

# Notes on Quantum Mechanics

Module 2 of Refresher course conducted by Indian Academies of Sciences at  
JSS Educational Institutions, Suttur, Mysore District, Karnataka, Dec 2-14, 2013  
Govind S. Krishnaswami, Chennai Mathematical Institute

- These are very brief and incomplete notes for lectures at the above Refresher Course. Please let me know (govind@cmi.ac.in) of any comments or corrections. 7 Apr, 2020.

## Contents

<b>1</b>	<b>References</b>	<b>2</b>
<b>2</b>	<b>Formalisms of classical and quantum mechanics</b>	<b>2</b>
2.1	Setup of classical mechanics . . . . .	2
2.2	Framework and postulates of quantum mechanics . . . . .	3
2.2.1	Hilbert Space of states of a quantum system . . . . .	3
2.2.2	Observables and hermitian linear operators on states . . . . .	5
2.2.3	Outer products of vectors and completeness relation . . . . .	6
2.2.4	Hermiticity of position and momentum operators . . . . .	7
2.2.5	Commutators of operators . . . . .	8
2.2.6	Eigenvalue problem for hermitian operators . . . . .	8
2.2.7	Measured value of observables in states and interpretation of expectation values . . . . .	11
2.2.8	Schrödinger time evolution of states . . . . .	12
2.2.9	Separation of variables, Stationary states, time-independent Schrodinger equation . . . . .	12
2.2.10	Conserved probability density and current . . . . .	13
2.2.11	Relation between wave function in position and momentum space . . . . .	15
2.3	Ehrenfest's theorem . . . . .	15
2.4	Generators of transformations, symmetries and conservation laws . . . . .	16
2.4.1	Generators of space translations . . . . .	16
2.4.2	Generator of time translation and time evolution operator . . . . .	17
2.4.3	Angular momentum as generator of rotations . . . . .	18
2.4.4	Symmetries and conservation laws . . . . .	18
<b>3</b>	<b>Harmonic oscillator</b>	<b>19</b>
3.1	Algebraic approach via creation and annihilation (ladder) operators . . . . .	20
<b>4</b>	<b>Heisenberg uncertainty principle (inequality)</b>	<b>23</b>
<b>5</b>	<b>Angular momentum</b>	<b>24</b>
5.1	Basic properties of angular momentum . . . . .	24
5.2	Eigenvalues of $L^2$ and $L_z$ by ladder operators . . . . .	25
5.3	Visualization of angular momentum and location in states $Y_{lm}$ . . . . .	26
5.4	Rigid Body . . . . .	27
5.5	Matrix elements of $L_{\pm}$ in the $ lm\rangle$ basis . . . . .	27
5.5.1	E.g.: Matrix representation of angular momenta for $l = 1$ . . . . .	28
<b>6</b>	<b>Spin angular momentum</b>	<b>29</b>
6.1	Spin half: Pauli spin matrices and spinor wave functions . . . . .	31
<b>7</b>	<b>Addition of angular momenta</b>	<b>31</b>
7.1	State space and observables for two particle systems . . . . .	31
7.2	Addition of two spin-half angular momenta . . . . .	33
7.3	Addition of two or more angular momenta . . . . .	34
<b>8</b>	<b>Multiparticle systems: Identical particles: bosons &amp; fermions</b>	<b>35</b>
8.1	Identical and indistinguishable particles . . . . .	35

## 1 References

- Here are some books on quantum mechanics.

1. E. Wichmann, Quantum Physics, Berkeley Physics Course, Vol 4.
2. H. S. Mani and G. K. Mehta, Introduction to Modern Physics.
3. Binayak Dutta-Roy, Elements of Quantum Mechanics.
4. L I Schiff, Quantum Mechanics, 3rd Ed. McGraw-Hill (1968).
5. P J E Peebles, Quantum Mechanics, Princeton Univ Press (1992).
6. B H Bransden and C J Joachain, Quantum Mechanics, 2nd Ed., Pearson (2000).
7. D. J. Griffiths, Introduction to Quantum Mechanics.
8. R. L. Liboff, Introductory Quantum Mechanics.
9. R Shankar, Principles of Quantum Mechanics, 2nd Ed. Plenum Press (1994).
10. P M Mathews and K Venkatesan, A textbook of quantum mechanics, Tata McGraw-Hill (1977).
11. P A M Dirac, The principles of quantum mechanics, 4th Ed., Oxford (1958).
12. W. Heitler, Elementary wave mechanics with applications to Quantum Chemistry.
13. Landau and Lifshitz, Quantum mechanics: Non-relativistic theory, 3rd Edition.

## 2 Formalisms of classical and quantum mechanics

### 2.1 Setup of classical mechanics

- The set of possible instantaneous locations of a classical particle is called its configuration space. This is usually three dimensional Euclidean space  $\mathbb{R}^3$ . The number of coordinates needed to specify the instantaneous configuration of a system is the number of degrees of freedom. A system consisting of a pair of particles has 6 degrees of freedom  $x_1, y_1, z_1, x_2, y_2, z_2$ , its configuration space is  $\mathbb{R}^3 \times \mathbb{R}^3 = \mathbb{R}^6$ . A particle attached to a fixed support by a rod of fixed length has two degrees of freedom, its configuration space is a sphere. The configuration space and number of degrees of freedom are kinematical notions. They do not depend on the nature of forces between the particles.

- If the forces acting on/between the particles are known, then we may determine the dynamical time evolution of the system by solving Newton's equations for the trajectories. For one particle,  $m\ddot{\mathbf{r}} = \mathbf{F}$ . Newton's equations are second order in time, they require two sets of initial conditions, the initial positions  $\mathbf{r}(0)$  and initial velocities  $\dot{\mathbf{r}}(0)$ . In other words the initial coordinates  $\mathbf{r}(0)$  and initial momenta  $\mathbf{p}(0) = m\dot{\mathbf{r}}(0)$  determine the future trajectory. We say that the instantaneous **state** of the system is specified by giving the coordinates and momenta of all the particles. The set of possible instantaneous states of a system is its **phase space**. For a particle moving along a line, its phase space is the  $x - p$  phase plane. Newton's equations may be formulated as Hamilton's equations for the time evolution of coordinates and momenta

$$\dot{x} = \frac{\partial H}{\partial p} \quad \text{and} \quad \dot{p} = -\frac{\partial H}{\partial x}. \quad (1)$$

For a particle in a potential  $H(x, p) = \frac{p^2}{2m} + V(x)$  and Hamilton's equations are a pair of first order equations

$$\dot{x} = \frac{p}{m} \quad \text{and} \quad \dot{p} = -\frac{dV}{dx}, \quad (2)$$

which may be written as a single second order equation expressing Newton's second law  $m\ddot{x} = -V'(x)$ . The curve in phase space  $(x(t), p(t))$  is called the phase trajectory. Draw the phase portrait for a free particle as well as for a simple harmonic oscillator, indicating the direction of trajectories. A dynamical variable that is constant along trajectories is called a constant of motion. Its value may differ from trajectory to trajectory. The hamiltonian  $H = T + V$  is a conserved quantity for conservative systems (i.e. where the force is the negative gradient of a scalar potential).

- Dynamical variables like angular momentum and the hamiltonian are functions of the basic dynamical variables position and momentum. In general, any real function of position and momentum is called an observable. Observables are simply real-valued functions on phase space. They must be real since observables are physical quantities that may be measured.

## 2.2 Framework and postulates of quantum mechanics

### 2.2.1 Hilbert Space of states of a quantum system

- States of a quantum system are vectors in a linear space ("vector space") called a complex Hilbert space  $\mathcal{H}$ . For a particle moving on a line, its configuration space is  $\mathbb{R}^1$ , parametrized by one coordinate  $x$ . Its quantum state space  $\mathcal{H} = L^2(\mathbb{R})$  is the space of square-integrable functions  $\psi(x)$  on the classical configuration space.  $\psi$  is called the state function or state vector or wave function of the particle.

- By Born's probability postulate,  $|\psi(x)|^2 dx$  is interpreted as the probability of finding the particle between  $x$  and  $x + dx$ . Since the total probability of the particle being somewhere should be one, we normalize the wave function  $\int_0^\infty |\psi(x)|^2 dx = 1$ . This is why we restrict to square-integrable wave functions.  $\psi(x)$  itself is called a **probability amplitude**, its square is a probability density.

- Unlike the classical space of states (phase space) which can be a non-linear manifold (e.g. if a particle is constrained to move on a circle), the quantum Hilbert space is always a linear space. The sum of two states  $\psi + \phi$  is a possible state and so is a complex multiple  $c\psi$  of any state. This is the principle of linear superposition of states, used to explain the interference of matter waves in the double slit experiment.

- A complex Hilbert space  $\mathcal{H}$  is a vector space over the complex numbers. It is a space of ket vectors  $|\psi\rangle$  closed under linear superposition. If  $|\psi\rangle$  and  $|\chi\rangle$  are state vectors, then so is  $\alpha|\psi\rangle + \beta|\phi\rangle$ , for any  $\alpha, \beta \in \mathbb{C}$ . A simple example is the two dimensional complex vector space of spin states of a spin half particle which are usually denoted as column vectors  $|\psi\rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$ . Notably, the space of states of a quantum system is a complex, rather than a real vector space.

- The quantum state space is equipped with an inner or dot product. The inner product of a

pair of vectors  $\psi, \chi$  is denoted  $\langle \psi | \chi \rangle$ . For the spin- $\frac{1}{2}$  Hilbert space, the inner product is

$$\langle \psi | \chi \rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}^\dagger \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = (\psi_1^* \quad \psi_2^*) \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \psi^\dagger \chi = \psi_1^* \chi_1 + \psi_2^* \chi_2. \quad (3)$$

$\psi^\dagger$  is called the hermitian adjoint, it is the complex conjugate transpose, it is a row vector. So associated with a vector space of column/ket vectors there is a ‘dual’ space of row/bra vectors, the adjoints of the kets  $|\psi\rangle^\dagger = \langle \psi| = (\psi_1^* \quad \psi_2^*)$ . The inner product may also be regarded as producing a complex number from a bra and a ket vector  $\langle \psi | \chi \rangle$ . However, the inner product of a non-zero vector with itself is always a positive real number  $\langle \psi | \psi \rangle > 0$ , it is called the square of the length of the vector.

- Another example is  $n$ -dimensional complex vector space  $\mathbb{C}^n$  with the inner product  $\langle u | v \rangle = \sum_i u_i^* v_i$ . The Hilbert space of a particle moving on a line is  $L^2(\mathbb{R})$  with  $\langle f | g \rangle = \int_{-\infty}^{\infty} f^*(x)g(x) dx$ .
- From these examples (keep  $\langle u | v \rangle = \sum_i u_i^* v_i$  in mind) we abstract the basic properties of the inner product (these are its defining properties in an axiomatic approach)

$$\langle \alpha u | v \rangle = \alpha^* \langle u | v \rangle, \quad \langle u | \beta v \rangle = \beta \langle u | v \rangle, \quad \langle u + v | w \rangle = \langle u | w \rangle + \langle v | w \rangle, \quad \langle u | v \rangle^* = \langle v | u \rangle. \quad (4)$$

$\langle u | v \rangle$  is linear in the second vector  $v$  and anti-linear in the first vector  $u$  on account of complex conjugation of the components of the first vector.

- The norm/length of a vector is  $\|v\| = \sqrt{\langle v | v \rangle}$ . The norm of a vector is unchanged upon multiplying by a phase  $e^{i\alpha}$ . If  $\langle u | v \rangle = 0$  then the vectors are orthogonal.
- Two state vectors that differ by multiplication by a non-zero complex number  $\psi_2(x) = c\psi_1(x)$  represent the **same physical state**. We often work with unit norm states.
- A basis for the Hilbert space is a set of vectors  $|e_i\rangle$  such that any vector  $|v\rangle$  may be expressed as a linear combination of  $|e_i\rangle$  in a unique way. The number of basis vectors is the dimension of the vector space. The standard basis vectors of the two dimensional spin Hilbert space  $\mathbb{C}^2$  are

$$|e_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |e_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \text{so} \quad \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = v_1 |e_1\rangle + v_2 |e_2\rangle. \quad (5)$$

The coefficients  $v_i$  in the expansion  $|v\rangle = \sum_i v_i |e_i\rangle$  are called the components of  $|v\rangle$ . The components of the adjoint are the complex conjugates:  $\langle v| = \sum_i \langle e_i | v_i^*$ . [We will often drop the summation symbol and assume repeated indices are summed.] E.g. the adjoints of the basis vectors are row bra-vectors

$$\langle e_1| = e_1^\dagger = (1 \quad 0), \quad \langle e_2| = e_2^\dagger = (0 \quad 1). \quad (6)$$

$\mathbb{C}^n$  is an  $n$ -dimensional vector space. The state space of a particle moving on a line,  $L^2(\mathbb{R})$  is infinite dimensional, it is called a function space. It is intuitively clear that this is an infinite dimensional space since the values of the function  $\psi(x)$  at each  $x \in \mathbb{R}$  can be freely specified (subject to normalizability).  $x$  here plays the role of the index  $i = 1, 2$  in the two dimensional spin-half vector space  $\mathbb{C}^2$ . A possible basis for a function space is the set of monomials  $\{1, x, x^2, x^3, x^4, \dots\}$ . Indeed, any function  $\psi$  that has a Taylor series around  $x = 0$  admits a expression as a linear combination of these. The coefficients are the derivatives of  $\psi$  at  $x = 0$ :

$$\psi(x) = \psi(0) + \psi'(0)x + \frac{1}{2}\psi''(0)x^2 + \frac{1}{3!}\psi'''(0)x^3 + \dots \quad (7)$$

However this basis of monomials is a bit inconvenient. In particular, the basis vectors are not orthogonal, in fact they are not even normalizable with respect to the above  $L^2$  inner product. A more convenient basis for  $L^2(\mathbb{R})$  consists of the energy eigenstates of the harmonic oscillator  $|n\rangle$ , which we will study in more detail later.

- It is often convenient to work with an orthonormal basis, i.e., a basis of vectors  $|e_i\rangle$  which are pairwise orthogonal and each normalized to have unit norm,  $\langle e_i|e_j\rangle = \delta_{ij}$ . The standard basis  $|e_i\rangle$  for  $\mathbb{C}^n$  with components  $|e_i\rangle_j = \delta_{ij}$  is orthonormal with respect to the usual inner product  $\langle u|v\rangle = \sum_i u_i^* v_j$ .
- A set of orthonormal vectors is said to be a complete orthonormal set if it forms a basis for the vector space, i.e., if we may write any vector as a linear combination.

### 2.2.2 Observables and hermitian linear operators on states

An observable  $A$  in quantum mechanics (e.g. hamiltonian, position, momentum, angular momentum, spin, magnetic moment) is a hermitian (self-adjoint) linear operator on the Hilbert space of states  $\mathcal{H}$ . Hermiticity is the quantum analogue of classical observables being real-valued functions. We will see that a hermitian operator has real eigenvalues, which are possible results when  $A$  is measured. To define a hermitian operator, we first note that a linear operator on a vector space takes vectors to vectors in a linear way:  $A(a|\psi\rangle + b|\chi\rangle) = aA|\psi\rangle + bA|\chi\rangle$ . When  $A$  acts on a vector  $|v\rangle$  it produces a new ket vector  $A|v\rangle$  which is also denoted  $|Av\rangle$ .

- A linear operator is an abstract concept, whose concrete realisation is a matrix. A linear operator on  $\mathbb{C}^2$  is simply a  $2 \times 2$  matrix, once we choose a basis to represent it. For example, the Pauli matrices  $\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ ,  $\sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ ,  $\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$  are linear operators represented as matrices in the standard basis for  $\mathbb{C}^2$ .
- If  $|e_j\rangle$  are a basis for  $\mathcal{H}$ , then a linear operator  $A$  is determined by how it acts on the basis vectors. Since  $A$  is linear  $A|e_j\rangle$  must be a linear combination of the basis vectors themselves

$$A|e_j\rangle = \sum_i |e_k\rangle A_{kj}. \quad (8)$$

$A_{kj}$  are the components of  $A$  in this basis, they may be written as entries in a matrix, with  $A_{kj}$  occupying the slot in the  $k^{\text{th}}$  row and  $j^{\text{th}}$  column. The vector that makes up the first column  $A_{k1}$  is the ‘image’ of  $e_1$  (i.e. coefficients in the linear combination appearing in  $A|e_1\rangle$ ), the second column  $A_{k2}$  is the image of  $e_2$  and so on.

- A matrix  $A$  is hermitian if it equals its own complex conjugate transpose. The latter is called its adjoint  $A^\dagger = (A^*)^t$ . So  $A$  is hermitian if  $A = A^\dagger$ , i.e., if it is self-adjoint. In terms of matrix entries,  $A_{ij}^* = A_{ji}$ . In particular, the diagonal entries of a hermitian matrix are real, while the off diagonal entries are complex conjugates of each other. The Pauli matrices are hermitian. Note that the adjoint of a product is the product of adjoints in the opposite order.  $(AB)^\dagger = B^\dagger A^\dagger$  and that  $(A|\psi\rangle)^\dagger = \langle\psi|A^\dagger$ . We also denote  $A|\psi\rangle = |A\psi\rangle$ , so that  $|A\psi\rangle^\dagger = \langle A\psi|$ .

- The concept of hermiticity makes sense for a linear operator, even if we have not represented it explicitly as a matrix by choosing a basis. To explain the concept, we need the idea of matrix elements between states. If  $u, v$  are a pair of states, then  $\langle u|A|v\rangle$  is called the **matrix element** of  $A$  between the states  $u$  and  $v$ . To know an operator is to know its matrix elements.

- The **adjoint** of  $A$  is the operator  $A^\dagger$  defined via its matrix elements  $\langle u|A^\dagger|v\rangle = \langle Au|v\rangle$ . So if we know the matrix elements of  $A$ , then we may find the matrix elements of  $A^\dagger$ . A linear operator is **hermitian** if  $\langle u|Av\rangle = \langle Au|v\rangle$  for all states  $u, v \in \mathcal{H}$ . A hermitian operator is also called symmetric by mathematicians since it does not matter whether  $A$  is written on the left or on the right.

