{p}(t) &= \hat{p}(0) \cos \omega t - m\omega \hat{x}(0) \sin \omega t. \end{aligned} \quad (4.2.14)$$

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

Alternatively, can write these as

$$\begin{aligned} \hat{x}(t) &= \left(\frac{\hbar}{2m\omega}\right)^{1/2} (a e^{-i\omega t} + a^\dagger e^{i\omega t}) \\ \hat{p}(t) &= \left(\frac{\hbar m\omega}{2}\right)^{1/2} \frac{1}{i} (a e^{-i\omega t} - a^\dagger e^{i\omega t}), \end{aligned} \quad (4.2.15)$$

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  $1 \leq i \leq N$  (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

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

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,

$$\{x_i, p_j\} = \delta_{ij}. \quad (4.3.2)$$

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

$$\frac{df}{dt} = \{f, H\}. \quad (4.3.3)$$

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

- $$\begin{array}{ccc} \text{classical} & & \text{quantum} \\ \text{functions} & f, g \longrightarrow & \text{operators} \end{array} \quad \hat{f}, \hat{g} \quad (4.3.4)$$

- Poisson brackets become commutators

$$[\hat{f}, \hat{g}] = i\hbar \widehat{\{f, g\}}. \quad (4.3.5)$$

In particular, get

$$[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij} \quad (4.3.6)$$

which are the canonical commutation relations.

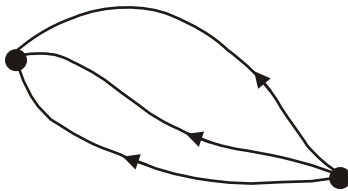
- Moreover, Hamilton's equations then become Heisenberg's equations

$$i\hbar \frac{d}{dt} \hat{f} = [\hat{f}, \hat{H}]. \quad (4.3.7)$$

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  $\hbar \rightarrow 0$ . 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

$$|\psi\rangle \in V_1, \quad |\phi\rangle \in V_2, \quad (5.1.1)$$

i.e., states in the spaces for two systems. The tensor product space

$$V = V_1 \otimes V_2 \quad (5.1.2)$$

consists of all linear combinations of tensor product states  $|\psi\rangle \otimes |\phi\rangle$  (duals  $\langle\psi| \otimes \langle\phi|$ ) subject to

$$\begin{aligned} (|\psi\rangle + |\psi'\rangle) \otimes |\phi\rangle &= |\psi\rangle \otimes |\phi\rangle + |\psi'\rangle \otimes |\phi\rangle \\ |\psi\rangle \otimes (|\phi\rangle + |\phi'\rangle) &= |\psi\rangle \otimes |\phi\rangle + |\psi\rangle \otimes |\phi'\rangle \\ (\alpha|\psi\rangle) \otimes |\phi\rangle &= \alpha|\psi\rangle \otimes (|\phi\rangle) = \alpha(|\psi\rangle \otimes |\phi\rangle), \end{aligned} \quad (5.1.3)$$

and similarly for duals. The inner product is

$$\left(\langle\psi'|\otimes\langle\phi'|\right)\left(|\psi\rangle\otimes|\phi\rangle\right)=\langle\psi'|\psi\rangle\langle\phi'|\phi\rangle, \quad (5.1.4)$$

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

$$\dim V = \dim V_1 \times \dim V_2. \quad (5.1.5)$$

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

$$(A\otimes B)\left(|\psi\rangle\otimes|\phi\rangle\right)=\left(A|\psi\rangle\right)\otimes\left(B|\phi\rangle\right)$$

and extend by linearity. In particular,

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

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

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

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

$$\begin{aligned} \left(\langle x_1|\otimes\langle x_2|\right)\left(|\psi\rangle\otimes|\phi\rangle\right) &= \langle x_1|\psi\rangle\langle x_2|\phi\rangle \\ &= \psi(x_1)\phi(x_2). \end{aligned} \quad (5.1.8)$$

