

Symmetries in Quantum Mechanics  
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## 2 Generators of transformations, symmetries and conservation laws

### 2.1 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 at the translated point is

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

It is in this sense that momentum generates an infinitesimal translation. More generally, for a finite translation one gets  $f(x + a) = e^{ipa/\hbar} f(x)$ , as we will see below. Physically,  $f$  could be a wave function or a potential. If  $pf = 0$  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. Similarly, 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

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

We can write this in terms of momentum

$$f(\mathbf{r} + \delta \mathbf{a}) \approx \left( 1 + \frac{i}{\hbar} \delta \mathbf{a} \cdot \hat{\mathbf{p}} \right) f(\mathbf{r}) \quad (2)$$

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  $\delta \mathbf{a}$  fixed

$$f(\mathbf{r} + \mathbf{a}) = \lim_{n \rightarrow \infty} \left( I + \frac{i}{\hbar} \frac{1}{n} \mathbf{a} \cdot \hat{\mathbf{p}} \right)^n f(\mathbf{r}) = e^{\frac{i}{\hbar} \mathbf{a} \cdot \hat{\mathbf{p}}} f(\mathbf{r}). \quad (3)$$

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

### 2.2 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

$$\psi(t + \delta t) \approx \psi(t) - \frac{iH\delta t}{\hbar} \psi(t) \quad \Rightarrow \quad \psi(t + \delta t) = \left[ 1 - \frac{iH\delta t}{\hbar} \right] \psi(t) \quad (4)$$

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  $U(t, 0) = e^{-iHt/\hbar}$  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

$$U(t, 0) = I - \frac{iHt}{\hbar} + \left(\frac{-it}{\hbar}\right)^2 \frac{1}{2!} H^2 + \left(\frac{-it}{\hbar}\right)^3 \frac{1}{3!} H^3 + \dots \quad (5)$$

- 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

$$U|\psi_n\rangle = e^{-iE_n t/\hbar} |\psi_n\rangle. \quad (6)$$

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  $\Psi_n(t) = \psi_n e^{-iE_n t/\hbar}$ .

### 2.3 Angular momentum as the generator of rotations

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

$$f(\vec{r} + \delta\vec{\phi} \times \vec{r}) \approx f(\vec{r}) + (\delta\vec{\phi} \times \vec{r}) \cdot \vec{\nabla} f(\vec{r}) \quad (7)$$

Now  $(\mathbf{A} \times \mathbf{B}) \cdot \mathbf{C} = \mathbf{A} \cdot (\mathbf{B} \times \mathbf{C})$  since both of them measure the volume of a parallelepiped defined by the vectors  $\mathbf{A}, \mathbf{B}, \mathbf{C}$  ordered so that  $\mathbf{C}$  has a positive component along  $\mathbf{A} \times \mathbf{B}$ . Thus using  $p = -i\hbar\nabla$ ,

$$f(\vec{r} + \delta\vec{\phi} \times \vec{r}) \approx f(\vec{r}) + \frac{i}{\hbar} \delta\vec{\phi} \cdot (\vec{r} \times p) f(\vec{r}) = \left( I + \frac{i}{\hbar} \delta\vec{\phi} \cdot \vec{L} \right) f(\vec{r}). \quad (8)$$

So angular momentum generates rotations. For a finite rotation counter clockwise about axis  $\vec{\phi}$  by angle  $|\vec{\phi}|$  we have

$$f(\vec{r}) \mapsto e^{\frac{i}{\hbar} \vec{\phi} \cdot \vec{L}} f(\vec{r}). \quad (9)$$

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  $z$  axis.

- 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  $[L_i, V(r)] = 0$  for each  $i$  and consequently that  $[L^2, V(r)] = 0$ . This result will be used in studying motion in a central potential, where one shows that  $L^2$  and (say)  $L_z$  commute with the hamiltonian (say of the hydrogen atom), and that  $L^2$ ,  $L_z$  and  $H$  are simultaneous observables.

### 2.4 Example of rotations generated by orbital and spin angular momentum

- **Orbital angular momentum:** Recall that a finite counter-clockwise rotation by angle  $|\alpha|$  about the axis  $\vec{\alpha}$  is effected by  $R_{\vec{\alpha}} = e^{\frac{i\vec{L} \cdot \vec{\alpha}}{\hbar}}$

$$\psi(\vec{r} + \vec{\alpha} \times \vec{r}) = e^{\frac{i\vec{L} \cdot \vec{\alpha}}{\hbar}} \psi(\vec{r}). \quad (10)$$

Of course, rotations do not affect  $r$ , they only affect the angles  $\theta, \phi$ . So we will focus on the angles and consider a wave function  $\psi(\theta, \phi)$ . Any such wave function can be expanded as a linear combination of spherical harmonics  $\psi(\theta, \phi) = \sum_{lm} c_{lm} \psi_{lm}(\theta, \phi)$ . The  $c_{lm}$  can be determined by using the orthogonality and normalization of  $Y_{lm}$ . We have seen that the angular momentum operators  $\vec{L}$  are each block diagonal in the spherical harmonic basis. This means  $L_x, L_y, L_z$  have zero matrix elements between spherical harmonics with different values of  $l$

$$\langle Y_{lm} | L_i | Y_{l'm'} \rangle \propto \delta_{ll'}. \quad (11)$$

So under a rotation,  $e^{\frac{i\vec{L}\cdot\vec{\alpha}}{\hbar}} \psi(\theta, \phi)$ , if the initial state  $\psi$  was one with a definite value of  $l$  then the transformed wave function will also have the same value of  $l$ .