- Now let us see how this abstract definition of hermiticity reduces to the formula  $A_{ij} = A_{ji}^*$  for hermitian matrices. We must equate the matrix elements of  $A$  and those of  $A^\dagger$ . Let  $e_i$  be an orthonormal basis, then the matrix element of  $A$  between the states  $e_i$  and  $e_j$  is just  $A_{ij}$ , as is seen by taking the inner product of the above equation with  $e_i$

$$\langle e_i|A|e_j\rangle = \sum_k \langle e_i|e_k\rangle A_{kj} = \sum_k \delta_{ik} A_{kj} = A_{ij}. \quad (9)$$

On the other hand, what are the matrix elements of  $A^\dagger$ ? By the definition of the adjoint,

$$\langle e_i|A^\dagger|e_j\rangle = \langle Ae_i|e_j\rangle = \langle e_j|Ae_i\rangle^* = (A_{ji})^* \quad (10)$$

So a linear operator is self-adjoint if its matrix elements in an orthonormal basis satisfy  $A_{ij} = (A_{ji})^*$ .

### 2.2.3 Outer products of vectors and completeness relation

- **Outer products of vectors:** Consider the vector space  $\mathbb{C}^n$  with standard basis  $|e_i\rangle$ . Just as we may ‘dot’ row and column  $n$ -vectors to get a scalar inner product, we may also form their ‘outer’ product (column times a row), to get an  $n \times n$  matrix. For  $n = 2$  show that

$$|e_1\rangle\langle e_1| = e_1 e_1^\dagger = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad |e_2\rangle\langle e_2| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \quad |e_1\rangle\langle e_2| = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad |e_2\rangle\langle e_1| = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (11)$$

More generally, check that  $|e_i\rangle\langle e_j|$  is a matrix with a 1 in the  $ij$ -entry and 0’s elsewhere. From this we see that a matrix whose entries are  $A_{ij}$  in the  $i^{\text{th}}$  row and  $j^{\text{th}}$  column, can be expressed as

$$A = \sum_{ij} A_{ij} |e_i\rangle\langle e_j| \quad (12)$$

Now let us use this expression to find how a matrix acts on a vector  $v = v_k |e_k\rangle$ . We get

$$Av = \sum_{ij} A_{ij} |e_i\rangle\langle e_j|v_k |e_k\rangle = A_{ij} v_k |e_i\rangle\langle e_j|e_k\rangle = A_{ij} v_k \delta_{jk} |e_i\rangle = A_{ik} v_k |e_i\rangle. \quad (13)$$

So the  $i^{\text{th}}$  component of  $Av$  is  $\sum_k A_{ik} v_k$ .

- In particular, the identity operator  $I$ , may be expressed as

$$I = \sum_i |e_i\rangle\langle e_i| = \sum_{ij} \delta_{ij} |e_i\rangle\langle e_j| \quad (14)$$

The identity operator has the components  $\delta_{ij}$  in any basis since it takes every vector to itself. This ‘resolution’ of the identity operator as a sum of outer products of a set of orthonormal basis vectors is called the **completeness relation**. It is quite useful in many physical problems and

calculations. E.g. the energy eigenstates of the Harmonic oscillator form a complete orthonormal set and satisfy the above completeness relation. Coherent states for the harmonic oscillator also satisfy a completeness relation even though they are not orthogonal and are in fact an over-complete set.

- An anti-hermitian operator is one that satisfies  $A^\dagger = -A$ . A unitary operator is one whose inverse is its adjoint,  $UU^\dagger = U^\dagger U = I$ . It is clear that the identity  $I$  is hermitian as well as unitary. If  $A$  is anti-hermitian, then  $iA$  is hermitian since  $(iA)^\dagger = A^\dagger i^\dagger = -A(-i) = A$ .

### 2.2.4 Hermiticity of position and momentum operators

- Physically interesting examples of hermitian operators for a particle with one degree of freedom moving on a line include the position operator  $\hat{x}\psi(x) = x\psi(x)$ , and momentum operator  $\hat{p}\psi(x) = -i\hbar\psi'(x)$ . Check that  $\hat{x}^\dagger = \hat{x}$  and  $\hat{d} = \frac{\partial}{\partial x}$  is anti-hermitian. We must show  $\langle f|\hat{x}g\rangle = \langle \hat{x}f|g\rangle$  for any two states  $f, g$ . This is seen as follows:

$$\langle f|\hat{x}g\rangle = \int f^*(x)xg(x) dx = \int (xf(x))^*g(x) dx = \langle \hat{x}f|g\rangle. \quad (15)$$

Showing hermiticity of  $\hat{p} = -i\hbar\frac{\partial}{\partial x}$  requires integration by parts. Let us show that  $\hat{d} = \frac{\partial}{\partial x}$  is anti-hermitian, from which it will follow that  $\hat{p} = -i\hbar\hat{d}$  is hermitian. Let us denote complex conjugate of  $f$  by  $\bar{f}$  here for convenience

$$\langle f|\hat{d}g\rangle = \int \bar{f}(x)g'(x)dx = - \int \bar{f}'(x)g(x) dx + [\bar{f}g]_{-\infty}^{\infty} = -\langle \hat{d}f|g\rangle. \quad (16)$$

Here we assumed  $f, g$  vanish at  $\pm\infty$ , which is the case for square-integrable functions. Boundary conditions play an important role in determining the hermiticity of momentum. If we have a particle moving on a finite interval  $[a, b]$  (as in a square well), then

$$\langle f|\hat{d}g\rangle = \int_a^b \bar{f}(x)g'(x)dx = - \int_a^b \bar{f}'(x)g(x) dx + [\bar{f}g]_a^b = -\langle \hat{d}f|g\rangle + [\bar{f}g]_a^b. \quad (17)$$

For  $\hat{d}$  to be anti-hermitian, the boundary term must vanish. This happens, for instance, if the functions vanish at the end points ( $f(a) = f(b) = 0$ , as in an infinite square well) or satisfy ‘periodic boundary conditions’  $f(a) = f(b)$ .

- Of particular importance is the concept of **expectation value** of an observable  $A$  in a state  $\psi$ , which is defined as the normalized diagonal matrix element of  $A$  in the state  $\psi$

$$\langle A\rangle_\psi = \frac{\langle \psi|A\psi\rangle}{\langle \psi|\psi\rangle} \quad (18)$$

The expectation value of a hermitian operator in any state is a real number. For, by hermiticity, and  $\langle u|v\rangle = \langle v|u\rangle^*$ , we have

$$\langle \psi|A\psi\rangle = \langle A\psi|\psi\rangle = \langle \psi|A\psi\rangle^* \quad (19)$$

In other words, the diagonal matrix element of  $A$  is equal to its own complex conjugate. We are familiar with this: the diagonal entries of a hermitian matrix in an orthonormal basis  $\langle e_i|A|e_i\rangle = A_{ii}$  are real.

### 2.2.5 Commutators of operators

- Multiplication of matrices/operators is in general not commutative  $AB \neq BA$  (in general). The amount by which  $AB - BA$  fails to vanish is called the commutator  $[A, B] = AB - BA$ . Any operator commutes with itself or any power of itself  $[A, A^n] = A^{n+1} - A^{n+1} = 0$ . On the other hand, check that  $xp - px = [x, p] = i\hbar I$  by acting on a state  $\psi(x)$ :

$$xp\psi = -i\hbar x\psi'(x), \quad \text{while} \quad px\psi = -i\hbar \frac{\partial}{\partial x}(x\psi) = -i\hbar x\psi'(x) - i\hbar\psi(x) \quad \Rightarrow \quad [x, p]\psi = i\hbar\psi. \quad (20)$$

- In QM, the commutator plays the role that the Poisson bracket plays in CM. Just as the Poisson bracket  $\{f, g\}$  of two observables is another observable,  $\frac{1}{i\hbar}[A, B]$  is again an observable (i.e., hermitian) if  $A, B$  are hermitian. To show this it suffices to check that  $[A, B]$  is anti-hermitian if  $A$  and  $B$  are hermitian.

$$([A, B])^\dagger = (AB - BA)^\dagger = B^\dagger A^\dagger - A^\dagger B^\dagger = BA - AB = -[A, B]. \quad (21)$$

An important property of the commutator is the product or Leibnitz rule, check that

$$[A, BC] = [A, B]C - B[A, C]. \quad (22)$$

- In three dimensions, we have three coordinate and momentum operators  $x, y, z$  and  $p_x = -i\hbar \frac{\partial}{\partial x}, p_y = -i\hbar \frac{\partial}{\partial y}, p_z = -i\hbar \frac{\partial}{\partial z}$ . It is easily seen that the momenta commute with each other and the coordinates commute among themselves, more over  $[x, p_x] = i\hbar$  while  $[x, p_y] = 0$  etc. These so-called **Heisenberg canonical commutation relations** may be summarised as  $[x_i, p_j] = i\hbar \delta_{ij}$ .

### 2.2.6 Eigenvalue problem for hermitian operators

- The **eigenvalue problem** for a linear operator (hermitian or not) is the equation  $A|\psi\rangle = \lambda|\psi\rangle$ . A non-zero vector  $|\psi\rangle \neq 0$  that satisfies this equation for some complex number  $\lambda$  is called an eigenvector of  $A$  with eigenvalue  $\lambda$ . Taking the adjoint of the eigenvalue equation we also have

$$(A|\psi\rangle)^\dagger = \langle\psi|A^\dagger = \lambda^* \langle\psi| \quad (23)$$

So if  $|\psi\rangle$  is an eigen-ket of  $A$  with eigenvalue  $\lambda$ , then  $\langle\psi|$  is an eigen-bra of  $A$  with eigenvalue  $\lambda^*$ . In particular, if  $A = A^\dagger$  is hermitian, then  $\langle\psi|A^\dagger = \langle\psi|A = \lambda^* \langle\psi|$ . In other words, if  $|\psi\rangle$  is an eigen-ket of  $A$ , then  $\langle\psi|$  is an eigen-bra of  $A$  with eigenvalue  $\lambda^*$ . We will soon show that  $\lambda \in \mathbb{R}$   $A$  is hermitian.

- The eigenstate of the position operator  $\hat{x}$  with eigenvalue  $x'$  is denoted  $|x'\rangle$ , i.e.,  $\hat{x}|x'\rangle = x'|x'\rangle$ . We will see that measurement of the position of a particle that is in state  $|x'\rangle$  is guaranteed to give the value  $x'$ . The ‘position-space’ or ‘coordinate-space’ wave function of any state  $|\psi\rangle$  is defined as the inner product  $\langle x|\psi\rangle = \psi(x)$ . It follows that  $\psi^*(x) = \langle\psi|x\rangle$ .

- Similarly, the eigenvalue problem for momentum is  $\hat{p}|k\rangle = \hbar k|k\rangle$ . It is conventional to write the momentum eigenvalue in terms of wave number as  $\hbar k$ . We will see that  $|k\rangle$  is a state in which a measurement of the particle’s momentum will give  $\hbar k$ . The momentum space wave function of a particle in state  $|\psi\rangle$  is defined as  $\tilde{\psi}(k) = \langle k|\psi\rangle$ .  $\tilde{\psi}$  is pronounced ‘psi-tilde’.

- Here are some **useful facts about hermitian matrices/operators**:



1. The eigenvalues of a hermitian operator are real. This is because the eigenvalues of a hermitian operator are simply the expectation values in the corresponding eigenstates

$$A|\psi\rangle = \lambda|\psi\rangle \quad \Rightarrow \quad \langle\psi|A|\psi\rangle = \langle\psi|\lambda\psi\rangle = \lambda\langle\psi|\psi\rangle \quad \Rightarrow \quad \lambda = \frac{\langle\psi|A|\psi\rangle}{\langle\psi|\psi\rangle}. \quad (24)$$

2. Eigenvectors  $|\chi\rangle, |\psi\rangle$  corresponding to distinct eigenvalues  $\mu \neq \lambda$  are orthogonal. To see this, we calculate  $\langle\chi|A\psi\rangle$  in two ways using hermiticity and reality of eigenvalues and subtract.

$$\langle\chi|A\psi\rangle = \lambda\langle\chi|\psi\rangle \quad \text{and} \quad \langle\chi|A\psi\rangle = \langle A\chi|\psi\rangle = \mu\langle\chi|\psi\rangle \quad (25)$$

Thus  $(\lambda - \mu)\langle\chi|\psi\rangle = 0$ . Since  $\lambda \neq \mu$  we must have  $\langle\chi|\psi\rangle = 0$ , i.e., eigenvectors corresponding to distinct eigenvalues are orthogonal.

3. It can be shown that a hermitian operator can be diagonalised by a unitary transformation  $U^\dagger H U = \Lambda$  where  $\Lambda$  is a diagonal matrix with eigenvalues along the diagonal. Moreover, the eigenvectors of a hermitian operator can be chosen to form a complete orthonormal basis for  $\mathcal{H}$

$$A|\psi_i\rangle = \lambda_i|\psi_i\rangle, \quad \langle\psi_i|\psi_j\rangle = \delta_{ij}, \quad \sum_i |\psi_i\rangle\langle\psi_i| = I, \quad . \quad (26)$$

Furthermore, two hermitian operators which commute can be simultaneously diagonalised. In other words, there is a basis of common eigenvectors in which both are diagonal. And if they do not commute, as in the case of  $[x, p] = i\hbar I$ , then they cannot be simultaneously diagonalised. Operators that commute are said to be compatible, we will see that they can be simultaneously measured.

4. The eigenvalue problem for the momentum operator is  $\hat{p}|k\rangle = \hbar k|k\rangle$ . The position space eigenfunction  $\langle x|k\rangle$  of the momentum operator is a plane wave.  $\hat{p}\psi(x) = \hbar k\psi(x)$  becomes  $-i\hbar\psi' = \hbar k\psi$  or  $\psi = Ae^{ikx}$ . We will choose  $A = 1$ . In other words  $\langle x|k\rangle = e^{ikx}$  and so  $\langle k|x\rangle = e^{-ikx}$ .
5. The position-space or coordinate-space eigenfunctions of the position operator are delta-functions. Let's see why. The eigenvalue problem is

$$\hat{x}\psi(x) = x\psi(x) = \lambda\psi(x) \quad \text{where} \quad \lambda \quad \text{is a constant.} \quad (27)$$

The only way this can be satisfied for all  $x$  is for  $\psi(x)$  to vanish at all  $x \neq \lambda$ . Now if  $\psi(x)$  were to vanish at  $x = \lambda$  as well, then it would be the zero function and not qualify as a non-trivial eigenvector. The value of  $\psi(x)$  at  $x = \lambda$  can be either  $\psi(\lambda) = \lambda$  or  $\psi(\lambda) = \infty$ . If  $\psi(\lambda) = \lambda$ , then the state will have zero norm. So it must be infinite at  $x = \lambda$ . In fact,  $\psi(x)$  is proportional to the Dirac delta function. It is normalized so that  $\psi(x) = \delta(x - \lambda)$ . It is conventional to denote the position eigenvalue by  $x'$  rather than  $\lambda$ . So  $\delta(x - x')$  is an eigenfunction of the position operator with eigenvalue  $x'$ , it is a function of  $x$  that is zero every where except at  $x'$ . Think of it as a limit of functions that are sharply peaked at  $x = x'$ . Thus the coordinate space wave function of the eigenstate  $|x'\rangle$  of  $\hat{x}$  is  $\langle x|x'\rangle = \delta(x - x')$ . Now if we have two position eigenstates  $|x'\rangle$  and  $|x''\rangle$ , then their coordinate space wave functions are  $\langle x|x'\rangle = \delta(x - x')$  and  $\langle x|x''\rangle = \delta(x - x'')$ . Their inner product is

$$\langle x''|x'\rangle = \int \delta(x - x'')\delta(x - x') dx = \delta(x' - x''). \quad (28)$$

So position eigenstates are orthogonal and ‘delta-normalized’. They form a complete set in the sense that they satisfy a completeness relation

$$\int dx |x\rangle\langle x| = I. \quad (29)$$

To see this, take the matrix elements of the LHS between coordinate basis states  $|x'\rangle$  and  $|x''\rangle$

$$\int dx \langle x'|x\rangle\langle x|x''\rangle = \int dx \delta(x-x')\delta(x-x'') = \delta(x'-x''). \quad (30)$$

On the other hand, the matrix elements of the identity are also the same  $\langle x'|I|x''\rangle = \langle x'|x''\rangle = \delta(x'-x'')$ . Since  $\int dx |x\rangle\langle x|$  and  $I$  have the same matrix elements, they are equal.

- Similarly, momentum eigenstates form a complete set

$$\int \frac{dk}{2\pi} |k\rangle\langle k| = I. \quad (31)$$

Check this by evaluating the matrix elements between position basis states  $|x'\rangle$  and  $|x''\rangle$ . On the rhs we get  $\langle x'|I|x''\rangle = \delta(x'-x'')$ . On the lhs we get the same using the Fourier representation of the delta function

$$\int_{-\infty}^{\infty} \frac{dk}{2\pi} \langle x'|k\rangle\langle k|x''\rangle = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ikx'} e^{-ikx''} = \delta(x'-x''). \quad (32)$$

How do we get the last equality? If  $x' = x''$  then we are integrating the function 1, and the answer should be infinite, and indeed  $\delta(0) = \infty$ . On the other hand, when  $x' \neq x''$ , then we have

$$\int \frac{dk}{2\pi} [\cos(k(x'-x'')) + i \sin(k(x'-x''))] = 0 \quad (33)$$

Since the average value of both the sine and cosine functions is zero.

- Momentum eigenstates with distinct wave numbers are orthogonal (as we expect for the eigenstates of a hermitian operator)

$$\langle k'|k''\rangle = \int dx \langle k'|x\rangle\langle x|k''\rangle = \int dx e^{-ik'x} e^{ik''x} = 2\pi \delta(k'-k''). \quad (34)$$

6. Among hermitian operators, the positive operators are particularly interesting physically. A hermitian operator is positive (or non-negative) if its expectation value in every state is non-negative  $\langle \psi|A|\psi\rangle \geq 0$ , for all  $\psi \in \mathcal{H}$ . Since eigenvalues are simply the expectation values in eigenstates, we see that positive operators have non-negative eigenvalues. If  $A$  is any linear operator, then we check that  $A^\dagger A$  and  $AA^\dagger$  are both hermitian and positive operators.

$$\text{E.g. } (AA^\dagger)^\dagger = A^{\dagger\dagger} A^\dagger = AA^\dagger. \quad (35)$$

To check positivity, we work out the expectation value in any state:

$$\langle \psi|A^\dagger A|\psi\rangle = \langle A\psi|A\psi\rangle = \|A\psi\|^2 \geq 0 \quad \text{and} \quad \langle \psi|AA^\dagger|\psi\rangle = \langle A^\dagger\psi|A^\dagger\psi\rangle = \|A^\dagger\psi\|^2 \geq 0. \quad (36)$$

An example is kinetic energy  $T = \frac{1}{2m}p^2 = \frac{1}{2m}p^\dagger p = \frac{1}{2m}pp^\dagger$ , since  $p = p^\dagger$  is hermitian. So we may conclude that the energy eigenvalues of a free particle must all be non-negative.