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

**Example:** two-dimensional oscillator.

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

with

$$\begin{aligned} H_i &= \frac{1}{2m}\hat{p}_i^2 + \frac{1}{2}m\omega^2\hat{x}_i^2 = \hbar\omega\left(N_i + \frac{1}{2}\right), \\ N_i &= a_i^\dagger a_i, \quad [a_i, a_j^\dagger] = \delta_{ij}. \end{aligned} \quad (5.1.11)$$

Simultaneous eigenstates of  $N_1, N_2$  constructed by

$$\begin{aligned} |n_1, n_2\rangle &= |n_1\rangle \otimes |n_2\rangle \\ \text{with } H|n_1, n_2\rangle &= \left(H_1|n_1\rangle\right) \otimes |n_2\rangle + |n_1\rangle \otimes \left(H_2|n_2\rangle\right) \\ &= E_{n_1 n_2}|n_1, n_2\rangle, \end{aligned} \quad (5.1.12)$$

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

$$|\mathbf{x}, r\rangle = |\mathbf{x}\rangle|r\rangle, \quad (5.2.1)$$

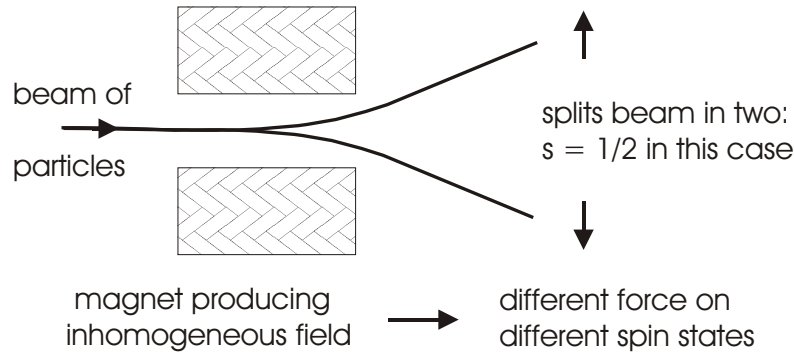
where  $r$  takes a finite set of values: the quantum numbers associated with **spin**. The particle is not ‘structureless’: the position operators,  $\hat{\mathbf{x}}$ , are not a complete commuting set by themselves – there are additional observables  $Q$  acting just on  $V_{\text{spin}}$  with  $[\hat{\mathbf{x}}_i, Q] = 0$ . 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  $0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ ; 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  $V_{\text{spin}}$  labelled by convention  $r = S, S - 1, \dots, -S$ . E.g.,

$$\begin{array}{lll} S & \text{basis states} & \\ 0 & |0\rangle & \\ \frac{1}{2} & |\frac{1}{2}\rangle, |-\frac{1}{2}\rangle & \text{also written } \underbrace{|\uparrow\rangle}_{\text{up}}, \underbrace{|\downarrow\rangle}_{\text{down}} \\ 1 & |1\rangle, |0\rangle, | - 1\rangle & \end{array} \quad (5.2.2)$$

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

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

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

$$\sum_r \psi(\mathbf{x}, r) |r\rangle . \quad (5.2.4)$$

### 5.3 Multiparticle states: bosons and fermions

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

$$V_1 \otimes V_2 \otimes \dots \otimes V_N , \quad (5.3.1)$$

with basis states

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

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:

$$W|\mathbf{x}_1, r_1; \mathbf{x}_2, r_2\rangle = |\mathbf{x}_2, r_2; \mathbf{x}_1, r_1\rangle . \quad (5.3.2)$$

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

$$W|\Psi\rangle = \eta|\Psi\rangle , \quad (5.3.3)$$

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

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

Thus, 2-particle states do not belong merely to

$$\begin{aligned}
 & V \otimes V && \text{spanned by } |\psi\rangle \otimes |\phi\rangle, \\
 \text{but to } & (V \otimes V)_S && \text{spanned by } |\psi\rangle \otimes |\phi\rangle + |\phi\rangle \otimes |\psi\rangle, \\
 & && \eta = 1 \quad \text{symm under } W \\
 \text{or to } & (V \otimes V)_A && \text{spanned by } |\psi\rangle \otimes |\phi\rangle - |\phi\rangle \otimes |\psi\rangle. \\
 & && \eta = -1 \quad \text{antisymm under } W
 \end{aligned} \tag{5.3.5}$$