• As an example, let us consider how a  $p$ -wave state  $\psi(r, \theta, \phi) = aY_{11} + bY_{10} + cY_{1,-1}$  transforms under a counter-clockwise rotation by angle  $\alpha$  about the  $z$ -axis. In the  $(Y_{11}, Y_{10}, Y_{1,-1})$  basis  $L_z$  is diagonal with diagonal entries  $(\hbar, 0, -\hbar)$ . Thus we have

$$\begin{aligned} R_{\alpha\hat{z}}(aY_{11} + bY_{10} + cY_{1,-1}) &= e^{iL_z\alpha/\hbar} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} ae^{i\alpha} \\ b \\ ce^{-i\alpha} \end{pmatrix} \\ R_{\alpha\hat{z}}Y_{11} &= e^{i\alpha}Y_{11}, \quad R_{\alpha\hat{z}}Y_{10} = Y_{10}, \quad \text{and} \quad R_{\alpha\hat{z}}Y_{1,-1} = e^{-i\alpha}Y_{1,-1}. \end{aligned} \quad (12)$$

In particular  $Y_{10}$  is unaffected by a rotation about  $z$ -axis, which is not surprising as it was independent of the azimuthal angle  $\phi$  to begin with. This is consistent with the coordinate space wavefunctions

$$Y_{10} \propto \cos\theta, \quad Y_{1,\pm 1} \propto \sin\theta e^{\pm i\phi} \quad (13)$$

if we observe that such a rotation augments the azimuthal angle  $\phi$  by  $\alpha$ . In particular, we observe that a rotation by  $\alpha = 2\pi$  brings us back to the initial state, as we would expect.

• **Remark:** Rotation of a physical vector can be thought of in two ways. (1) A rotation of the corresponding position vector  $\vec{r}$  holding the surroundings (axes) fixed. Or (2) a rotation (by the negative angle) of the ambient space (i.e., the axes) holding  $\vec{r}$  fixed. In both points of view, a rotation by  $\alpha = 2\pi$  about any axis acts as the identity transformation for any function  $\psi(\vec{r})$ .

• **Spin angular momentum:** By analogy with the rotations generated by orbital angular momentum, we may consider the transformations generated by spin  $e^{\frac{i\vec{S}\cdot\vec{\sigma}}{\hbar}}$ . For spin half, these become  $e^{\frac{i\vec{\sigma}\cdot\vec{\phi}}{2}}$  where  $\vec{\sigma}$  is the vector of Pauli matrices. These rotations act on the spin wave function (e.g.  $a|\uparrow\rangle + b|\downarrow\rangle$ ), which however, is not a function of the spatial coordinates.

• So a rotation about an axis in ordinary three dimensional space has two effects. On the one hand, it transforms the coordinate wave function  $\psi(\vec{r})$  via the angular momentum operator. It also transforms the spinorial wave function via the spin operator. This transformation generated by spin acts on the ‘internal’ spin degrees of freedom.

• For example, calculate the  $2 \times 2$  matrix representing a c.c. rotation by angle  $\phi$  about the  $\hat{n}$  direction, on the spin wavefunction. Show that

$$e^{i\phi\vec{\sigma}\cdot\hat{n}/2} = I \cos\frac{\phi}{2} + i\vec{\sigma}\cdot\hat{n} \sin\frac{\phi}{2}. \quad (14)$$

Though not needed here, we note that  $e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}$  if  $[A, B]$  commutes with both  $A$  and  $B$ . As a consequence, show that the spin wavefunction changes sign (though it represents the same physical state) under a rotation by  $2\pi$ , unlike the coordinate wave function.

- Use this to find how an ‘up spin’  $|\uparrow\rangle$  transforms under a rotation by  $\pi$  about the  $y$  axis.

## 2.5 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

$$i\hbar \frac{\partial}{\partial t} \langle \psi | A | \psi \rangle = \langle \psi | [A, H] | \psi \rangle. \quad (15)$$

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  $A$

$$A|\psi(t)\rangle = Ae^{-iHt/\hbar} |\psi(0)\rangle = e^{-iHt/\hbar} A|\psi(0)\rangle = e^{-iHt/\hbar} a|\psi(0)\rangle = a|\psi(t)\rangle. \quad (16)$$

• 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.