### 2.2.7 Measured value of observables in states and interpretation of expectation values

- Measurement of an observable  $A$  in state  $\psi$  of unit norm produces a real number that is one of the eigenvalues of  $A$ . Born's probability postulate: If we have several identically prepared systems in the same state  $\psi$  and we measure the value of  $A$  in each system and collect the values. Then the frequency of occurrence of the measured value  $\lambda$  is  $p_\lambda = |\langle\psi_\lambda|\psi\rangle|^2$  where  $\psi_\lambda$  is the unit norm eigenstate corresponding to the eigenvalue  $\lambda$ .

- The expectation value of an observable  $A$  in a state  $\psi$  is the mean value obtained when  $A$  is measured on many copies of the system prepared in the same state  $\psi$ . How do we see this? Each measurement gives a (possibly different) eigenvalue  $\lambda$  with probability  $p_\lambda$ . So the mean measured value is a sum over the eigenvalues of  $A$  (counted with multiplicity)

$$\sum_\lambda p_\lambda \lambda = \sum_\lambda \lambda |\langle\psi|\psi_\lambda\rangle|^2 = \sum_\lambda \lambda \langle\psi|\psi_\lambda\rangle \langle\psi|\psi_\lambda\rangle^* = \sum_\lambda \lambda \langle\psi|\psi_\lambda\rangle \langle\psi_\lambda|\psi\rangle = \sum_\lambda \langle\psi|A|\psi_\lambda\rangle \langle\psi_\lambda|\psi\rangle = \langle\psi|A|\psi\rangle. \quad (37)$$

We used the eigenvalue equation and completeness of the eigenvectors  $\sum_\lambda |\psi_\lambda\rangle \langle\psi_\lambda| = I$ .

- **Physical interpretation** of  $\langle x|k'\rangle = e^{ik'x}$  and  $\langle x|x'\rangle = \delta(x-x')$  in the context of probability of results of measurements. Suppose a particle is in a position eigenstate  $|x'\rangle$ . Then its coordinate space wave function is  $\langle x|x'\rangle = \delta(x-x')$ . Now suppose we make a measurement of its position. Then the probability of getting the value  $x$  is  $p_x \propto |\langle x|x'\rangle|^2$ . Notice that  $p_x = 0$  for  $x \neq x'$ . So if we measure the position of a particle known to be in the position eigenstate  $|x'\rangle$ , then the only value of position that can result is  $x'$  itself.

- Suppose a particle is in a position eigenstate  $|x'\rangle$ . Then its momentum space wave function is  $\langle k|x'\rangle = e^{ikx'}$ . Suppose we make a measurement of its momentum. Then the probability of getting the value  $\hbar k$  is  $p_k \propto |\langle k|x'\rangle|^2 = |e^{ikx'}|^2 = 1$ . In other words, all momenta are equally probable. This makes physical sense in light of the Heisenberg uncertainty principle. If the particle is in a position eigenstate, then its position is known with perfect accuracy. So we would expect its momentum to be maximally uncertain. And indeed, what we find is that all possible momenta are equally likely, so we have no knowledge as to what the result of a momentum measurement may give.

- After measuring an observable  $A$  and getting the eigenvalue  $\lambda$ , the state of the system 'collapses' from state  $\psi$  to eigenstate  $\psi_\lambda$  corresponding to the eigenvalue  $\lambda$  ( $A|\psi_\lambda\rangle = \lambda|\psi_\lambda\rangle$ ).

- **Reproducibility of measurements:** If  $A$  is measured again, soon after a previous measurement of  $A$ , then the same value  $\lambda$  will be obtained and the system will remain in the same eigenstate of  $A$ . If a system is in an eigenstate  $|\psi_0\rangle$  of energy, then we know in advance that measurement of energy will result only in the eigenvalue  $E_0$  and that the state will not change after the measurement.

- If two observables (hermitian operators  $A, B$ ) commute, they have common eigenvectors and are simultaneously diagonalisable. We say they are simultaneously measurable or compatible. What this means is that if  $A$  has been measured, and a value  $a$  obtained, then a measurement of  $B$  will not affect the state  $|\psi_a\rangle$  to which the system had collapsed. This is because  $|\psi_a\rangle$  is an eigenstate of  $B$  as well. A measurement of  $B$  will result in the eigenvalue of  $B$  corresponding to the eigenvector  $\psi_a$ .

- It is worth noting that measurement of an observable in a state  $\psi$  is a complicated process that is still not well-understood, and is certainly not the multiplication of the operator  $A$  with the state vector  $\psi$ .

### 2.2.8 Schrödinger time evolution of states

- When left to itself, the state of the system evolves according to the Schrödinger equation  $i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H|\psi(t)\rangle$ .  $H$  is the hermitian hamiltonian. Given the initial state  $|\psi(0)\rangle$ , the SE determines the state at subsequent times, just as Hamilton's equations  $\dot{x} = \frac{\partial H}{\partial p}$ ,  $\dot{p} = -\frac{\partial H}{\partial x}$  do in classical mechanics.

- In the position basis, the SE is

$$i\hbar \frac{\partial}{\partial t} \langle x|\psi(t)\rangle = \langle x|H\psi(t)\rangle \quad \text{or} \quad i\hbar \frac{\partial \psi(x,t)}{\partial t} = (H\psi)(x,t) \quad (38)$$

For a particle in a potential  $(H\psi)(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t)$ , and we get

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi(x). \quad (39)$$

- We often need to work with the adjoint of the Schrodinger equation, which is obtained using  $H = H^\dagger$

$$-i\hbar \frac{\partial}{\partial t} \langle \psi(t)| = \langle \psi(t)|H. \quad (40)$$

In the coordinate basis, the adjoint of the SE reads

$$-i\hbar \frac{\partial}{\partial t} \langle \psi(t)|x\rangle = \langle \psi(t)|H|x\rangle = \langle \psi(t)|H|x\rangle = \langle H\psi|x\rangle = \langle x|H\psi\rangle^* \Rightarrow -i\hbar \frac{\partial}{\partial t} \psi^*(x,t) = ((H\psi)(x))^* \quad (41)$$

or  $-i\hbar \frac{\partial}{\partial t} \psi^*(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi^*(x)}{\partial x^2} + V(x)\psi^*(x)$  for a particle in a real potential  $V(x)$ .

### 2.2.9 Separation of variables, Stationary states, time-independent Schrodinger equation

- The problem of time-evolution is to solve the Schrodinger equation  $i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = \hat{H}|\Psi(t)\rangle$  given the initial state  $|\Psi(t=0)\rangle$ . For a particle in a potential  $V(x)$ , the SE is a LINEAR partial differential equation for the unknown function  $\Psi(x,t) = \langle x|\Psi(t)\rangle$ .

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = (H\Psi)(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t). \quad (42)$$

To solve it we use the method of separation of variables. We look for separable solutions in the form a product  $\Psi(x,t) = \psi(x)T(t)$ . Now, not every solution of the SE is such a product. But due to the linearity of the equation linear combinations of solutions are again solutions. The idea is to find sufficiently many separable solutions so that every solution can be written as a linear combination of separable solutions. Putting the 'ansatz' (guess)  $\Psi(x,t) = \psi(x)T(t)$  into the equation, we get

$$i\hbar \dot{T}(t)\psi(x) = T(t)(H\psi)(x). \quad (43)$$

Dividing by  $T\psi$  we get

$$i\hbar \frac{\dot{T}(t)}{T(t)} = \frac{(H\psi)(x)}{\psi(x)} = E. \quad (44)$$

LHS depends only on time while the RHS depends only on position. The only way these can be equal is for both to equal the same constant, say  $E$ , so-named, since it turns out to have the

physical meaning of energy eigenvalue. Now we have two separate equations. The one for  $T(t)$  has the solution  $T(t) = c \exp(-iEt/\hbar)$ . The other equation

$$(H\psi)(x) = E\psi(x) \quad \text{or} \quad \langle x|H|\psi\rangle = E\langle x|\psi\rangle \quad \text{or} \quad H|\psi\rangle = E|\psi\rangle \quad (45)$$

is simply the eigenvalue equation for the hamiltonian operator. It is also called the time-independent Schrodinger eigenvalue equation. It typically has lots of solutions, namely all the eigenstates  $|\psi_n\rangle$  of the hamiltonian, with their corresponding energy eigenvalues  $E_n$ . As for any hermitian operator, we can take these  $|\psi_n\rangle$  to be orthonormal. Thus the separable solutions of the Schrodinger equation are

$$\Psi_n(x, t) = c_n \psi_n(x) e^{-iE_n t/\hbar}. \quad (46)$$

where  $\psi_n$  are eigenstates of the hamiltonian. These separable solutions are called stationary states since the probability density in these states  $P(x, t) = |\Psi(x, t)|^2 = |c_n|^2 |\psi_n(x)|^2$  are independent of time. Stationary states have the simplest possible time dependence of all solutions of the Schrodinger equation, i.e., sinusoidal or harmonic time dependence.

- Now the general solution of the SE is got by taking a linear combination of stationary states

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}. \quad (47)$$

To find the solution of the initial value problem, we must choose the  $c_n$  so that the initial state is  $|\Psi(0)\rangle$ . In other words, we must have

$$\sum_n c_n |\psi_n\rangle = |\Psi(0)\rangle \quad (48)$$

To find the  $c_n$  we take the inner product with  $|\psi_m\rangle$ , and use orthogonality of energy eigenstates

$$\sum_n c_n \langle \psi_m | \psi_n \rangle = \sum_n \delta_{mn} c_n = c_m = \langle \psi_m | \Psi(0) \rangle \quad \Rightarrow \quad c_m = \int \psi_m^*(x) \Psi(x, 0) dx. \quad (49)$$

Thus we have solved the initial value problem for the Schrodinger equation.

### 2.2.10 Conserved probability density and current

- The absolute square of the wave function  $|\psi(x, t)|^2 = \psi^*(x, t)\psi(x, t)$  gives the probability density for finding the particle at location  $x$  at time  $t$ . Suppose  $n$  copies of a system are prepared in the same quantum mechanical state  $\psi(x)$ . (For example, we could have a hydrogen atom in its ground state in each of 100 different boxes) Then a measurement of the position of each particle (at the same time) gives a (possibly) different result (this is an experimental fact). Born's statistical interpretation of the wave function is that, as  $n \rightarrow \infty$ , the distribution of position measurements approaches the probability density  $|\psi(x, t)|^2$ .

- To qualify as a probability density, the total probability of finding the particle anywhere must be one. In other words, we need  $\int |\psi|^2 = \int dx |\psi(x, t)|^2 = 1$ . However, there could be a problem. For consistency, the total probability of finding the particle *somewhere* must remain equal to

one at all times, total probability must be conserved. This is indeed the case, as is checked using the Schrödinger equation and its adjoint

$$i\hbar \frac{\partial}{\partial t} \langle \psi | \psi \rangle = i\hbar \langle \psi | H \psi \rangle - i\hbar \langle \psi H | \psi \rangle = 0. \quad (50)$$

In other words, if the wave function is normalized to one initially ( $t = 0$ ), then it continues to have norm one in the future. This is called global conservation of probability. But it is not merely the total probability that is conserved. Probability cannot jump from one place to another, it flows continuously like a fluid. There is a local conservation of probability just like for mass in a fluid. The rate of increase of mass of fluid in a box is equal to the inward flux of fluid across the walls of the box (provided there isn't a source/sink of fluid inside the box). The probability density  $|\psi(x, t)|^2$  satisfies a continuity equation with an associated probability current. Consider a particle in a potential

$$\begin{aligned} i\hbar \partial_t (\psi^* \psi) &= i\hbar (\psi_t^* \psi + \psi^* \psi_t) = \left( \frac{\hbar^2}{2m} \psi^{*''} - V \psi^* \right) \psi + \psi^* \left( -\frac{\hbar^2}{2m} \psi'' + V \psi \right) \\ &= \frac{\hbar^2}{2m} [\psi^{*''} \psi - \psi^* \psi''] = \frac{\hbar^2}{2m} \partial_x (\psi^{*'} \psi - \psi^* \psi') \end{aligned} \quad (51)$$

Let  $P(x, t) = |\psi(x, t)|^2$  and define the probability current density

$$j(x, t) = \frac{\hbar}{2mi} (\psi^* \psi' - \psi^{*'} \psi), \quad \text{then} \quad \partial_t P(x, t) + \partial_x j(x, t) = 0. \quad (52)$$

The last equation is called the law of local conservation of probability (in differential form) or a continuity equation. To interpret this formula we consider how the probability for the particle to be in an interval  $[x_0, x_1]$  changes with time. So integrate  $\partial_t P + \partial_x j = 0$  over this interval at a fixed time  $t$  to get the law of local conservation of probability in integral form:

$$\partial_t \int_{x_0}^{x_1} P(x) dx + \int_{x_0}^{x_1} \frac{\partial j(x)}{\partial x} dx = 0 \quad \Rightarrow \quad \partial_t \int_{x_0}^{x_1} P(x) dx = j(x_0) - j(x_1) \quad (53)$$

by the fundamental theorem of calculus. This equation says the rate of increase of probability in  $[x_0, x_1]$  equals the probability current flowing in at  $x_0$  minus that flowing out at  $x_1$ .

- All of this also works in three dimensions. The rate of increase of probability in a region (volume)  $\Omega$  must equal the inward flux of probability across the surface  $\partial\Omega$  that borders  $\Omega$ .

$$\begin{aligned} P(\vec{r}, t) &= \psi^*(\vec{r}, t) \psi(\vec{r}, t), & \vec{j} &= \frac{\hbar}{2mi} [\psi^* (\nabla \psi) - (\nabla \psi^*) \psi] = \frac{\hbar}{m} \Im \psi^* \nabla \psi \\ \partial_t P(\vec{r}, t) + \nabla \cdot \vec{j}(x, t) &= 0, \quad \text{i.e.} \quad \frac{\partial \rho}{\partial t} + \frac{\partial j_1}{\partial x} + \frac{\partial j_2}{\partial y} + \frac{\partial j_3}{\partial z} = 0. \\ \partial_t \int_{\Omega} P(\vec{r}, t) d^3 r + \int_{\Omega} d^3 r \nabla \cdot \vec{j} &= 0 \quad \text{or} \quad \partial_t \int_{\Omega} P(\vec{r}, t) d^3 r + \int_{\partial\Omega} \vec{j} \cdot d\vec{S} = 0. \end{aligned} \quad (54)$$

$d\vec{S}$  is the outward pointing area element on the bounding surface  $\partial\Omega$ . It says that the rate of increase of probability in a region plus the outward flux of probability current must vanish. We used the divergence theorem to write the volume integral of a divergence as a surface integral.

### 2.2.11 Relation between wave function in position and momentum space

- The wave function is a complete specification of the state of a quantum mechanical system, just as giving the position and momentum of a particle completely specifies its classical state. For a particle moving in 3-space, the coordinate space wave function is  $\psi(x, y, z; t)$ . For a system of  $n$  particles, the coordinate space wave function is a function of the three coordinates of each of the  $n$  particles  $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n; t)$ . In other words, the coordinate space wave function is a (time-dependent) function on the classical configuration space of the system.

- We have seen that the position space wave function of a state  $|\psi\rangle$  is defined as  $\psi(x) = \langle x|\psi\rangle$ . Let us denote a momentum eigenstate with momentum eigenvalue  $p = \hbar k$  by  $|k\rangle$ , where  $k$  is the wave number. Then the momentum space wave function of the same state  $|\psi\rangle$  is  $\tilde{\psi}(k) = \langle k|\psi\rangle$ . The point is that  $|\psi\rangle$  is an abstract state vector. We can study it ('represent it') via its components in any basis. In particular, we may look at its components  $\langle x|\psi\rangle = \psi(x)$  in the basis of position eigenstates or its components  $\langle k|\psi\rangle = \tilde{\psi}(k)$  in the basis of momentum eigenstates. Let us see how  $\psi(x)$  is related to  $\tilde{\psi}(k)$ .

- Now inserting a complete set of momentum eigenstates and using  $\langle x|k\rangle = e^{ikx}$ ,

$$\psi(x) = \langle x|\psi\rangle = \int \frac{dk}{2\pi} \langle x|k\rangle \langle k|\psi\rangle = \int \frac{dk}{2\pi} e^{ikx} \tilde{\psi}(k) \quad (55)$$

So the position space wave function is the inverse-Fourier transform of the momentum space wave function. Similarly, we have the Fourier transform

$$\tilde{\psi}(k) = \int dx e^{-ikx} \psi(x). \quad (56)$$

- $\psi(x)$  and  $\tilde{\psi}(k)$  are to be compared with the state of a classical mechanical system, which is given by a *simultaneous* specification of coordinates **and** momenta. In the quantum theory,  $\psi$  cannot depend on both the coordinates and momenta (in an arbitrary manner). This is related to the uncertainty principle.

- The absolute square of the wave function  $|\psi(x, t)|^2 = \psi^*(x, t)\psi(x, t)$  gives the probability density for finding the particle at location  $x$  at time  $t$ . Similarly,  $|\tilde{\psi}(k, t)|^2 \frac{dk}{2\pi}$  is the probability of finding the particle in momentum interval  $[k, k + dk]$  at time  $t$ .

### 2.3 Ehrenfest's theorem

- The expectation values  $\langle x \rangle$ ,  $\langle p \rangle$ ,  $\langle E \rangle$  etc are functions of time (space has been integrated over). The average position and momentum of an electron will depend on time in a way governed by the Schrödinger equation. According to Ehrenfest's theorem, these expectation values evolve as do the corresponding classical variables, whose evolution is given by Newton's/Hamilton's equations! E.g.  $\frac{d\langle x \rangle}{dt} = \frac{\langle p \rangle}{m}$ , so the average position evolves in the same way as given by the first of Hamilton's equations. To see this and related results, we first derive a general equation for the time evolution of expectation value of an observable  $A$  in a unit-norm state that evolves via the SE

$$i\hbar \frac{\partial}{\partial t} \langle \psi|A|\psi \rangle = -\langle \psi|HA|\psi \rangle + \langle \psi|AH|\psi \rangle = \langle \psi|[A, H]|\psi \rangle. \quad (57)$$

- Putting  $A = H$  and using  $[H, H] = 0$  shows that the average energy (expectation value of hamiltonian) is constant  $\frac{\partial \langle \hat{H} \rangle}{\partial t} = 0$ . This is the analogue of the classical constancy of energy along a trajectory.
- Taking  $A = p$  we find the time evolution of mean momentum for a particle subject to the hamiltonian  $H = \frac{p^2}{2m} + V$ . Show that

$$[p, H] = [p, V] = -i\hbar V' \quad (58)$$

Thus we have

$$\frac{\partial \langle p \rangle}{\partial t} = \langle -V' \rangle. \quad (59)$$

Thus Newton's second law (or the second of Hamilton's equations)  $\dot{p} = -V'(x)$  continues to hold in quantum mechanics, but in the sense of expectation values. The average momentum evolves as though it is a classical variable subject to an 'average force'!