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

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

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

For any permutation  $\pi$  of  $\{1, 2, \dots, N\}$  define

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

on the basis states. On a general state

$$W_\pi|\Psi\rangle = \eta_\pi|\Psi\rangle \quad \text{for some } \eta_\pi. \tag{5.3.8}$$

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 particles are identical and the initial choice for the labelling is not unique. Then, since any  $\pi$  can be obtained as a sequence of swaps, we have alternative outcomes

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

with the same alternative for all  $\pi$ . 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  $(V \otimes V \otimes \dots \otimes V)_S$ .

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

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

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 uncertainty principle.

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

## 5.4 Spin and statistics

Integral spin particles ( $S = 0, 1, 2, \dots$ ) are **bosons**.

$\frac{1}{2}$ -integral spin particles ( $S = \frac{1}{2}, \frac{3}{2}, \dots$ ) 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 known 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,  $\tau$  – 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.,  $\pi, K$  are spin 0, the  $\rho$  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

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

It is convenient to construct these spaces by first taking

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

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

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

$$H(\hat{\mathbf{x}}_1, \hat{\mathbf{p}}_1) + H(\hat{\mathbf{x}}_2, \hat{\mathbf{p}}_2) , \quad (5.5.3)$$

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

$$\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) \quad E = E_i + E_j . \quad (5.5.4)$$

- Ground state,  $E = 2E_0$ :

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

which is automatically ( $S$ )ymmetric.

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

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

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

$$\Psi_1^S(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}(\psi_0(\mathbf{x}_1)\psi_1(\mathbf{x}_2) + \psi_1(\mathbf{x}_1)\psi_0(\mathbf{x}_2)), \quad (5.5.7)$$

$$\Psi_1^A(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}(\psi_0(\mathbf{x}_1)\psi_1(\mathbf{x}_2) - \psi_1(\mathbf{x}_1)\psi_0(\mathbf{x}_2)), \quad (5.5.8)$$

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:**  $V_{\text{spin}}$  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

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

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

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

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

**or** normalized combinations with definite symmetry are

$$\begin{array}{ll} |\uparrow\rangle|\uparrow\rangle & \\ \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle) & \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle) \\ |\downarrow\rangle|\downarrow\rangle & \\ (V_{\text{spin}} \otimes V_{\text{spin}})_S & (V_{\text{spin}} \otimes V_{\text{spin}})_A \end{array} \quad (5.5.11)$$

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

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

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

★ Ground state,  $E = 2E_0$ :

$$\Psi_0^S(\mathbf{x}_1, \mathbf{x}_2) \frac{1}{\sqrt{2}} \left( |\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle \right) \quad (5.5.13)$$

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

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

$$\Psi_1^S(\mathbf{x}_1, \mathbf{x}_2) \frac{1}{\sqrt{2}} \left( |\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle \right) \quad (5.5.14)$$

$$\Psi_1^A(\mathbf{x}_1, \mathbf{x}_2) \begin{pmatrix} |\uparrow\rangle|\uparrow\rangle \\ \frac{1}{\sqrt{2}} \left( |\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle \right) \\ |\downarrow\rangle|\downarrow\rangle \end{pmatrix} \quad (5.5.15)$$

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  $(V \otimes \dots \otimes V)_A$ . 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  $(V \otimes \dots \otimes V)_A$  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

$$H(\hat{\mathbf{x}}_1, \hat{\mathbf{p}}_1) + \dots + H(\hat{\mathbf{x}}_N, \hat{\mathbf{p}}_N), \quad (5.6.1)$$

where a single electron Hamiltonian is

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

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

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

where

$$\begin{aligned}
 E_n &= -\frac{m}{2} \left( \frac{Ze^2}{4\pi\epsilon_0\hbar} \right)^2 \frac{1}{n^2} = \alpha^2 \frac{Z^2}{2n^2} mc^2, \\
 n &= 1, 2, \dots \quad \text{principal quantum number,} \\
 l &= 0, 1, \dots, n-1 \quad m = \underbrace{0, \pm 1, \pm 2, \dots, \pm l}_{2l+1 \text{ states}},
 \end{aligned} \tag{5.6.4}$$