- If  $A = x$ , then  $[x, H] = [x, \frac{p^2}{2m}] = \frac{i\hbar p}{m}$ . So

$$\frac{\partial \langle x \rangle}{\partial t} = \left\langle \frac{p}{m} \right\rangle. \quad (60)$$

This is the first of Hamilton's equations  $\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}$ , but now in the sense of expectation values.

- So if the electron is in the initial state  $\psi(x, t = 0)$ , Schrödinger's equation tells us how the state evolves in time. We have used this to determine the motion of the average position of the electron and found that it is related to the average momentum in the same way as the actual position and momentum of a particle are related by Hamilton's equation of classical mechanics. To the extent that the expectation value of  $x$  provides an approximate position for a localized electron wave packet, we see that the quantum mechanical motion of the wave-packet mimics the classical motion of a particle. However, the wave packet typically spreads out in time, and ceases to be well-described by merely its mean position. This reduces the utility of the Ehrenfest result in determining where a quantum particle may be found at later times, based purely on its classical motion.

## 2.4 Generators of transformations, symmetries and conservation laws

### 2.4.1 Generators of space translations

- What does it mean to say that momentum  $\hat{p}$  generates translations, angular momentum generates rotations and the hamiltonian generates time translations?
- Consider first a system with one degree of freedom so that the wave function or potential is a function of one variable  $f(x)$ . Recall that  $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ . Under a translation  $x \mapsto x + \delta a$ , the function becomes

$$f(x + \delta a) = f(x) + \delta a f'(x) + \frac{1}{2}(\delta a)^2 f''(x) + \dots = f(x) - \delta a \frac{1}{i\hbar} (-i\hbar) \frac{\partial}{\partial x} f(x) + \dots = \left( I + \frac{i\hat{p} \delta a}{\hbar} + \dots \right) f.$$

It is in this sense that momentum generates an infinitesimal translation. More generally, for a finite translation one gets  $f(x + a) = e^{i\hat{p}a/\hbar} f(x)$ , as we will see below. Physically,  $f$  could be a wave function or a potential. If  $\hat{p}f = 0$  we say that  $f$  is translation invariant since  $f(x + \delta x) = f(x)$ . For example, a constant potential  $V(x) = V_0$  is translation invariant. Or



a potential  $V(x, y)$  is translation invariant in the z-direction. We say it is annihilated by  $p_z$ , since  $p_z V(x, y) = 0$ .

- In 3d, under an infinitesimal translation  $\mathbf{r} \rightarrow \mathbf{r} + \delta\mathbf{a}$ , a function changes to  $f(\mathbf{r} + \delta\mathbf{a})$ . Using the Taylor expansion

$$f(\mathbf{r} + \delta\mathbf{a}) = f(\mathbf{r}) + \delta\mathbf{a} \cdot \nabla f(\mathbf{r}) + \frac{1}{2} \delta a_i \delta a_j \partial_i \partial_j f(\mathbf{r}) + \dots \quad (61)$$

We can write this in terms of momentum

$$f(\mathbf{r} + \delta\mathbf{a}) \approx \left(1 + \frac{i}{\hbar} \delta\mathbf{a} \cdot \hat{\mathbf{p}}\right) f(\mathbf{r}) \quad (62)$$

And for a finite translation by  $\mathbf{a} = n \delta\mathbf{a}$  we apply the infinitesimal translation  $n$  times and let  $n \rightarrow \infty$  holding  $\mathbf{a}$  fixed

$$f(\mathbf{r} + \mathbf{a}) = \lim_{n \rightarrow \infty} \left(1 + \frac{i}{\hbar} \frac{1}{n} \mathbf{a} \cdot \hat{\mathbf{p}}\right)^n f(\mathbf{r}) = e^{\frac{i}{\hbar} \mathbf{a} \cdot \hat{\mathbf{p}}} f(\mathbf{r}). \quad (63)$$

We say that  $\hat{\mathbf{p}}$  is the infinitesimal generator of translations. If we expand the exponential we will recover the Taylor expansion.

#### 2.4.2 Generator of time translation and time evolution operator

- To find the generator of time translations, we observe that the Schrödinger equation  $i\hbar\dot{\psi} = H\psi$  may be solved for short times to write

$$\psi(t + \delta t) \approx \psi(t) - \frac{iH\delta t}{\hbar} \psi(t) \quad \Rightarrow \quad \psi(t + \delta t) = \left[1 - \frac{iH\delta t}{\hbar}\right] \psi(t) \quad (64)$$

In this sense, the hamiltonian generates infinitesimal time-translations of the wave function. As above, a finite time-translation is given by composing a succession of infinitesimal time-evolutions  $|\psi(t)\rangle = e^{-i\hat{H}t/\hbar} |\psi(0)\rangle$ . The operator  $U(0, t) = e^{-iHt/\hbar}$  is called the time evolution operator. It is unitary if the hamiltonian is hermitian, since then  $U^\dagger U = e^{iHt/\hbar} e^{-iHt/\hbar} = I$ . We may write the time evolution operator as an infinite exponential series

$$U(0, t) = I - \frac{iHt}{\hbar} + \left(\frac{-it}{\hbar}\right)^2 \frac{1}{2!} H^2 + \left(\frac{-it}{\hbar}\right)^3 \frac{1}{3!} H^3 + \dots \quad (65)$$

- Though  $U$  is not an observable, it is still an important operator in quantum mechanics. It is easy to find its eigenstates and eigenvalues. Suppose the eigenstates of the hamiltonian are  $H|\psi_n\rangle = E_n|\psi_n\rangle$ . Then one finds that the energy eigenstates are also eigenstates of the time evolution operator and that

$$U|\psi_n\rangle = e^{-iE_n t/\hbar} |\psi_n\rangle. \quad (66)$$

The eigenvalues of  $U$  are complex numbers of unit magnitude  $e^{-iE_n t/\hbar}$ . The eigenvalues of the time evolution operator give the time evolution of stationary states  $\Psi_n(t) = \psi_n e^{-iE_n t/\hbar}$ .

### 2.4.3 Angular momentum as generator of rotations

- The change in  $\vec{r}$  upon making a rotation by angle  $\delta\phi$  counter clockwise about the axis  $\hat{\phi}$  is  $\delta\vec{r} = \delta\vec{\phi} \times \vec{r}$ .

$$f(\vec{r} + \delta\vec{\phi} \times \vec{r}) = f(\vec{r}) + (\delta\vec{\phi} \times \vec{r}) \cdot \vec{\nabla} f(\vec{r}) \quad (67)$$

Now  $(A \times B) \cdot C = A \cdot (B \times C)$  since both of them measure the volume of a parallelepiped defined by the vectors  $A, B, C$ . Thus using  $p = -i\hbar\nabla$ ,

$$f(\vec{r} + \delta\vec{\phi} \times \vec{r}) \approx f(\vec{r}) + \frac{i}{\hbar} \delta\vec{\phi} \cdot (r \times p) f(\vec{r}) = \left( I + \frac{i}{\hbar} \delta\vec{\phi} \cdot \vec{L} \right) f(\vec{r}). \quad (68)$$

So angular momentum generates rotations. For a finite rotation we have

$$f(\vec{r} + \vec{\phi} \times \vec{r}) = e^{\frac{i}{\hbar} \vec{\phi} \cdot \vec{L}} f(\vec{r}). \quad (69)$$

Here  $\mathbf{L} \cdot \phi = L_x \phi_x + L_y \phi_y + L_z \phi_z$ . We say that  $L_x$  generates a rotation about the  $x$  axis,  $L_y$  generates a rotation about the  $y$  axis and  $L_z$  generates a counter clockwise rotation about the  $z$ .

- Now if  $V(r)$  is a spherically symmetric (central) potential, then we know it is unaffected by rotations. It follows that  $\mathbf{L}V(r) = 0$ . In other words,  $L_i V(r) = 0$ , or the angular momentum operators annihilate the potential. It follows that  $L^2 = \sum_i L_i^2$  also annihilates a spherically symmetric potential. Check that this implies  $[L^2, V(r)] = 0$ . This result will be used in studying motion in a central potential, where one shows  $L^2$  commutes with the hamiltonian (say of the hydrogen atom), so that  $L^2$  and  $H$  are simultaneous observables.

### 2.4.4 Symmetries and conservation laws

- An observable  $A$  (not explicitly dependent on time) is said to generate a symmetry of the hamiltonian  $H$  if it commutes with the hamiltonian  $[A, H] = 0$ . A symmetry leads to a conserved quantity in the following sense: the expectation value of  $A$  in any state (evolving via the Schrödinger equation) is independent of time. Let us see why. Recall from Ehrenfest's theorem, that

$$i\hbar \frac{\partial}{\partial t} \langle \psi | A | \psi \rangle = \langle \psi | [A, H] | \psi \rangle. \quad (70)$$

In addition, we know that time evolution does not change the norm of a state,  $\partial_t \langle \psi | \psi \rangle = 0$ . So if  $[A, H] = 0$ , then the expectation value  $\langle A \rangle_\psi = \frac{\langle \psi | A | \psi \rangle}{\langle \psi | \psi \rangle}$  is time-independent.

- The classical version of this relation between symmetries and conservation laws is called Noether's theorem.
- E.g., consider a particle moving in a potential  $V(\mathbf{r})$ . If the potential is independent of the  $z$ -coordinate, then  $V(\mathbf{r} + a\hat{z}) = V(\mathbf{r})$  so that  $\hat{z} \cdot \nabla V = 0$  or  $p_z(V) = 0$ . It follows that  $[p_z, V] = 0$  and since  $[p_z, \frac{\mathbf{p}^2}{2m}] = 0$ ,  $[p_z, H] = 0$ . So if the potential is  $z$ -translation-invariant then  $\langle \psi | p_z | \psi \rangle$  is conserved in time.
- Similarly, if the potential is invariant under rotations (a central potential), then each component of angular momentum is conserved in the sense of expectation values  $\partial_t \langle \psi | \mathbf{L} | \psi \rangle = 0$ .

- Another consequence of a symmetry ( $[A, H] = 0$ ), is that if the initial state  $\psi(0)$  is an eigenstate of  $A$  with eigenvalue  $a$ , then the system remains in that eigenstate and measurement of  $A$  at any time will result in the value  $a$ . Indeed, suppose the initial state is  $\psi(0)$ , then we know that  $|\psi(t)\rangle = e^{-iHt/\hbar}|\psi(0)\rangle$ . If  $[A, H] = 0$ , it is easily checked that  $|\psi(t)\rangle$  is an eigenvector of  $A$

$$A|\psi(t)\rangle = Ae^{-iHt/\hbar}|\psi(0)\rangle = e^{-iHt/\hbar}A|\psi(0)\rangle = e^{-iHt/\hbar}a|\psi(0)\rangle = a|\psi(t)\rangle. \quad (71)$$

- If  $A$  is a symmetry of the hamiltonian  $H$ , then  $A$  and  $H$  are commuting observables  $[A, H] = 0$  and therefore have a common basis of eigenvectors where both operators are diagonal<sup>1</sup>. It follows that energy eigenstates can be labelled by energy as well as by the eigenvalue of the symmetry  $A$ . This is particularly important when there are several energy levels that are degenerate. The degenerate levels can often be distinguished by the eigenvalue of a symmetry generator. For example, the hamiltonian of the hydrogen atom commutes with  $L_z$  as well as with  $L^2$ , which are a set of three commuting operators. So energy levels can be labelled with the eigenvalues  $\hbar m$  and  $\hbar l(l+1)$  of  $L_z$  and  $L^2$  in addition to the energy eigenvalue  $E_n$  which depends only on the principal quantum number.

### 3 Harmonic oscillator

- Small oscillations of a spring about equilibrium are governed by Hooke's restoring force  $-kx$  or potential energy  $\frac{1}{2}kx^2$ . Classical eq.  $\ddot{x} = -kx$  has solution  $x(t) = A \cos(\omega t) + B \sin(\omega t)$  where the angular freq.  $\omega = \sqrt{k/m}$ . So the hamiltonian is  $H = p^2/2m + \frac{1}{2}m\omega^2x^2$ . Large oscillations require corrections to Hooke's law, and the inclusion of anharmonic forces. Hooke's law is called the linearized (since force is linear in displacement and equation of motion is linear) or harmonic approximation.
- Approximation applies to oscillations of many systems about a point of equilibrium. For example, for small amplitude motion in neighborhood of a minimum  $x_0$  of a potential  $V(x) = V(x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \dots$ , as long as the second derivative of the potential is non-zero at  $x_0$ . The omitted higher order terms in the potential are 'anharmonic' terms.
- Classically, for fixed energy, motion lies between the turning points, where the particle comes instantaneously to rest. The turning points are the solutions of  $E = V(x_0) = \frac{1}{2}kx_0^2$ . All classical trajectories are bound, the particle cannot escape to  $|x| \rightarrow \infty$  for any fixed energy, unlike the free particle. Newton's equation  $m\ddot{x} = -kx$  has solutions  $x(t) = x_0 \cos(\omega t + \delta)$  where the amplitude  $x_0$  and phase  $\delta$  are determined by initial conditions.
- Quantum mechanically, to study the dynamics we reduce the time-dependent Schrodinger equation to the time-independent one for energy eigenstates by separation of variables. The Schrodinger eigenvalue problem is

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + \frac{1}{2}m\omega^2x^2\psi(x) = E\psi(x). \quad (72)$$

---

<sup>1</sup>Suppose  $A\psi = \lambda\psi$  and for simplicity assume that  $\lambda$  is a non-degenerate eigenvalue of  $A$ . Then  $A(H\psi) = HA\psi = \lambda(H\psi)$  so that  $H\psi$  is also an eigenvector of  $A$  with the same eigenvalue  $\lambda$ . As this we assumed  $\lambda$  was a nondegenerate eigenvalue, we must have  $H\psi = \mu\psi$  for some  $\mu$ . So  $\psi$  is a common eigenvector of both  $A$  and  $H$ .

### 3.1 Algebraic approach via creation and annihilation (ladder) operators

- We will find all the energy eigenstates of the SHO by solving  $H\psi = E\psi$ . Rather than solving this second order differential equation directly, we follow a different approach. The ground state will be found by solving a *first order* differential equation. Then we will create all the excited states by suitably modifying the ground state. This may seem an odd way to proceed. But the method works in many quantum mechanical systems and is justified by its success.

- We change to dimensionless variables using  $\beta = \sqrt{m\omega/\hbar}$  which has dimensions of  $L^{-1}$ . So let

$$\xi = \beta x, \quad \mathbf{p} = \frac{p}{\hbar\beta} = -i\frac{\partial}{\partial\xi}, \quad \Rightarrow \quad H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = \frac{\hbar\omega}{2} (\xi^2 + \mathbf{p}^2) \quad (73)$$

$\xi, \mathbf{p}$  are dimensionless. Being the sum of two squares, the hamiltonian is a positive function on phase space. Now, to the extent possible, we wish to factorize the hamiltonian as the product of an operator and its adjoint, which would automatically be a positive operator. To this end, define the dimensionless annihilation (lowering) and creation (raising) operators

$$a = \frac{\xi + i\mathbf{p}}{\sqrt{2}}, \quad a^\dagger = \frac{\xi - i\mathbf{p}}{\sqrt{2}} \quad \Rightarrow \quad a^\dagger a = \frac{1}{2} (\xi^2 + \mathbf{p}^2 + i[\xi, \mathbf{p}]) = \frac{1}{2} (\xi^2 + \mathbf{p}^2 - 1) \quad (74)$$

Here we used  $[\xi, \mathbf{p}] = i$ . Thus, up to an additive constant, the hamiltonian has been factorized:

$$H = \hbar\omega \left( a^\dagger a + \frac{1}{2} \right) = \hbar\omega \left( a a^\dagger - \frac{1}{2} \right), \quad a = \frac{1}{\sqrt{2}} \left( \xi + \frac{\partial}{\partial\xi} \right), \quad a^\dagger = \frac{1}{\sqrt{2}} \left( \xi - \frac{\partial}{\partial\xi} \right). \quad (75)$$

- $a, a^\dagger$  do not commute, their commutator is  $[a, a^\dagger] = a a^\dagger - a^\dagger a = 1$ . In terms of  $x$  and  $p$

$$a^\dagger = \frac{1}{\sqrt{2}} \left( \beta x - \frac{ip}{\hbar\beta} \right) = \frac{1}{\sqrt{2}} \left( \beta x - \frac{1}{\beta} \frac{\partial}{\partial x} \right), \quad a = \frac{1}{\sqrt{2}} \left( \beta x + \frac{1}{\beta} \frac{\partial}{\partial x} \right) \quad (76)$$

- Now suppose  $\psi$  is an energy eigenstate  $H\psi = E\psi$ . The main virtue of the creation and annihilation operators is that they act on  $\psi$  to produce energy eigenstates with higher ( $E + \hbar\omega$ ) and lower ( $E - \hbar\omega$ ) energies. Using  $[a, a^\dagger] = 1$  we find

$$H(a^\dagger\psi) = (E + \hbar\omega)(a^\dagger\psi), \quad H(a\psi) = (E - \hbar\omega)(a\psi). \quad (77)$$

Now by repeated application of  $a$ , we can produce states with negative energy. However, we already saw that  $\langle H \rangle \geq 0$ . A way around this problem is that by repeated application of  $a$  we must eventually reach a state  $\psi_0$  that is annihilated by  $a$ :  $a\psi_0 = 0$ .  $\psi_0$  is the ground state. By repeated application of  $a^\dagger$  on  $\psi_0$  we get all the excited states. Repeated application of  $a$  on  $\psi_0$  gives the zero vector.

- $a\psi_0(x) = 0$  leads to the first order differential equation  $(\xi + \frac{\partial}{\partial\xi})\psi_0(\xi) = 0$  or

$$\xi\psi_0 = -\psi_0' \Rightarrow \log \psi_0 = -\frac{-\xi^2}{2} + c \Rightarrow \psi_0 = A e^{-\xi^2/2} \Rightarrow \psi_0(x) = A e^{-\beta^2 x^2/2}, \quad A = \frac{\sqrt{\beta}}{\pi^{1/4}}$$

The g.s. energy is  $\frac{1}{2}\hbar\omega$ . Why?  $H\psi_0 = \hbar\omega(a^\dagger a + \frac{1}{2})\psi_0 = \frac{1}{2}\hbar\omega\psi_0$ .

- The classical ground state is the static solution of Hamilton's equations,  $x(t) = 0, p(t) = 0$ , where the particle is eternally at rest at the equilibrium point. The quantum g.s. energy  $\frac{1}{2}\hbar\omega$

is not zero, it is called the zero point energy. Classically, the ground state wave function has zero width, it is concentrated at the point  $x = 0$ . Let us indicate why the ground state wave function cannot be too narrow or too broad. The g.s. energy is the expectation value of the hamiltonian in the normalised ground state. Integrate by parts to show that it can be written as

$$\langle H \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} |\psi'(x)|^2 dx + \frac{1}{2} m \omega^2 \int x^2 |\psi(x)|^2 dx. \quad (78)$$

- We introduced  $\beta = \sqrt{\frac{m\omega}{\hbar}}$  which is a constant with dimensions of inverse length.  $\beta$  controls the rate of decay of the position space probability distribution. The larger  $\beta$  is, the less probable it is to find the particle far from the point of equilibrium  $x = 0$ .  $\beta^2 = \frac{\sqrt{mk}}{\hbar}$  is large if the force constant or mass is large, both of which prevent the particle from going far from  $x = 0$ . This is true both quantum mechanically as well as classically. But unlike classically, in QM, the particle in the g.s. has a non-zero probability to be found beyond the classical turning points. The probability for a particle in the ground state to be found beyond the classical turning points  $x_0$  is

$$P(|x| > x_0) = 2 \int_{x_0}^{\infty} |\psi_0(x)|^2 dx \quad (79)$$

This can be evaluated using the error function, it is a very small number for macroscopic  $m, \omega$  and  $E$ . Now if  $\psi(x)$  is very wide, then the mean potential energy would become large, since large values of  $x$  contribute more to the potential energy. On the other hand, if  $\psi(x)$  is very narrow, it must also rise and fall very steeply, resulting in large values of  $\psi'(x)$ , which would make the mean kinetic energy very large. The ground state wave function must strike a balance between these two competing tendencies, the gaussian with width  $1/\beta$  is neither too broad nor too narrow and results in a minimum possible energy expectation value.

- All the excited states are obtained as  $\psi_n(x) = A_n (a^\dagger)^n \psi_0(x)$ , for  $n = 1, 2, 3, \dots$  for appropriate normalization constants shown below to be  $A_n = \frac{1}{\sqrt{n!}}$  to ensure  $\|\psi_n\| = 1$ .

- Since  $a^\dagger \psi_0$  is an eigenstate with energy  $\hbar\omega$  more than that of  $\psi_0$ , the energy level obtained by  $n$ -fold application of  $a^\dagger$  is  $E_n = \frac{1}{2}\hbar\omega + n\hbar\omega = \hbar\omega (n + \frac{1}{2})$ . This is the energy spectrum of the SHO.

- Define the number operator  $\hat{N} = a^\dagger a$ , then  $\hat{H} = \hbar\omega (\hat{N} + \frac{1}{2})$ . So  $\hat{N}\psi_n = n\psi_n$  for  $n = 0, 1, 2, \dots$ .

- To find normalization constants  $A_n$  so that  $\|\psi_n\| = 1$  for  $n = 1, 2, 3, \dots$ . We first note that though  $\psi_0$  may have norm one,  $a^\dagger \psi_0$  need not have norm one, so let us write

$$a^\dagger \psi_n = c_n \psi_{n+1}, \quad \text{and} \quad a \psi_n = d_n \psi_{n-1} \quad (80)$$

To find  $d_n$ , we observe that (use the fact that  $a$  and  $a^\dagger$  are adjoints)

$$1 = \langle \psi_{n-1} | \psi_{n-1} \rangle = \left\langle \frac{a \psi_n}{d_n} \middle| \frac{a \psi_n}{d_n} \right\rangle \Rightarrow |d_n|^2 = \langle \psi_n | a^\dagger a \psi_n \rangle = \langle \psi_n | \hat{N} \psi_n \rangle = n \|\psi_n\|^2 = n. \quad (81)$$

Thus  $d_n = \sqrt{n}$ . Similarly we find that  $c_n = \sqrt{n+1}$ . So

$$a^\dagger \psi_0 = c_0 \psi_1 = \psi_1. \quad a^\dagger \psi_1 = \sqrt{2} \psi_2 \Rightarrow \psi_2 = \frac{1}{\sqrt{2!}} a^\dagger a^\dagger \psi_0, \dots \Rightarrow \psi_n = \frac{1}{\sqrt{n!}} (a^\dagger)^n \psi_0. \quad (82)$$

- For example, the normalized 1st excited state is ( $A_1 = 1$ )

$$\psi_1 = A_1 a^\dagger \psi_0 = \frac{A_1 A}{\sqrt{2}} \left( \xi - \frac{\partial}{\partial \xi} \right) e^{-\xi^2/2} = A\sqrt{2}\xi e^{-\xi^2/2} = \sqrt{2}\beta \frac{\sqrt{\beta}}{\pi^{1/4}} x e^{-\beta^2 x^2/2} = \sqrt{\frac{2m\omega}{\hbar}} \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} x e^{-\frac{m\omega x^2}{2\hbar}}$$

In particular, the first excited state wave function is odd, it has one node ( $\psi_1(0) = 0$ ).

- The excited states are  $\psi_n = A_n \frac{1}{\sqrt{2^n}} \left( \xi + \frac{\partial}{\partial \xi} \right)^n \psi_0 \propto H_n(\xi) e^{-\xi^2/2}$  for some polynomials  $H_n(\xi)$ , which turn out to be the Hermite polynomials. It is clear that  $H_n$  is even in  $\xi$  (parity even) for  $n$  even and odd in  $\xi$  (parity odd) for  $n$  odd since it involves  $\left( \xi + \frac{\partial}{\partial \xi} \right)^n$ . The particle has zero probability density to be found at the equilibrium point  $x = 0$  in all the odd stationary states! In general, the  $n^{\text{th}}$  excited state has  $n$  nodes. Precisely,

$$\psi_n(\xi) = \sqrt{\frac{\beta}{\sqrt{\pi}}} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2} \quad (83)$$

The  $\sqrt{2^n}$  is because Hermite polynomials are conventionally normalized to have leading coefficient  $2^n$ . The first few Hermite polynomials are

$$H_0 = 1, \quad H_1 = 2\xi, \quad H_2 = 4\xi^2 - 2, \quad H_3 = 8\xi^3 - 12\xi. \quad (84)$$

- Let us define the parity operator  $\mathbb{P}f(x) = f(-x)$ . It may be seen to be a hermitian operator on  $L^2(\mathbb{R})$

$$\langle f | \mathbb{P} | g \rangle = \langle \mathbb{P}f | g \rangle = \int_{-\infty}^{\infty} f^*(x) g(-x) dx = \int_{-\infty}^{\infty} f^*(-x) g(x) dx. \quad (85)$$

$\mathbb{P}^2 = I$  so the eigenvalues of parity are  $\pm 1$ . The eigenfunctions of parity with eigenvalue one are the even functions ( $\mathbb{P}f(x) = f(x)$  called even parity functions) and the eigenfunctions with eigenvalue  $-1$  are the odd functions,  $\mathbb{P}f(x) = f(-x) = -f(x)$ . Since  $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2$  is unchanged under  $x \rightarrow -x$  one can show that  $[\mathbb{P}, H] = 0$ . Indeed,

$$\mathbb{P}(H\psi) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(-x)}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 \psi(-x) = H(\mathbb{P}\psi) \quad (86)$$

So parity is a symmetry, and its expectation value in any state is preserved in time. Moreover  $\mathbb{P}$  and  $H$  are simultaneously diagonalisable. So energy eigenfunctions can be labelled by the energy as well as parity eigenvalue. The  $n^{\text{th}}$  state has energy eigenvalue  $E_n = \hbar\omega(n + \frac{1}{2})$  and parity eigenvalue  $(-1)^n$ .

- The energy eigenstates are orthogonal. For  $m, n \neq 0$ , we calculate  $\langle \psi_n | \psi_m \rangle$  in two different ways, by inserting the number operator  $N/n = a^\dagger a/n$  which acts as the identity on the  $n^{\text{th}}$  eigenstate  $N\psi_n = n\psi_n$ :

$$\langle \psi_n | \psi_m \rangle = \frac{1}{m} \langle \psi_n | a^\dagger a \psi_m \rangle = \frac{1}{m} \langle a \psi_n | a \psi_m \rangle \quad (87)$$

On the other hand,

$$\langle \psi_n | \psi_m \rangle = \frac{1}{n} \langle a^\dagger a \psi_n | \psi_m \rangle = \frac{1}{n} \langle a \psi_n | a \psi_m \rangle \quad (88)$$

To be equal,  $m = n$  or if  $m \neq n$ ,  $\langle \psi_n | \psi_m \rangle = 0$ . Combining with normalization,  $\langle \psi_n | \psi_m \rangle = \delta_{mn}$ , for  $m, n \neq 0$  (they cannot be zero since we divided by them). Now, if one of the states is the

ground state, then  $\langle 0|n\rangle = \frac{1}{\sqrt{n!}}\langle 0|(a^\dagger)^n|0\rangle = \langle a^n\psi_0|\psi_0\rangle = 0$  since  $a\psi_0 = 0$ . So all excited states are orthogonal to the ground state. Of course, the g.s. has been normalised to 1, so it follows that  $\langle m|n\rangle = \delta_{mn}$  for all  $m, n = 0, 1, 2, 3, \dots$

- The higher excited states are increasingly oscillatory between the classical turning points. But they decay exponentially to zero outside the classical turning points. As the quantum number  $n$  grows, the probability density in the  $n^{\text{th}}$  excited state begins to approach (in a coarse-grained sense) a classical probability density. By the latter we mean: suppose we have several springs with the same force constant and same energy (large compared to  $\hbar\omega$ ), but let them start oscillating at different times. Then at a common time, we measure the location of each classical oscillator and plot the distribution of positions. We are likely to find fewer oscillators near their points of equilibrium and more near their turning points. This is because the oscillator slows down as it approaches the turning point and speeds up near the equilibrium point. The classical probability distribution is the one to which  $|\psi_n(x)|^2$  tends (provided we do not look too close to see the rapid oscillations). The appearance of classical behaviour in the limit of large quantum numbers is one manifestation of Bohr's correspondence principle.

#### 4 Heisenberg uncertainty principle (inequality)

- Given an observable  $A$  and a unit norm state  $|\psi\rangle$ , we have the variance of  $A$  in the state  $\psi$  (or the square of the standard deviation or simply the square of the uncertainty of  $x$ )

$$(\Delta A)^2 = \langle \psi|(A - \langle A\rangle)^2|\psi\rangle = \langle A^2\rangle - \langle A\rangle^2 \quad (89)$$

The uncertainty in  $A$  measures the spread/width of the distribution of possible measured values of  $A$  in the state  $|\psi\rangle$ . It depends both on  $A$  and  $|\psi\rangle$ . If  $\psi$  is an eigenstate of  $A$  with eigenvalue  $a$ , then the uncertainty of  $A$  is zero. We say that  $A$  takes a definite value  $a$  in an eigenstate.

- Suppose  $\psi$  is a unit norm state, then the Heisenberg uncertainty inequality is  $\Delta x\Delta p \geq \frac{1}{2}\hbar$ . It says that if you prepare a large number of copies of a system in the same state  $\psi$ , and make measurements of position on half of them and momentum on the other half, the product of standard deviations in the measurements of position and momentum is bounded below by  $\hbar/2$ .

- To show this we define an uncertainty functional  $U$  in a state  $\psi$  for a pair of observables  $A, B$  with  $[A, B] = iC$ . Later we will specialize to  $A = x, B = p, C = \hbar I$ .

$$U(\psi) = (\Delta A)^2(\Delta B)^2 = \langle \psi|(A - \bar{A})^2|\psi\rangle\langle \psi|(B - \bar{B})^2|\psi\rangle = \langle \alpha|\alpha\rangle\langle \beta|\beta\rangle \quad (90)$$

where  $|\alpha\rangle = (A - \bar{A})|\psi\rangle \equiv \delta A|\psi\rangle$  and  $|\beta\rangle = (B - \bar{B})|\psi\rangle = \delta B|\psi\rangle$ . By the Cauchy-Schwarz inequality,

$$U \geq |\langle \alpha|\beta\rangle|^2 = |\langle \psi|\delta A \delta B|\psi\rangle|^2 \quad (91)$$

We bring in the commutator and the anticommutator via

$$\delta A\delta B = \frac{1}{2}[\delta A, \delta B] + \frac{1}{2}\{\delta A, \delta B\} = \frac{1}{2}iC + \frac{1}{2}\{\delta A, \delta B\}. \quad (92)$$

Now  $C$  is hermitian as is  $\{\delta A, \delta B\}$ . It follows that  $\frac{1}{2}\langle iC\rangle$  is purely imaginary and  $\frac{1}{2}\langle \{\delta A, \delta B\}\rangle$  is real. So the absolute square of the sum is just the sum of the squares of the imaginary and real parts:

$$U \geq \left| \frac{i}{2}\langle C\rangle + \langle \{\delta A, \delta B\}\rangle \right|^2 = \frac{1}{4}\langle C\rangle^2 + \frac{1}{4}\langle \psi|\{\delta A, \delta B\}|\psi\rangle^2. \quad (93)$$

The second term is  $\geq 0$ . So we get

$$(\Delta A)^2(\Delta B)^2 = U \geq \frac{1}{4}\langle C \rangle_\psi^2. \quad (94)$$

Specializing to  $A = x, B = p, C = \hbar I$  we get the Heisenberg uncertainty inequality  $\Delta x \Delta p \geq \hbar/2$ .

## 5 Angular momentum

### 5.1 Basic properties of angular momentum

- Classically angular momentum  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ . Its cartesian components are

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = zp_y - yp_x \quad \text{Cyclic: } x \rightarrow y \rightarrow z \rightarrow x \quad (95)$$

We could also write them in terms of the Levi-Civita tensor  $\epsilon_{ijk}$  which is anti-symmetric under interchange of any pair of neighbouring indices.

$$L_i = \epsilon_{ijk} r_j p_k, \quad \epsilon_{123} = +1, \epsilon_{132} = -1, \dots \quad (96)$$

- We saw that each component of angular momentum generates a symmetry and is a conserved quantity (in the sense of expectation values), for a particle in a central potential  $V(r)$ .
- In QM, angular momentum is represented in the position basis by the operators

$$L_x = \hat{y}p_z - \hat{z}p_y = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \dots \quad (97)$$

Note that  $y$  and  $p_z$  commute so it does not matter whether we write  $yp_z$  or  $p_z y$  etc. Angular momentum has the dimensions of  $\hbar$ . As a vector  $\hat{\mathbf{p}} = -i\hbar(\partial_x, \partial_y, \partial_z) = -i\hbar\nabla$ . So  $L = -i\hbar\mathbf{r} \times \nabla$ . Check that the angular momentum operators  $L_x, L_y, L_z$  are hermitian:  $L_x^\dagger = L_x$  etc. This is because  $y$  and  $p_z$ , for instance, are hermitian and commute. It follows that  $\vec{L}$  is also hermitian.

- The square of total angular momentum  $L^2$  is defined as the square of the length of the vector  $\vec{L} = (L_x, L_y, L_z)$ .  $L^2 = L_x^2 + L_y^2 + L_z^2$ .  $L^2$  is also hermitian.
- Angular momentum commutation relations. Using the commutators of  $x, y, z, p_x, p_y, p_z$  we show

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y \quad \text{cyclic.} \quad (98)$$

The components of angular momentum aren't simultaneously diagonalizable:

$$(\Delta L_x)^2(\Delta L_y)^2 \geq -\frac{1}{4}\langle [L_x, L_y] \rangle^2 = \frac{\hbar^2}{4}\langle L_z \rangle^2 \Rightarrow \Delta L_x \Delta L_y \geq \frac{\hbar}{2}|\langle L_z \rangle|. \quad (99)$$

$L_x$  and  $L_y$  can't take definite values in the same state, except if  $\langle L_z \rangle = 0$  in that state.