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

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

Now, including  $V_{\text{spin}}$  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.

$$\begin{aligned}
 E_1 \text{ filled for } Z = 2 &\rightarrow \text{He} \\
 E_1 \text{ \& } E_2 \text{ filled for } Z = 10 &\rightarrow \text{Ne}
 \end{aligned} \tag{5.6.6}$$

- Chemical reactivity is controlled by the **valency** which is given by the number of electrons in an almost empty outer shell ( $\text{Ca}^{2+}$ ) or the number of unoccupied states in a nearly filled outer shell ( $\text{F}^-$ ).
- 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 no.	n element	1		2		3			4			
		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](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

$$H|n\rangle = E_n|n\rangle, \quad (6.1)$$

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

$$(H + \mu V)|\psi\rangle = E|\psi\rangle, \quad (6.2)$$

order-by-order in parameter  $\mu$  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  $\mu$ . 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  $\mu \rightarrow 0$

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

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

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

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

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

Aim is to calculate the coefficients in these expansions

$$\begin{aligned} E &= E_r + E_r^{(1)}\mu + E_r^{(2)}\mu^2 + \dots \\ \alpha &= 1 + a_1\mu + a_2\mu^2 + \dots \\ \gamma_j &= c_{j1}\mu + c_{j2}\mu^2 + \dots \end{aligned} \quad (6.1.4)$$

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

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

cancelling overall factor of  $\alpha$ . Rewrite as

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

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

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

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

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

Thus, already know first-order energy shift

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

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

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

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

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

and so substituting in Eq. (6.1.8) we find

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

In summary,

$$E = E_r + \mu \langle r|V|r\rangle + \mu^2 \sum_{j \neq r} \frac{|\langle j|V|r\rangle|^2}{E_r - E_j} + \dots, \quad (6.1.13)$$

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



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

**Example:**

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = \hbar\omega \left( a^\dagger a + \frac{1}{2} \right) \quad (6.1.15)$$

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

$$\text{Perturb with } V = m\omega^2\hat{x}^2 = \frac{\hbar}{2m\omega} (a^2 + a^{\dagger 2} + 2a^\dagger a + 1). \quad (6.1.16)$$

Have

$$\begin{aligned} \langle n|V|n\rangle &= \frac{1}{2}\hbar\omega(2n+1) \\ \langle n+2|V|n\rangle &= \frac{1}{2}\hbar\omega\sqrt{n+1}\sqrt{n+2} \\ \langle n-2|V|n\rangle &= \frac{1}{2}\hbar\omega\sqrt{n}\sqrt{n-1} \\ \langle m|V|n\rangle &= 0 \quad \text{all other } m \end{aligned} \quad (6.1.17)$$

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

$$\begin{aligned} E_n &+ \mu\langle n|V|n\rangle + \mu^2 \sum_{m \neq n} \frac{|\langle m|V|n\rangle|^2}{E_n - E_m} \\ &= \hbar\omega\left(n + \frac{1}{2}\right) + \mu\hbar\omega\left(n + \frac{1}{2}\right) + \mu^2 \left( \frac{\hbar\omega}{2} \right)^2 \left( \frac{(n+1)(n+2)}{-2\hbar\omega} + \frac{n(n-1)}{2\hbar\omega} \right) \\ &= \hbar\omega \left( n + \frac{1}{2} \right) \left( 1 + \mu - \frac{1}{2}\mu^2 \right) . \end{aligned} \quad (6.1.18)$$

But this problem can be solved exactly:

$$H \rightarrow H + \mu V \quad \text{equivalent to} \quad \omega \rightarrow \omega' = \omega\sqrt{1+2\mu} . \quad (6.1.19)$$

New energies are exactly

$$\begin{aligned} \hbar\omega' \left( n + \frac{1}{2} \right) &= \hbar\omega \left( n + \frac{1}{2} \right) (1 + 2\mu)^{\frac{1}{2}} \\ &= \hbar\omega \left( n + \frac{1}{2} \right) \left( 1 + \mu - \frac{1}{2}\mu^2 + O(\mu^3) \right) . \end{aligned} \quad (6.1.20)$$