- However, check that  $[L^2, \vec{L}] = 0$ . In other words, each component of angular momentum  $L_x, L_y, L_z$  commutes with the square of the total angular momentum. E.g.,  $L^2$  and  $L_z$  may be simultaneously diagonalized, but not  $L^2, L_z$  and  $L_x$ .
- We may also express angular momentum in spherical polar coordinates

$$z = r \cos \theta, \quad x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi. \quad (100)$$



Calculate derivatives by the chain rule to get

$$L_z = -i\hbar \frac{\partial}{\partial \phi}, \quad L_x = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right), \quad L_y = i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \quad (101)$$

For example,  $x_\phi = -y, y_\phi = x, z_\phi = 0$  where subscripts denote partial derivatives. So

$$-i\hbar \partial_\phi = -i\hbar \left( \frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \phi} \frac{\partial}{\partial z} \right) = -i\hbar (-y \partial_x + x \partial_y) = L_z. \quad (102)$$

- We may also express  $L^2$  in spherical coordinates

$$L^2 \psi = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right]. \quad (103)$$

## 5.2 Eigenvalues of $L^2$ and $L_z$ by ladder operators

- We seek simultaneous eigenstates  $\psi$  of  $L^2$  and  $L_z$  with eigenvalues  $\lambda \hbar^2$  and  $\hbar m$

$$L^2 \psi = \hbar^2 \lambda \psi, \quad L_z \psi = \hbar m \psi \quad (104)$$

To find the allowed values of  $\lambda, m$  we use the ladder operator method. Define  $L_\pm = L_x \pm L_y$ . The virtue of  $L_\pm$  is that if  $\psi$  is one such simultaneous eigenstate, then so are  $L_\pm \psi$ . Indeed, we check using the commutation relations  $[L^2, L_\pm] = 0$  and  $[L_z, L_\pm] = \pm \hbar L_\pm$  that

$$L^2 (L_\pm \psi) = \hbar^2 \lambda (L_\pm \psi), \quad L_z (L_\pm \psi) = \hbar (m \pm 1) (L_\pm \psi). \quad (105)$$

So  $L_\pm$  raises/lowers the eigenvalue of  $L_z$  by  $\hbar$  while leaving the eigenvalue of  $L^2$  unchanged. However, by positivity of  $L_x^2, L_y^2, L_z^2$  and  $L^2 = \vec{L} \cdot \vec{L}$  it follows that the eigenvalues of  $L_z$  for *fixed*  $\lambda$  cannot get too big or too small. So starting with a common eigenfunction  $\psi$  and repeatedly applying  $L_+$ , there must be a state ( $\psi_h$ ) with highest eigenvalue of  $L_z$  (say,  $\hbar l$ ), which is annihilated by  $L_+$

$$L_z \psi_h = \hbar l \psi_h, \quad L_+ \psi_h = 0. \quad (106)$$

But  $\psi_h$  must also be an eigenfunction of  $L^2$ . To see how  $L^2$  acts on  $\psi_h$  we express it in terms of  $L_\pm$

$$L^2 = L_- L_+ + L_z^2 + \hbar L_z \Rightarrow L^2 \psi_h = (\hbar^2 l^2 + \hbar^2 l) \psi_h = \hbar^2 l(l+1) \psi_h \quad (107)$$

So if  $\hbar l$  is the largest eigenvalue of  $L_z$ , then the corresponding eigenvalue of  $L^2$  must be  $\hbar^2 l(l+1)$ . But what are the allowed values of  $l$ ? To find out, we note that there is also a state with lowest eigenvalue of  $L_z$  which is annihilated by  $L_-$

$$L_z \psi_{low} = \hbar l' \psi_{low}, \quad L_- \psi_{low} = 0, \quad l' \leq l \quad (108)$$

But  $\psi_{low}$  must also be an eigenfunction of  $L^2$ . Using

$$L^2 = L_+ L_- + L_z^2 - \hbar L_z \Rightarrow L^2 \psi_{low} = (\hbar^2 l'^2 - \hbar^2 l') \psi_{low} = \hbar^2 l'(l'-1) \psi_{low} \quad (109)$$

However, raising and lowering does not change the eigenvalue of  $L^2$ , so

$$l(l+1) = l'(l'-1), \quad l \geq l'. \quad (110)$$

The solutions are  $l' = -l$  and  $l' = l + 1$ . The latter solution is disallowed since it would imply  $l' > l$ . Thus  $l' = -l$ . So for fixed  $\lambda$ , i.e., fixed  $l$ , the eigenvalues of  $L_z$  go in integer steps from  $l$  to  $-l$ . But this is possible only if  $l - (-l)$  is itself an integer, i.e., if  $l$  is half an integer

$$l = 0, \pm\frac{1}{2}, \pm 1, \pm\frac{3}{2}, \pm 2 \dots \quad (111)$$

And for each such value of  $l$ , the possible eigenvalues of  $L_z$  are  $\hbar(-l, -l + 1, \dots, l - l, l)$ . However, there is a small problem with the non-integer values of  $l$ . We already saw in the last section that the eigenvalues of  $L_z$  are  $\hbar m$  where  $m$  is an integer, if  $m$  was half an odd integer, then  $\Phi(\phi) \neq \Phi(\phi + 2\pi)$  would not be single-valued. Only the integer values  $l = 0, 1, 2, \dots$  lead to simultaneous eigenfunctions of  $L^2$  and  $L_z$ . To summarize, the spectrum of  $L^2$  consists of the numbers  $\hbar^2 l(l + 1)$  where  $l = 0, 1, 2, \dots$ . For each such  $l$ , the spectrum of  $L_z$  consists of the numbers  $\hbar m$  where  $m$  is an integer satisfying  $-l \leq m \leq l$ . So the degeneracy of each eigenvalue of  $L^2$  is  $2l + 1$ . The simultaneous eigenstates are denoted  $|lm\rangle$ , they are orthonormal  $\langle lm|l'm'\rangle = \delta_{mm'}\delta_{ll'}$ .

- We observe that the largest eigenvalue of  $L_z$  among states with square of total angular momentum  $\hbar^2 l(l + 1) > 0$  is  $\hbar l$ . But  $l < \sqrt{l(l + 1)}$  for  $l > 0$ . This means in a state of definite  $L^2$  and  $L_z$ , measured values of  $L_z$  can never equal the (non-zero) total angular momentum. This is different from the classical situation where all the angular momentum can be pointing in (say) the  $z$  direction. Quantum mechanically there cannot be any simultaneous eigenstate where the eigenvalues of  $L_x, L_y$  are zero and that of  $L_z$  and  $L$  equal (and non-zero). Such a state would violate  $\Delta L_x \Delta L_y \geq \frac{\hbar}{2} |\langle L_z \rangle|$ .

### 5.3 Visualization of angular momentum and location in states $Y_{lm}$

- Classically, suppose we are in a stationary state of angular momentum, i.e., one where  $\vec{L}$  points in a fixed direction with fixed magnitude over time. For example, we can be in a classical state where  $L_z = 10^5 \hbar, L_y = 0, L_x = 0$ . We can visualize this in terms of a rigid body that is rotating with constant angular speed about an axis pointing along  $\hat{z}$ . Quantum mechanically, the stationary states may be taken as simultaneous eigenstates  $\psi = Y_{lm}$  of  $L^2$  and  $L_z$ . In such a state we can imagine the angular momentum vector as having length equal to the square-root of the eigenvalue of  $L^2$ , i.e.,  $\sqrt{\hbar^2 l(l + 1)}$ . Moreover, this vector has projection on the  $z$ -axis of  $\hbar m$ . So we know its angle with the  $z$ -axis. But that is as much as we can say. We cannot unambiguously specify its projections on  $x$  or  $y$  axes since  $L_x$  and  $L_y$  do not have definite values in this state. To visualize the ‘angular momentum vector’ in this state, we can think of it as the cone of vectors from the origin whose lengths are  $\sqrt{\hbar^2 l(l + 1)}$  and projection  $\hbar m$  on the  $z$ -axis. This hand-waving visualization can be a useful aid to memory. There are as many vectors on the cone with  $x$ -component of angular momentum equal to  $\hbar m_x$  as  $-\hbar m_x$ . So by symmetry we would expect the expectation value of  $L_x$  in the state  $Y_{lm}$  to vanish, as it does. It is important to realize that this cone *does not* tell us where the particle is likely to be found, it only gives some crude information on the likely values that may be obtained upon a measurement of various components of angular momentum.

- To visualize where the particle is likely to be found if its angular position is measured in state  $Y_{lm}$ , we must plot the probability density  $|Y_{lm}(\theta, \phi)|^2$  on the surface of a unit sphere in polar coordinates  $r = 1, \theta, \phi$ . For example, in the S-wave state  $Y_{00} = \frac{1}{\sqrt{4\pi}}$ , this probability density is constant, indicating that the particle is equally likely to be found at all angular locations. More

generally,  $Y_{lm}(\theta, \phi) \propto e^{im\phi} P_{lm}(\cos \theta)$ . So  $|Y_{lm}|^2 \propto |P_{lm}(\theta)|^2$ . Thus the angular probability distribution is azimuthally symmetric (independent of  $\phi$ ). For example,  $|Y_{10}|^2 \propto \cos^2 \theta$ . So in this state, the particle is more likely to be found near the north pole ( $\theta = 0$ ) or south pole ( $\theta = \pi$ ), than along the equator  $\theta = \pi/2$ . Polar plots of  $P_{lm}(\theta)$  are given in many text books.

## 5.4 Rigid Body

- A molecule can be crudely modelled as rigid body if we are interested in its rotational spectrum. Consider an isotropic rigid body, (i.e., one whose principal moments of inertia are equal) e.g., a spherical ball free to rotate about its center, which is held fixed, to a cube shaped molecule or a tetrahedral molecule. Its rotational kinetic energy is  $H = \frac{L^2}{2I}$  where  $I$  is its moment of inertia about *any* axis passing through its center. Classically, its rotational energy is any positive number, depending on its angular velocity  $\omega = L/I$ . For an isotropic rigid body, in quantum mechanics,  $H$ ,  $L^2$  and  $L_z$  commute and are simultaneously diagonal in the basis of spherical harmonics. The spectrum of energies is discrete,  $E_{lm} = \frac{l(l+1)\hbar^2}{2I}$  where the angular momentum quantum number  $l = 0, 1, 2, \dots$ . The corresponding eigenfunctions are the spherical harmonics  $Y_{lm}(\theta, \phi)$ . The energies are independent of the magnetic quantum number  $m$ . This is because of spherical symmetry. All  $2l + 1$  states  $Y_{lm}$ , for  $m = -l, \dots, l$ , irrespective of their  $z$ -component of angular momentum ( $L_z Y_{lm} = \hbar m Y_{lm}$ ) are degenerate in energy. This is due to the spherical symmetry of the hamiltonian.  $L_x, L_y$  and  $L_z$  are symmetries of  $H$ , they commute with it. The independence of  $E$  on  $m$  means the rotational energy of the body does not depend on its orientation (i.e., independent of the projection of the angular momentum on the  $z$ -axis). In general, symmetries imply degeneracies. And when symmetries are broken, the degeneracy is lost.

- More generally, the rotational kinetic energy of a rigid body free to rotate about a point is  $H = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3}$  where  $I_1, I_2, I_3$  are the principal moments of inertia about the three principal axes of inertia of the body. For an isotropic body,  $I_1 = I_2 = I_3$ .

- The next simplest case is a top, a rigid body with an axis of symmetry, which we can take as the third principal axis. Then  $I_1 = I_2 = I$  and the hamiltonian becomes

$$H = \frac{L_1^2 + L_2^2}{2I} + \frac{L_3^2}{2I_3} = \frac{L^2 - L_3^2}{2I} + \frac{L_3^2}{2I_3}. \quad (112)$$

Written this way, we see that  $[H, L^2] = 0$  and  $[H, L_3] = 0$ , so the hamiltonian is again diagonal in the basis of spherical harmonics. The energy spectrum is

$$E_{lm} = \frac{\hbar^2 l(l+1) - \hbar^2 m^2}{2I} + \frac{\hbar^2 m^2}{2I_3}. \quad (113)$$

Due to lack of isotropy, energy levels now depend on the magnetic quantum number  $m$ . In a sense, the energy depends on the orientation of the rigid body. The  $2l + 1$ -fold degeneracy of energy in the  $m$  quantum number is lost. We still have a 2-fold  $m \rightarrow -m$  degeneracy in the energy spectrum, corresponding. The isotropic case is obtained by putting  $I_3 = I$ .

## 5.5 Matrix elements of $L_{\pm}$ in the $|lm\rangle$ basis

- Let  $|l, m\rangle$  be the normalized simultaneous eigenstates of  $L^2$  and  $L_z$ ,  $\langle lm|l'm'\rangle = \delta_{ll'}\delta_{mm'}$ .

- We already know that

$$\begin{aligned} L^2|lm\rangle &= \hbar^2 l(l+1)|lm\rangle \quad \text{and} \quad L_z|lm\rangle = \hbar m|lm\rangle \\ \text{So } \langle lm|L^2|l'm'\rangle &= \hbar^2 l(l+1)\delta_{ll'}\delta_{mm'} \quad \text{and} \quad \langle lm|L_z|l'm'\rangle = \hbar m\delta_{ll'}\delta_{mm'}. \end{aligned} \quad (114)$$

- Moreover,  $L_{\pm} = L_x \pm iL_y$  raise and lower the value of  $m$  by one, so for some dimensionless constants  $C_{lm}^{\pm}$  we must have

$$L_{\pm}|lm\rangle = \hbar C_{lm}^{\pm}|l, m \pm 1\rangle. \quad (115)$$

- To find  $C^-$ , we use the identity  $L^2 = L_+L_- + L_z^2 - \hbar L_z$  to evaluate the diagonal matrix elements  $\langle lm|L^2|lm\rangle$  in two different ways. We get

$$\begin{aligned} \hbar^2 l(l+1) &= \langle L_-lm|L_-lm\rangle + \langle lm|L_z^2 - \hbar L_z|lm\rangle = \hbar^2 |C_{lm}^-|^2 + \hbar^2 m^2 - \hbar^2 m \\ \Rightarrow |C_{lm}^-|^2 &= l(l+1) - m(m-1) \quad \Rightarrow |C_{lm}^-|^2 = l(l+1) - m(m-1) \end{aligned} \quad (116)$$

Similarly<sup>2</sup>, using  $L^2 = L_-L_+ + L_z^2 + \hbar L_z$  we get  $|C_{lm}^+|^2 = l(l+1) - m(m+1)$ . Thus for some phases  $e^{i\phi_{lm}}$ , we have

$$C_{lm}^- = \sqrt{l(l+1) - m(m-1)}e^{-i\phi_{lm}} \quad \text{and} \quad C_{lm}^+ = \sqrt{l(l+1) - m(m+1)}e^{i\phi_{lm}}. \quad (118)$$

It is possible to absorb these phases into the wave functions and take  $C^{\pm}$  to be real.

$$C_{lm}^{\pm} = \sqrt{l(l+1) - m(m \pm 1)} \quad (119)$$

Thus the matrix elements of  $L_{\pm}$  are

$$\langle l'm'|L_{\pm}|lm\rangle = \hbar\sqrt{l(l+1) - m(m \pm 1)} \delta_{l'l}\delta_{m',m \pm 1}. \quad (120)$$

Using these we can easily get the matrix elements of  $L_x$  and  $L_y$ .

### 5.5.1 E.g.: Matrix representation of angular momenta for $l = 1$

- Let us illustrate with the  $l = 1$  subspace which is  $2l + 1 = 3$  dimensional and is spanned by the orthonormal spherical harmonics  $Y_{1m}(\theta, \phi)$  for  $m = 1, 0, -1$  which we denote  $|m\rangle$  and represent by the column vectors

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (121)$$

In this basis  $L_z|m\rangle = \hbar m|m\rangle$  and  $L^2|m\rangle = l(l+1)\hbar^2|m\rangle$  are represented by the diagonal matrices

$$L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{and} \quad L^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (122)$$

<sup>2</sup>Alternatively, we may use hermiticity  $L_+^\dagger = L_-$ , to get  $C_{lm}^- = (C_{l,m-1}^+)^*$ . To see this, we note that

$$\langle l'm'|L_-|lm\rangle = C_{lm}^- \delta_{l'l'}\delta_{m',m-1} = \langle L_+l'm'|lm\rangle = \langle lm|L_+|l'm'\rangle^* = C_{l'm'}^{+*} \delta_{l'l'}\delta_{m,m'+1} = C_{l,m-1}^{+*} \delta_{l'l'}\delta_{m',m-1} \quad (117)$$

Since these must be equal for all  $l, l', m, m'$  we have  $C_{lm}^- = (C_{l,m-1}^+)^*$ .

$L_{\pm}$  have the action  $L_{\pm}|m\rangle = \sqrt{2 - m(m \pm 1)} \hbar |m \pm 1\rangle$  and are adjoints of each other, so

$$\begin{pmatrix} L_+|1\rangle = 0 \\ L_+|0\rangle = \sqrt{2}\hbar|1\rangle \\ L_+|-1\rangle = \sqrt{2}\hbar|0\rangle \end{pmatrix} \Rightarrow L_+ = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad L_- = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}. \quad (123)$$

Notice that  $L_{\pm}$  are strictly upper/lower triangular and not hermitian. They are not observables. But using them we find the matrices for  $L_x$  and  $L_y$

$$L_x = \frac{L_+ + L_-}{2} = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad L_y = \frac{L_+ - L_-}{2i} = \frac{\hbar}{\sqrt{2}i} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}. \quad (124)$$

- The eigenvalues of  $L_z$  are  $\hbar, 0, -\hbar$ . Since there is nothing special about the  $z$ -direction we should expect the eigenvalues of  $L_y$  and  $L_z$  to also be the same. Check if this is so!
- However,  $L_x$  is not diagonal in the eigenbasis of  $L_z$ . Suppose an atom in the  $l = 1$  state is in the  $m = 0$  eigenstate  $|10\rangle$  or  $Y_{10}(\theta, \phi)$  of  $L_z$ . A measurement of  $L_x$  is made. What are the probabilities of various outcomes of the measurement?
- Measurement of  $L_x$  can result in any one of the eigenvalues  $\hbar m_x = \hbar, 0, -\hbar$ , after which the state collapses to the corresponding eigenstate  $X_+, X_0, X_-$ , which in this case are (show it!)

$$X_+ = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}, \quad X_0 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \quad X_- = \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}. \quad (125)$$

The measurement postulate further tells us that the probability of each outcome is the absolute square of the projection of the initial state  $|0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$  on the final eigenstate. We find

$$\text{prob}(l_x = 0) = |\langle X_0|0\rangle|^2 = 0, \quad \text{prob}(l_x = \hbar) = |\langle X_+|0\rangle|^2 = \frac{1}{2}, \quad \text{prob}(l_x = -\hbar) = |\langle X_-|0\rangle|^2 = \frac{1}{2}. \quad (126)$$

Interestingly, this means measurement of  $L_x$  for a particle in the state  $L_z = 0$  cannot result in the value zero while the values  $\pm\hbar$  occur with equal probability. So if a beam of particles in the  $l = 1, m = 0\rangle$  state enters a Stern-Gerlach apparatus with an inhomogeneous magnetic field component  $B_x$  that couples to the  $L_x$  component of angular momentum via the magnetic moment, then two beams will emerge, corresponding to the  $l_x = \pm\hbar$  values. Different values of  $L_x$  feel different magnetic dipole forces.

## 6 Spin angular momentum

- Spin was initially discovered (by the work of many physicists, culminating in the work of Goudsmit and Uhlenbeck) through a detailed study of atomic spectral lines. Certain forbidden/additional spectral lines were seen (e.g. where one line was expected, two closely spaced lines were seen). To account for these, a new ‘spin’ quantum number  $m_s = \pm\frac{1}{2}$  was introduced, in addition to the  $n, l, m$  quantum numbers used to label the energy levels of the hydrogen atom.

It is interesting to read the translation of a lecture by Goudsmit on the history of the discovery of electron spin, see <http://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html>

- Subsequently, a theory of spin was developed (among others by Pauli), wherein it is treated as another type of angular momentum. The initial analogy was with the spinning of the Earth about its axis, while orbital angular momentum was compared with the motion of the center of mass of the Earth around the sun. However, no such mechanical model for the spin of the electron has been successful. The electron is point-like to current experimental accuracy and even extended particles like the proton (which are not point-like), have intrinsic spin which has not been explained by mechanical analogies. Quantum mechanical spin is regarded as an ‘intrinsic spin’ represented by a vector observable  $\vec{S} = (S_x, S_y, S_z)$ . Intrinsic means not of ‘ $\mathbf{r} \times \mathbf{p}$ ’ origin, i.e., not having to do with movement in three dimensional space. In fact, a massive particle at rest can have a magnetic moment! This magnetic moment must necessarily be of non-orbital origin. Such a magnetic moment is ascribed to its spin. The spin observables are postulated to satisfy the same commutation relations as angular momentum

$$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k \quad (127)$$

Unlike  $L_i$ ,  $S_i$  are not expressible in terms of position and momentum, spin is a new degree of freedom. To make sense of spin in the quantum theory, we need to represent  $S_i$  as hermitian operators acting on some Hilbert space of spin states. In fact, we have already learned how to do this in the context of orbital angular momentum.  $S^2 = S_x^2 + S_y^2 + S_z^2$  and  $S_z$  are simultaneously diagonalizable and their common eigenbasis is denoted  $|s, m\rangle$ .

$$S^2|sm\rangle = s(s+1)\hbar^2|sm\rangle, \quad S_z|sm\rangle = \hbar m|sm\rangle. \quad (128)$$

$S_{\pm}|sm\rangle = (S_x \pm iS_y)|sm\rangle$  are found to be eigenvectors of  $S^2$  with the same eigenvalue  $s(s+1)\hbar^2$ , but eigenvectors of  $S_z$  with eigenvalue raised/lowered by  $\hbar$ ,  $S_{\pm}|sm\rangle \propto |s, m \pm 1\rangle$ . The largest and smallest possible values of  $m$  must be  $s$  and  $-s$  and since  $S_+$  raises  $m$  in steps of 1,  $2s = N$  for some non-negative integer  $N = 0, 1, 2, \dots$ . Thus

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \dots \quad \text{and} \quad m = -s, -s+1, \dots, s-1, s. \quad (129)$$

However, unlike for orbital angular momentum where  $L_z = -i\hbar\frac{\partial}{\partial\phi}$ ,  $S_z$  is not a differential operator in the coordinates of the particle. There is no restriction on the allowed values of  $m$  being integral rather than half integral. Indeed, in nature,  $s$  is found to take on both integer and half odd-integer values.  $s$  is referred to as the spin of the particle. Unlike the orbital angular momentum quantum number  $l$ , a given type of particle (say electron) has a fixed value of spin  $s$ , irrespective of its state of motion or location.

- Electrons, protons, neutrons, muons, neutrinos, quarks all have spin  $s = \frac{1}{2}$ . Mesons like pions and kaons have spin zero, as does the proposed Higgs particle. Rho mesons, photons, gluons and the weak gauge bosons  $W^{\pm}, Z^0$  have spin 1, Delta baryons have spin 3/2, gravitons would have spin two. Atoms as a whole can also have non-zero spin arising collectively from the spins of the electrons protons and neutrons. There are particles with higher spin as well, but we will focus on spin  $s = \frac{1}{2}$ , which is relevant to electrons.

- For each value of spin  $s$ , we need to find a representation of the spin observables  $S_x, S_y, S_z$  as hermitian operators on some Hilbert space. The relevant Hilbert spaces are  $2s+1$  dimensional. This representation may be built up from the lowest state  $|s, -s\rangle$  by repeatedly applying  $S_+$ .

## 6.1 Spin half: Pauli spin matrices and spinor wave functions

Here the Hilbert space of spin states is  $2s + 1 = 2$  dimensional and has basis  $|\frac{1}{2}, \frac{1}{2}\rangle$  and  $|\frac{1}{2}, -\frac{1}{2}\rangle$  which are also denoted  $|\uparrow\rangle$  and  $|\downarrow\rangle$ . The general spin state of a spin half particle is  $a|\uparrow\rangle + b|\downarrow\rangle$ . In this basis,

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \Rightarrow S^2 = \frac{3\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (130)$$

To find the matrix representation of  $S_x$  and  $S_y$  we recall that

$$S_{\pm}|sm\rangle = \hbar\sqrt{s(s+1) - m(m \pm 1)}|s, m \pm 1\rangle. \quad (131)$$

Thus  $S_+|\uparrow\rangle = 0, S_+|\downarrow\rangle = \hbar|\uparrow\rangle$  and

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \Rightarrow S_x = \frac{S_+ + S_-}{2} = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \text{and} \quad S_y = \frac{S_+ - S_-}{2i} = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

The traceless hermitian matrices  $\sigma_i = \frac{2}{\hbar}S_i$  are called Pauli matrices.

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (132)$$

Check that they satisfy

$$[\sigma_i, \sigma_j] = 2\sqrt{-1}\epsilon_{ijk}\sigma_k, \quad \text{and} \quad \sigma_i\sigma_j = \delta_{ij} + i\epsilon_{ijk}\sigma_k. \quad (133)$$

If  $S_z$  is measured in the above general state  $a|\uparrow\rangle + b|\downarrow\rangle$  then the possible values obtained are  $\pm\frac{1}{2}\hbar$  with probabilities given by the absolute squares of the projections of the normalized initial state with the corresponding normalized eigenvectors of  $S_z$ . These probabilities are  $\frac{|a|^2}{|a|^2+|b|^2}$  and  $\frac{|b|^2}{|a|^2+|b|^2}$ . On the other hand, if we measure  $S_x$ , the possible values obtained are again  $\pm\frac{1}{2}\hbar$  but with probabilities  $\frac{1}{2}|a+b|^2$  and  $\frac{1}{2}|a-b|^2$ , where we assume the state has been normalized so that  $|a|^2 + |b|^2 = 1$ .

- The hydrogen atom hamiltonian commutes not just with  $L^2, L_z$  but also  $S^2$  and  $S_z$ . All these operators commute pairwise. So we can label stationary states by their eigenvalues,  $n, l, m$  and also  $s, m_s$ . Of course  $s = \frac{1}{2}$  is fixed for electrons and the energy eigenvalues are independent of  $l, m, m_s$ . So accounting for the two possible spin projections of an electron, the degeneracy of the hydrogen energy levels is  $2n^2$ .

## 7 Addition of angular momenta

### 7.1 State space and observables for two particle systems

So far we dealt with 1-particle systems (electron in an atom, spin in a magnetic field e.t.c.). Now suppose we have a system of two particles, each of whose space of quantum states are the Hilbert spaces  $\mathcal{H}_1$  and  $\mathcal{H}_2$ . For example,  $\mathcal{H}_1$  could be specified by a basis, i.e.,  $\mathcal{H}_1$  is the linear span of a collection of basis vectors, which may be the energy eigenstates of an SHO if we have a particle in one dimension. Similarly, we specify  $\mathcal{H}_2$  as the linear span of a set of basis vectors.

Then the space of states of the combined system is the so-called tensor/direct product Hilbert space  $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$ . If  $\psi_n$  and  $\phi_m$  are a basis for  $\mathcal{H}_1$  and  $\mathcal{H}_2$  respectively, then a basis for  $\mathcal{H}_1 \otimes \mathcal{H}_2$  is given by the vectors  $\psi_n \otimes \phi_m$ . So any state of the combined system is a linear combination of tensor products of basis states of the individual systems.

- This definition is imposed on us by the superposition principle of quantum mechanics. In classical mechanics, the state of a system of 2 particles is given by specifying the state of each particle  $(x_1, p_1, x_2, p_2)$ . Analogously in quantum mechanics we might expect the state of the system to be specified by giving the states of each particle, say  $|\psi_1\rangle|\phi_2\rangle$ . However, the superposition principle says that these cannot be all the states, since a linear combination of states is also an allowed state. This directly leads to the conclusion that arbitrary linear combinations of product states are allowed states of the combined system. Now the tensor product is merely a notation for writing these product states. The definition of tensor product Hilbert space is merely kinematical, it does not presuppose any particular interaction between the particles.

- E.g., if we have two spin half particles, a basis for their combined spinorial Hilbert space is given by

$$|\uparrow\rangle \otimes |\uparrow\rangle \equiv |\uparrow\uparrow\rangle, \quad |\uparrow\rangle \otimes |\downarrow\rangle \equiv |\uparrow\downarrow\rangle, \quad |\downarrow\rangle \otimes |\uparrow\rangle \equiv |\downarrow\uparrow\rangle, \quad |\downarrow\rangle \otimes |\downarrow\rangle \equiv |\downarrow\downarrow\rangle. \quad (134)$$

We sometimes abbreviate by dropping the  $\otimes$  symbol as above. The dimension of the tensor product Hilbert space is the product of dimensions.

- Observables for the two particle system are (hermitian) operators acting on the tensor product Hilbert space. Examples of such operators are tensor products of operators acting on each particle separately. For example, if  $\vec{S}_1$  and  $\vec{S}_2$  are the spin operators for each, then we have the total spin operator

$$\vec{S} = \vec{S}_1 \otimes 1 + 1 \otimes \vec{S}_2 \quad (135)$$

The identity operator for the combined system is  $1 \otimes 1$ . We often drop the  $\otimes$  symbol and suppress the identity operators and write  $\vec{S} = \vec{S}_1 + \vec{S}_2$ . The  $z$ -component of the first spin is  $S_{1z} \otimes 1$ . The total  $z$ -component of spin is  $S_z = S_{1z} \otimes 1 + 1 \otimes S_{2z} \equiv S_{1z} + S_{2z}$ . A tensor product operator  $A \otimes B$  acts on a basis state of the tensor product Hilbert space by

$$(A \otimes B)(u \otimes v) = (Au) \otimes (Bv) \quad (136)$$

The composition of a pair of tensor product operators is given by

$$(A \otimes B)(C \otimes D) = AC \otimes BD \quad (137)$$

This is what you get if you keep in mind that  $C$  acts on the state of the first particle followed by  $A$ , again on the first particle. Similarly,  $D$  acts on the state of the second particle followed by the action of  $B$ . For example, the square of total spin works out to be

$$S^2 = \left( \vec{S}_1 + \vec{S}_2 \right)^2 = S_1^2 \otimes 1 + 1 \otimes S_2^2 + 2\vec{S}_1 \cdot \vec{S}_2. \quad (138)$$

Make sense of this formula and work out how it acts on the above-mentioned tensor product states.

- The tensor product carries a natural inner product induced by the inner products on the individual Hilbert spaces. On basis states, the inner product is

$$\langle u \otimes v | w \otimes z \rangle = \langle u | w \rangle \langle v | z \rangle. \quad (139)$$

For example,  $\langle \uparrow \otimes \uparrow | \uparrow \otimes \downarrow \rangle = \langle \uparrow | \uparrow \rangle \langle \uparrow | \downarrow \rangle = 0$ .



## 7.2 Addition of two spin-half angular momenta

The sum of two spins operators  $\vec{S} = \vec{S}_1 + \vec{S}_2$  satisfies the same angular momentum algebra as each of the individual spins. Check that

$$[S_x, S_y] = [S_{1x} + S_{2x}, S_{1y} + S_{2y}] = i\hbar(S_{1z} + S_{2z}) = i\hbar S_z, \quad \text{e.t.c.} \quad (140)$$

In particular we can carry over all our results on the matrix representation of spin observables which depend only on these commutation relations. In particular,  $[S^2, S_z] = 0$  and we have raising and lowering operators  $S_{\pm} = S_{1\pm} + S_{2\pm}$  which raise or lower the eigenvalue of  $S_z$  by  $\hbar$ . We may denote the simultaneous eigenstates of  $S^2$  and  $S_z$  by  $|sm\rangle$  and as before we must have highest/lowest weight states  $|ss\rangle, |s, -s\rangle$  that are annihilated by  $S_{\pm}$ . Of course, there could be more than one highest weight state labelled by different values of  $s$ . From each highest weight state we can build a representation of spin operators by acting repeatedly with  $S_-$ . Now we want to know what possible values  $s$  can take given that  $\vec{S} = \vec{S}_1 + \vec{S}_2$  is the sum of two spin half observables. For each value of  $s$ , the allowed values of  $m$  will be as before, running from  $-s$  to  $s$  in steps of one.

- Since  $|sm\rangle$  is a state of a two-spin system, it must be expressible as a linear combination of tensor products of states of single spins. There are four tensor product basis vectors

$$|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle \quad (141)$$

We find that all of these are eigenstates of  $S_z = S_{1z} + S_{2z}$  which just adds the  $z$ -components of the two spins. The corresponding values of  $m$  are 1, 0, 0, -1. So it would appear that the value of  $s$  is either 1 or 0, as we will see.

- Now  $S_+|\uparrow\uparrow\rangle = 0$ . So we can build one representation by successively applying  $S_- = S_{1-} + S_{2-}$  to  $|\uparrow\uparrow\rangle$

$$S_-|\uparrow\uparrow\rangle = \hbar|\downarrow\uparrow\rangle + \hbar|\uparrow\downarrow\rangle; \quad S_- (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) = 2\hbar|\downarrow\downarrow\rangle, \quad S_-|\downarrow\downarrow\rangle = 0. \quad (142)$$

These three basis states are found to be eigenstates of  $S^2$  with eigenvalue  $2\hbar^2$  (show this, using the formulae  $S^2 = S_+S_- + S_z^2 - \hbar S_- = S_-S_+ + S_z^2 + \hbar S_+$ ). Thus we have a spin  $s = 1$  three dimensional ‘triplet’ representation on the states

$$|11\rangle = |\uparrow\uparrow\rangle, \quad |10\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad |1, -1\rangle = |\downarrow\downarrow\rangle. \quad (143)$$

The remaining orthogonal state with  $m = 0$ ,

$$|00\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (144)$$

is annihilated by both  $S_-$  and  $S_+$  and therefore furnishes a 1-dimensional representation of total spin. It is shown to be an eigenstate of  $S^2$  and  $S_z$  with eigenvalues 0 and 0. Thus it corresponds to  $s = 0, m_s = 0$  and is called the singlet state  $|00\rangle$ .

- To summarize, the total spin of a composite system consisting of two spin half particles can be either  $s = 0$  or  $s = 1$ . This is expressed in the formula  $\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$ . The four dimensional Hilbert space of the composite system splits into the *direct sum* of a one dimensional subspace spanned by the singlet state with  $s = 0$  and a three dimensional subspace spanned by the

triplet states with  $s = 1$ . Notice that the spin singlet state is anti-symmetric under exchange of particles while the spin triplet states are all symmetric under exchange of particles; this will be exploited when we discuss the Pauli principle.

- The Hilbert space of the combined system has two interesting bases. The first is the ‘uncoupled’ basis of tensor product states  $\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$  which are common eigenstates of  $S_{1z}, S_{2z}, S_1^2$  and  $S_2^2$ , which are all simultaneously diagonalizable. (In fact  $S_1^2$  and  $S_2^2$  are just proportional to the identity). The uncoupled basis states may be denoted  $|s_1, m_1, s_2, m_2\rangle$ .

- Then there is the ‘coupled’ basis of eigenstates of  $S^2, S_z$  (and  $S_1^2$  and  $S_2^2$ ) which we could denote  $|s, m, s_1, s_2\rangle$ . Here  $s_1 = s_2 = \frac{1}{2}$  are constant so we usually suppress them. The coupled basis states consist of the triplet and singlet states.

- We can express the basis vectors of the coupled basis as linear combinations of the uncoupled basis vectors and vice versa.

$$|s, m, s_1, s_2\rangle = \sum_{m_1, m_2} C_{m_1, m_2}^{s, m} |s_1, m_1\rangle \otimes |s_2, m_2\rangle. \quad (145)$$

The coefficients in these linear combinations are called Clebsch-Gordan coefficients. We have obtained a few of them above.

### 7.3 Addition of two or more angular momenta

- More generally, we can combine two spins or angular momenta  $l_1$  and  $l_2$ . The result is that the angular momentum  $l$  of the combination takes each value from  $|l_1 - l_2|$  to  $l_1 + l_2$  in integer steps. This is expressed in the formula

$$l_1 \otimes l_2 = (l_1 + l_2) \oplus (l_1 + l_2 - 1) \oplus \cdots \oplus |l_1 - l_2|. \quad (146)$$

For example, if we form a composite system from two spin one particles, the combined system again behaves like a spin system, but with spin either 2 or 1 or 0. The Clebsch-Gordan coefficients for combining angular momenta are tabulated in various quantum mechanics books. To combine three spins, we first combine two of them and then the third and so on.

- This quantum mechanical procedure for finding the resultant spin is to be contrasted with the vector addition formula for combining angular momenta in classical mechanics. However, there is some similarity. Classically, the resultant angular momentum  $\vec{L} = \vec{L}_1 + \vec{L}_2$  can take a maximum magnitude equal to  $|\vec{L}_1| + |\vec{L}_2|$  when the angular momenta are parallel and a minimal value  $||\vec{L}_1| - |\vec{L}_2||$  when the angular momenta are anti-parallel. These maximal and minimal values are analogous to the quantum mechanical result that the maximum angular momentum quantum number is  $l_1 + l_2$  and minimal value is  $|l_1 - l_2|$ . Of course, classically every value in between is also a possibility depending on the relative orientations of the two angular momentum vectors. Quantum mechanically, only certain intermediate values of  $l$  are allowed, in integer steps! The classical limit is obtained in the limit of large quantum numbers  $l(l+1)\hbar^2 \gg \hbar^2, l_1, l_2 \gg 1$ . In this limit,  $\sqrt{\hbar^2 l(l+1)} \approx \hbar l \rightarrow |\vec{L}|$  e.t.c. Moreover the size of the small integer steps in units of  $\hbar$  is very small compared to the angular momentum and a continuum of values is approximately obtained.