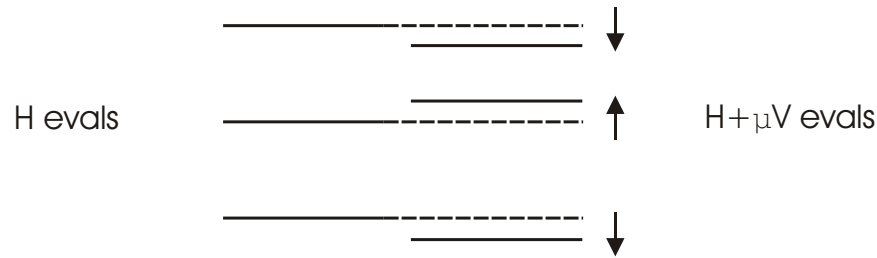
### Validity/usefulness of perturbation theory

If  $\mu$  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

$$\left| \mu \frac{\langle i|V|j\rangle}{E_i - E_j} \right| \quad i \neq j , \quad (6.1.21)$$

and similar quantities. Condition for accuracy is therefore qualitatively

$$|\text{energy shifts}| \ll |\text{original energy differences}| . \quad (6.1.22)$$



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

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

Single electron states and energies are

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

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

$$\begin{aligned} |\Psi\rangle &= |100\rangle \otimes |100\rangle \otimes |\chi\rangle \\ \text{with } |\chi\rangle &= \frac{1}{\sqrt{2}} (|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle) \quad \text{the spin state.} \end{aligned} \quad (6.1.25)$$

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

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2) &= \psi_{100}(\mathbf{x}_1)\psi_{100}(\mathbf{x}_2) \\ \psi_{100}(\mathbf{x}) &= \frac{1}{\sqrt{\pi}} \left( \frac{2}{a_2} \right)^{\frac{3}{2}} e^{-|\mathbf{x}|/a_2} \\ \text{with } (Z=2) \quad a_2 &= \frac{1}{2} \left( \frac{\hbar}{\alpha mc} \right) = \frac{1}{2} * (\text{Bohr radius}) \end{aligned} \quad (6.1.26)$$

The two-electron unperturbed energy is

$$2E_1 = -4\alpha^2 mc^2 \approx -108.8 \text{ eV}. \quad (6.1.27)$$

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:

$$\frac{e^2}{4\pi\epsilon_0 |\hat{\mathbf{x}}_1 - \hat{\mathbf{x}}_2|}. \quad (6.1.28)$$

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

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

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

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

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  $\alpha$  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

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

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**  $\alpha$  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  $V_\lambda$  be  $N$  with common eigenvalue  $\lambda$ . Then use notation

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

and suppose that as  $\mu \rightarrow 0$

$$E \rightarrow \lambda, \quad |\psi\rangle \rightarrow \sum_r a_r |r\rangle. \quad (6.2.2)$$

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

$$\begin{aligned} E &= \lambda + \mu E^{(1)} + \mu^2 E^{(2)} + \dots, \\ |\psi\rangle &= \sum_r \alpha_r |r\rangle + \sum_j \beta_j |j\rangle. \end{aligned} \quad (6.2.3)$$

with  $\alpha_r = a_r + O(\mu), \quad \beta_j = O(\mu).$

Note that for  $\mu \rightarrow 0$ ,  $|\psi\rangle \rightarrow |\psi_0\rangle \in V_\lambda$  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  $V_\lambda$ . Take the inner product of  $\langle s|$  with  $(**)$  to get (remember  $E_r = \dots = E_s \dots = E_N = \lambda$ )

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

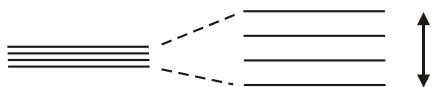
but the second term on RHS is  $O(\mu^2)$  and  $\alpha_r = a_r + O(\mu)$ , and so hence to leading order

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

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  $\Rightarrow \mathbf{L}^2, L_3$  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 split 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,  $0 \leq x, y \leq a$ . The unperturbed problem is the free particle with states  $|p, q\rangle$  and

$$\begin{aligned} \text{wavefns} \quad \psi_{pq}(x, y) &= \frac{2}{a} \sin \frac{p\pi x}{a} \sin \frac{q\pi y}{a} \\ \text{energies} \quad E_{pq} &= \frac{\hbar^2 \pi^2}{2ma^2} (p^2 + q^2) \quad p, q = 1, 2, \dots \end{aligned} \quad (6.2.8)$$

- 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  $\mu$  has dimensions of energy.

- The shift in the lowest energy level is given by

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

$$(6.2.10)$$

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

- Shifts in next level given by eigenvalues of

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

with

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

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

$$(6.2.14)$$

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

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

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

Collecting results:

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

$$\begin{array}{ll} \text{energies} & \frac{5\hbar^2 \pi^2}{2ma^2} + \frac{\mu}{4} \pm \mu \frac{256}{81\pi^4} \\ \text{states} & |\psi\rangle = \frac{1}{\sqrt{2}}(|12\rangle \pm |21\rangle). \end{array} \quad (6.2.16)$$

Note that the state is unperturbed at first order in  $\mu$  but the perturbation **does** determine the **choice** of basis in  $V_\lambda$  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.

$$\mathbf{L} = \hat{\mathbf{x}} \wedge \hat{\mathbf{p}} \quad \text{or} \quad L_i = \varepsilon_{ijk} \hat{x}_j \hat{p}_k \quad \mathbf{L}^2 = L_i L_i. \quad (7.1.1)$$

Then

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

In addition to these fundamental commutation relations we have

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

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

$$\nabla^2 = \underbrace{\frac{1}{r} \frac{\partial^2}{\partial r^2} r}_{\text{radial}} - \underbrace{\frac{1}{r^2 \hbar^2} \mathbf{L}^2}_{\text{angular}}. \quad (7.1.4)$$

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

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

$$\begin{aligned} P_l(u) & \text{ is a Legendre polynomial} \\ P_l^m(u) & \text{ is an associated Legendre function .} \end{aligned}$$

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

$$l = 0, 1, 2, 3, \dots \quad \text{and} \quad m = 0, \pm 1, \pm 2, \dots, \pm l . \quad (7.1.6)$$

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

$$\psi_{lm}(\mathbf{x}) = R_l(r)Y_{lm}(\theta, \phi) , \quad (7.1.7)$$

where

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

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

$$r \mapsto r, \quad \theta \mapsto \pi - \theta, \quad \phi \mapsto \phi + \pi . \quad (7.1.9)$$

Then, under parity map have

$$\begin{aligned} Y_{lm}(\pi - \theta, \phi + \pi) & = (-1)^l Y_{lm}(\theta, \phi) \\ \Rightarrow \psi_{lm}(-\mathbf{x}) & = (-1)^l \psi_{lm}(\mathbf{x}) . \end{aligned} \quad (7.1.10)$$

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

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

where

$$\begin{aligned} \hat{\mathbf{X}} & = \frac{m_1 \hat{\mathbf{x}}_1 + m_2 \hat{\mathbf{x}}_2}{M} & \hat{\mathbf{x}} & = \hat{\mathbf{x}}_1 - \hat{\mathbf{x}}_2 \\ \hat{\mathbf{P}} & = \hat{\mathbf{p}}_1 + \hat{\mathbf{p}}_2 & \hat{\mathbf{p}} & = \frac{m_2 \hat{\mathbf{p}}_1 - m_1 \hat{\mathbf{p}}_2}{M} \\ M & = m_1 + m_2 & m & = \frac{m_1 m_2}{M} \text{ reduced mass} \end{aligned} \quad (7.1.12)$$

CoM degrees of freedom

relative degrees of freedom

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

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

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

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

## 7.2 General analysis of angular momentum eigenstates

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

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

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

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

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

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

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

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

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

Furthermore, we find

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

Furthermore, we find that

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

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

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

Compare with the harmonic oscillator where

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