- More generally we may combine any number of spins/angular momenta  $s_1 \otimes s_2 \otimes \dots \otimes s_n$ . Then there is a unique (up to normalization) highest weight state (annihilated by  $S_+$ )  $\psi_{hws}$

with maximal spin projections  $S_z|s_1, \dots, s_n\rangle = \hbar(s_1 + \dots + s_n)|s_1, \dots, s_n\rangle$ . Applying  $S_-$  to this state produces an eigenstate of  $S_z$  with eigenvalue  $\hbar(s_1 + \dots + s_n - 1)$  which is  $\hbar$  less than maximal. This is the symmetric state

$$\psi_S \propto |s_1 - 1, s_2, \dots, s_n\rangle + |s_1, s_2 - 1, \dots, s_n\rangle + \dots + |s_1, s_2, \dots, s_n - 1\rangle \quad (147)$$

We may successively apply  $S_-$  to this to produce a spin  $s_1 + \dots + s_n$  representation. However the space of states with spin projection  $\hbar$  less than maximal is  $n$  dimensional with basis

$$|s_1 - 1, s_2, \dots, s_n\rangle, |s_1, s_2 - 1, \dots, s_n\rangle, \dots, |s_1, s_2, \dots, s_n - 1\rangle. \quad (148)$$

Any state  $\psi$  in this subspace that is orthogonal to  $\psi_S$  is automatically annihilated by  $S_+$  and furnishes a highest weight state for a new spin  $s_1 + \dots + s_n - 1$  representation. This procedure is then repeated. Let us see why  $S_+\psi = 0$ . Since  $S_z(S_+\psi) = \hbar(s_1 + \dots + s_n)S_+\psi$ , and the space of states with maximal spin projection is one dimensional we must have for some constant  $c$

$$S_+\psi = c\psi_{hws} \quad (149)$$

We will show that  $c = 0$  if  $\psi \perp \psi_S$ . Taking an inner product

$$\langle \psi_{hws} | S_+ | \psi \rangle = \langle \psi_{hws} | c \psi_{hws} \rangle = c \Rightarrow c = \langle S_- \psi_{hws} | \psi \rangle = \langle \psi_S | \psi \rangle = 0. \quad (150)$$

The possible resultant spins of a composite system of three spin half particles (e.g. the three electrons in a Lithium atom) can be worked out by combining two of the spins first and then the third

$$\frac{1}{2} \otimes \left( \frac{1}{2} \otimes \frac{1}{2} \right) = \frac{1}{2} \otimes (0 \oplus 1) = \frac{1}{2} \oplus \frac{1}{2} \otimes 1 = \frac{1}{2} \oplus \frac{1}{2} \oplus \frac{3}{2}. \quad (151)$$

So a system of three spin half particles can behave as a spin half particle in two different ways and also as a spin 3/2 particle. The  $\otimes$  can be read as ‘and’, and  $\oplus$  as ‘or’, they are the direct product (tensor product) and direct sum, respectively. So when reading  $\frac{1}{2} \otimes \frac{1}{2}$  we say that if a system consists of a spin half particle AND another spin half particle, then the composite system behaves either as a spin zero system OR as a spin one system.

## 8 Multiparticle systems: Identical particles: bosons & fermions

### 8.1 Identical and indistinguishable particles

In classical physics we can distinguish a pair of tennis balls since they may not have exactly the same mass or number of fibres. Classical objects may be identified/labelled by their intrinsic properties detected by their different interactions with various measuring devices (like light (for color) or smell or mass). By intrinsic properties we mean charge, mass, shape or inertia tensor etc, not the position or speed of the particle. Even if the masses, shapes and inertia tensors were the same to the accuracy of our devices (i.e., the balls seem identical) we could still distinguish the two tennis balls by keeping track of their historical trajectories  $(x(t), p(t))$ , ball A was the one that left the factory at 10am on 23/4/10 etc while ball B had a slightly different trajectory (after all we have never found two tennis balls with coincident trajectories even for a short duration).

- The situation with objects needing a quantum mechanical treatment is somewhat different. No experiment so far has been able to distinguish one electron from another, they all have the

same mass, charge, spin, magnetic moment and interactions with light, atoms etc. What is more, the possibility of distinguishing two electrons based on their semi-classical trajectories may seem to work approximately for some time, but can easily fail. The electron wave packets, if they come quite close, would overlap, interfere and we would not be able to unambiguously label the electrons when the wave packets separate.

- This is a particularly severe problem when we are dealing with atoms with several electrons. The electrons do not have well-defined orbits, their wave functions overlap and it has not been possible to keep track of which electron is which as time progresses. There are many other examples of identical particles in nature including photons in a black body cavity, neutrons in a neutron star, Rubidium atoms in a laser trap etc.
- Contrast this with the situation with planets in the solar system where we can distinguish them by their color/mass/temperature/support for life/historical trajectories etc. So quantum mechanically electrons are identical and indistinguishable. Of course, not all particles are identical and indistinguishable. We *can* tell a proton apart from an electron by its mass.
- The state of a multi-particle system is a ray in the tensor product Hilbert space. Let us consider two identical particles for simplicity. Since the particles are identical, their individual Hilbert spaces of states can be taken to be the same  $\mathcal{H}_1 \cong \mathcal{H}_2$ . If  $\phi_a$  is a basis for the individual Hilbert space, a vector in the tensor product  $\mathcal{H}_1 \otimes \mathcal{H}_2$  is of the form

$$\psi(x_1, x_2) = \sum_{a,b} c_{ab} \phi_a(x_1) \otimes \phi_b(x_2) \quad (152)$$

Define the permutation or exchange operator (not to be confused with parity)  $P\psi(x_1, x_2) = \psi(x_2, x_1)$  which exchanges the coordinates (and spins if we were keeping track of the spins). Check that this implies that  $P$  is hermitian. To implement the identical and indistinguishable nature of the particles, we postulate that the vector  $\psi$  and the vector  $P\psi$  must represent the same physical state. This implies that

$$\psi(x_1, x_2) = e^{i\theta} \psi(x_2, x_1) \quad (153)$$

for some phase  $e^{i\theta}$ . We will find that  $e^{i\theta} = \pm 1$  are the allowed values, corresponding to bosons and fermions respectively. In particular,

$$P\psi(x_1, x_2) = \psi(x_2, x_1) = e^{-i\theta} \psi(x_1, x_2). \quad (154)$$

From the definition of  $P$  we also see that  $P^2 = I$  is the identity. Thus we have

$$P^2\psi(x_1, x_2) = \psi(x_1, x_2) \quad \text{and} \quad P^2\psi(x_1, x_2) = e^{-2i\theta} \psi(x_1, x_2). \quad (155)$$

Comparing we find  $e^{-2i\theta} = 1$  or  $e^{i\theta} = \pm 1$ , which means there are only two possibilities

$$\psi(x_1, x_2) = \pm \psi(x_2, x_1) \quad (156)$$

and we say that wavefunctions of a system of two (though it is true also for more than two) identical particles must be either symmetric or antisymmetric under exchange. Note that this applies to all states, not just energy eigenstates!

- In addition we postulate that exchange of particles must be a symmetry of the dynamics, i.e., classically the forces and energy must not be affected by a permutation of the particles (if

this weren't true we could distinguish the particles). This means the classical hamiltonian is symmetric

$$H(x_1, p_1; x_2, p_2) = H(x_2, p_2; x_1, p_1) \quad (157)$$

In the quantum theory this means  $[P, H] = 0$ . Thus,  $P$  and  $H$  are simultaneously diagonalizable. Energy eigenstates may therefore be chosen to be eigenstates of the exchange operator and must be either symmetric or anti-symmetric functions of the coordinates.

- The symmetric and anti-symmetric functions describe different types of particles. Fermionic particles are those with anti-symmetric wave functions while bosonic particles are those with symmetric wave functions. Electrons in an atom need to be described by anti-symmetric wave functions to match the measured atomic spectra and periodic table. They are fermions. Photons and many isotopes of alkali metal atoms need to be described by symmetric wave functions to match their experimental properties such as Bose condensation. They are bosons. Remarkably, it is found that particles with integer spin  $s = 0, 1, 2, \dots$  are bosons and those with half-odd-integer spin  $s = \frac{1}{2}, \frac{3}{2}, \dots$  are fermions.

- What is more,  $[H, P] = 0$  implies that if the initial state is an eigenstate of  $P$ , then it will remain an eigenstate of  $P$  under Schrödinger evolution with the same eigenvalue. So a system of identical bosons remains this way at all times. We may build multi-particle wave functions by taking products of single particle orbitals and either symmetrizing or anti-symmetrizing for bosons and fermions respectively.

- Examples of symmetrized and antisymmetrized wave functions for two particles are

$$\psi_S(x_1, x_2) = \phi_a(x_1)\phi_b(x_2) + \phi_a(x_2)\phi_b(x_1), \quad \psi_A(x_1, x_2) = \phi_a(x_1)\phi_b(x_2) - \phi_a(x_2)\phi_b(x_1). \quad (158)$$

We remark that this anti-symmetric state could also be written as a 'Slater' determinant.

$$\psi_A(x_1, x_2) = \det \begin{pmatrix} \phi_a(x_1) & \phi_a(x_2) \\ \phi_b(x_1) & \phi_b(x_2) \end{pmatrix} \quad (159)$$

Written this way, antisymmetry is equivalent to the statement that the determinant changes sign under a permutation of two columns. This way of writing anti-symmetric states is particularly useful when there are more than two particles.

- Of course, these are just the simplest examples of (anti-)symmetrized wave functions built out of a pair of single particle wavefunctions. More generally we could take linear combinations of (anti-)symmetric wavefunctions to produce new (anti-)symmetric wave functions. E.g. we may build a fermionic state from four one particle wavefunctions

$$\psi_A(x_1, x_2) = N_1 \det \begin{pmatrix} \phi_a(x_1) & \phi_a(x_2) \\ \phi_b(x_1) & \phi_b(x_2) \end{pmatrix} + N_2 \det \begin{pmatrix} \phi_c(x_1) & \phi_c(x_2) \\ \phi_d(x_1) & \phi_d(x_2) \end{pmatrix} \quad (160)$$

- Symmetric and anti-symmetric wave functions have rather different physical features. For example, the probability amplitude to find both particles at the same location  $x_1 = x_2 = x$  in an anti-symmetrized state is zero  $\psi_A(x, x) = 0$ , though it can be non-zero in a symmetrized state. Alternatively  $\psi_A = 0$  if  $\phi_a = \phi_b = \phi$ . This is loosely stated as 'two identical fermions (e.g. electrons) *cannot* occupy the same 1-particle state  $\phi$ '. On the other hand, two identical bosons (e.g. photons) *can* occupy the same state. We use this while obtaining the distribution of photons in a black body cavity.

- This property of electrons had been postulated by Pauli (even before the development of Schrodinger's equation), in an attempt to explain atomic spectra and the periodic table. Pauli's exclusion principle stated that there was at most one electron per state in an atom. The states could be labelled by the same quantum numbers as appearing in the hydrogen atom  $n, l, m$  and an extra quantum number with two possible values. The latter quantum number was subsequently identified as the electron spin projection  $m_s$ . Of course, the hydrogen atom stationary state wave functions do not account for electron-electron repulsion, and cannot just be taken over to construct the wave function of a many-electron atom. However, there are ways to do this approximately. In any case, the Pauli-exclusion principle in the form 'multi-electron wave functions must be anti-symmetric' under exchange of quantum numbers (coordinates, spins) of any pair of electrons, has stood the test of time.

- For a system of  $N$  identical particles, we define the exchange operators which permute the quantum numbers of  $i^{\text{th}}$  and  $j^{\text{th}}$  particle (coordinates and spin projections)

$$P_{ij}\psi(\cdots, x_i, \cdots, x_j, \cdots) = \psi(\cdots, x_j, \cdots, x_i, \cdots), \quad \text{for } 1 \leq i, j \leq N. \quad (161)$$

Then each  $P_{ij}$  must commute with the hamiltonian. Every energy eigenstate  $\psi(x_1, \cdots, x_n)$  can be taken as either symmetric or antisymmetric under *every* such permutation. Symmetric states describe bosons and anti-symmetric ones describe fermions.

- For three identical particles we have three exchange operators  $P_{12}, P_{23}, P_{31}$ . Note that  $P_{12} = P_{21}$  etc. The action of a permutation operator on a state vector  $\psi(x_1, x_2, x_3)$  must produce a state vector that differs from the original one at most by a phase:  $P_{ij}\psi = e^{i\theta_{ij}}\psi$ . Each permutation operator  $P_{ij}$  squares to the identity  $P_{ij}P_{ij} = I$ , proceeding as before, we find  $e^{i\theta_{ij}} = \pm 1$ .

- In other words, every state of a system of identical and indistinguishable particles must be an eigenstate of all the  $P'_{ij}$ s with eigenvalues  $\pm 1$ . Note that the permutation operators pairwise commute  $P_{ij}P_{kl} = e^{i(\theta_{ij} + \theta_{kl})} = P_{kl}P_{ij}$ . So they are simultaneously diagonalizable. Now a question arises whether a quantum mechanical system of identical and indistinguishable particles can be in a state where some of the  $P_{ij}$ 's have eigenvalue one and some other permutations have eigenvalue minus one. This is not allowed since if there were such a state where, say,  $P_{12}\psi = \psi$  and  $P_{13}\psi = -\psi$  then we could use these eigenvalues to distinguish between particle 2 and particle 3, violating the indistinguishability. So the only allowed states of identical particles are those that are symmetric under *every* exchange and those that are anti-symmetric under *every* exchange. Moreover, since permutations of particles must be symmetries of the dynamics, we must also have  $[P_{ij}, H] = 0$  for all  $i, j$ . Thus, the states which are symmetric under every exchange are preserved under time evolution; they are called systems of bosons. The anti-symmetric states are also preserved under time evolution and are called systems of fermions.

- An example of a fermionic state of  $N$  particles is given by the Slater determinant, which is constructed using  $N$  one particle wave functions ('orbitals'). For  $N = 3$  let  $\phi_a, \phi_b, \phi_c$  be three one-particle wave functions ('orbitals')

$$\psi_A(x_1, x_2, x_3) = \det \begin{pmatrix} \phi_a(x_1) & \phi_a(x_2) & \phi_a(x_3) \\ \phi_b(x_1) & \phi_b(x_2) & \phi_b(x_3) \\ \phi_c(x_1) & \phi_c(x_2) & \phi_c(x_3) \end{pmatrix} \quad (162)$$

To build an example of a bosonic state of three identical particles we only need a single 1-particle orbital  $\psi_S(x_1, x_2, x_3) = \phi(x_1)\phi(x_2)\phi(x_3)$ .

- We may also consider what happens to the state vector of a system of identical particles under permutations that are not simple exchanges of particles. An example is a cyclic permutation of the particles. However, every permutation can be built by composing exchanges, so these new permutations do not contain new information. One finds that wave functions of systems of fermions are anti-symmetric under odd-permutations, such as pairwise exchanges. Under even permutations such as  $P_{12}P_{23}$ , wave functions of systems of fermions are unchanged. Wave functions of systems of bosons are unchanged under all permutations, irrespective of whether they are even or odd.

## 8.2 Application: electronic configuration of light elements and periodic table

- Now let us briefly apply the ideas of identical and indistinguishable particles and Pauli's principle to the  $n$ -electrons in an atom, governed by the hamiltonian

$$H = \sum_{i=1}^N \left( \frac{p_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_i|} \right) + \sum_{1 \leq i < j \leq N} \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} \quad (163)$$

The determine and understand the ground (and excited states) of the atom is a very challenging problem, which occupied and continues to occupy many physicists and chemists. To find the ground state, we may (as a first approximation) ignore the inter-electron repulsion. In this approximation, it would seem that each electron 'sees' only the nucleus in a hydrogenic atom with nuclear charge  $Z$ . But there is a crucial difference. The  $N$ -electron wave function  $\psi(\vec{r}_1, m_1; \dots, \vec{r}_N, m_N)$  depends on the positions  $x_i$  and spin projections  $m_i$  of each of the electrons. By Pauli's principle, it must be antisymmetric under exchange of any pair of electrons. A simple way of constructing such an antisymmetric wave function is to choose  $n$  one-particle wave functions or orbitals  $\phi_1, \dots, \phi_n$  and form their Slater determinant, e.g.,

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = A \det \begin{pmatrix} \phi_1(r_1) & \phi_1(r_2) & \phi_1(r_3) \\ \phi_2(r_1) & \phi_2(r_2) & \phi_2(r_3) \\ \phi_3(r_1) & \phi_3(r_2) & \phi_3(r_3) \end{pmatrix} \quad (164)$$

We suppress the spin projections  $m_i$  so  $r_i$  refers to  $\vec{r}_i, m_i$ . Now the orbitals must be chosen carefully to ensure that the energy is minimized (this is the statement of the variational principle). An example of an orbital is the ground state wave function of hydrogen.

$$\phi_1(r) = \langle r | n = 1, l = 0, m_l = 0, s = \frac{1}{2}, m_s = \frac{1}{2} \rangle \propto e^{-r/a_0} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (165)$$

We could equally well have chosen  $m_s = -\frac{1}{2}$ . The ground state electronic configuration of hydrogen is called  $1s^1$ , one electron in the  $n = 1$  shell with zero angular momentum ( $s = 0$ ). For Helium, we select a second hydrogenic orbital with as little energy as possible  $|\phi_2\rangle = |n = 1, l = 0, m_l = 0, s = \frac{1}{2}, m_s = -\frac{1}{2}\rangle$ , different from  $\phi_1$  to implement Pauli's principle.  $\phi_1$  and  $\phi_2$  are anti-symmetrized via a  $2 \times 2$  Slater determinant, resulting in

$$\psi = \phi_{n=1, l=0, m=0}(r_1)\phi_{n=1, l=0, m=0}(r_2) \frac{1}{\sqrt{2}} (\uparrow\downarrow - \downarrow\uparrow) \sim e^{-(r_1+r_2)/a} (\uparrow\downarrow - \downarrow\uparrow). \quad (166)$$

This wave function is symmetric under exchange of spatial variables but anti-symmetric under exchange of spins, it is the singlet spin-zero state obtained from combining two spin halves. It

is called para helium. The electronic configuration of Helium is  $1s^2$ , two  $S$ -wave electrons in the  $K(n = 1)$  shell. Helium has a filled  $K$ -shell.

- For Lithium, we could select the next orbital as  $|\phi_3\rangle = |n = 2, l = 0, m_l = 0, m_s = \frac{1}{2}\rangle$  resulting in  $1s^2 2s^1$ . Proceeding in this way, we get  $1s^2 2s^2 2p^6$  for Neon and  $1s^2 2s^2 2p^6 3s^2 3p^6$  for Argon. But the configurations of potassium  $4s^1$  and magnesium  $4s^2$  are somewhat anomalous, the  $4s$  shell is filled before the  $3d$  shell, as it is energetically favourable to do so, when one includes the effect of inter-electron repulsion. Let us crudely indicate why. In general, the  $n = 4$  shell has a higher energy than the  $n = 3$  shell, since the hydrogenic energies are  $E \sim -\frac{1}{n^2}$ . On the other hand, in a higher angular momentum orbital (e.g.  $l = 2$  d-orbital), the electron probability density is concentrated farther from the nucleus than in a lower angular momentum orbital (say s-orbital,  $l = 0$ ). This is seen from the  $\psi \sim r^l$  behaviour of hydrogenic wave functions, they are more strongly suppressed for small  $r$  if  $l$  is larger. In a multi-electron atom, like potassium, the nuclear charge is partly screened by the inner shell electrons ('Neon core'), and it is energetically favourable for the valence electron of Potassium to be more tightly bound to the nucleus by occupying the  $4s$  orbital rather than the  $3d$  orbital. For further discussion of the periodic table, see the books by Griffiths, Liboff, Schiff, Heitler etc mentioned in the list of reference books and the books cited therein.