<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 Parity: A discrete symmetry

- The parity operator is defined on position space wave functions by reflection about  $x = 0$

$$\mathbb{P}\psi(x) = \psi(-x) \quad (17)$$

In three dimensions, it is defined as  $\mathbb{P}\psi(\mathbf{r}) = \psi(-\mathbf{r})$ . Applying it twice, we see that  $\mathbb{P}^2 = I$  is the identity. The eigenvalues  $\mathbb{P}\psi(x) = \lambda\psi(x)$  must satisfy  $\lambda^2 = 1$ , i.e.  $\lambda = \pm 1$ . Even functions of  $x$  are eigenfunctions of parity with eigenvalue  $+1$  and odd functions of  $x$  are eigenfunctions corresponding to eigenvalue  $-1$ .

- A state is said to have definite parity if it is an eigenstate of parity, i.e. if its position space wave function is either even or odd. Most states do not have definite parity.
- The g.s. of the SHO  $Ae^{-\beta^2 x^2/2}$  has even parity  $\mathbb{P}\psi_0(x) = \psi_0(x)$ . The excited states alternate in parity, odd and even. Time evolution doesn't change the parity of a stationary state  $\psi_n(x)e^{-iE_n t/\hbar}$ .
- $\mathbb{P}$  is hermitian on square-integrable functions on any even interval  $(-L, L)$  or on  $(-\infty, \infty)$  as a change of variable  $y = -x$  shows

$$\langle \phi | \mathbb{P} | \psi \rangle = \int_{-L}^L \phi^*(x) \psi(-x) dx = \int_L^{-L} \phi^*(-y) \psi(y) (-dy) = \int_{-L}^L \phi^*(-y) \psi(y) dy = \langle \mathbb{P}\phi | \psi \rangle. \quad (18)$$

As parity is hermitian & has a complete set of eigenfunctions (on  $L^2(-L, L)$ ), parity is an observable.

- We can write the matrix representation of parity in any basis. Suppose we pick the basis of energy eigenstates of the SHO. In this basis  $P$  is diagonal. If we order the eigenstates according to  $\cdots \psi_5, \psi_3, \psi_1, \psi_0, \psi_2, \psi_4, \cdots$ , then in this basis  $\mathbb{P} = \begin{pmatrix} -I & 0 \\ 0 & I \end{pmatrix}$ .
- Parity does not commute with position or momentum. So momentum and parity (or position and parity) are not simultaneously measurable. Parity in fact anti-commutes with both position and momentum. Check that  $[\mathbb{P}, x]\psi = -x\psi(-x) - x\psi(-x) = -2x\psi(x) \neq 0$  so that  $[\mathbb{P}, x]_+\psi = (\mathbb{P}x + x\mathbb{P})\psi = 0$ . As for momentum, let  $D$  be the operator that acts by differentiation on position space functions.  $(Df)(x) = f'(x)$ .  $\mathbb{P}D + D\mathbb{P} = 0$  or  $[\mathbb{P}, D]_+ = 0$ . To see this:

$$((\mathbb{P}D)f)(x) = (\mathbb{P}f')(x) = \frac{\partial f(y)}{\partial y} \Big|_{y=-x}; \quad ((D\mathbb{P})f)(x) = \frac{\partial f(-x)}{\partial x} = -\frac{\partial f(y)}{\partial y} \Big|_{y=-x} \quad (19)$$

So  $[\mathbb{P}, p]_+ = 0$  as well. We use  $p\mathbb{P} + \mathbb{P}p = 0$  to show that  $\mathbb{P}$  commutes with  $p^2$  or kinetic energy

$$[\mathbb{P}, p^2] = \mathbb{P}p^2 - p^2\mathbb{P} = -p\mathbb{P}p - p^2\mathbb{P} = p\mathbb{P}p - p^2\mathbb{P} = 0. \quad (20)$$

- Parity commutes with the potential energy operator for an even potential  $V(x) = V(-x)$ :

$$(\mathbb{P}V - V\mathbb{P})f(x) = V(-x)f(-x) - V(x)f(-x) = 0. \quad (21)$$

Thus parity commutes with the hamiltonian  $H = p^2/2m + V$  for even  $V(x)$ . So we expect parity and energy to be simultaneously diagonalizable and measurable. In other words, eigenstates of energy can be taken to have definite parity: i.e., either even or odd. We saw that energy

eigenstates of the SHO are either even or odd. The same was true for the square well (reflection about center of the well). More generally, if  $\psi(x)$  is an energy eigenfunction but does not have definite parity, then we can add to it  $\psi(-x)$  (which can be seen to also be an energy eigenfunction with the same energy) to get an even parity energy eigenfunction. Similarly,  $\psi(x) - \psi(-x)$  has odd parity. Illustrate this with the free particle energy eigenfunctions  $e^{ikx}$  and  $e^{-ikx}$ . It may seem as if we have shown that there is always both an even and an odd eigenfunction for each energy. This is not the case. Often, one of the above two combinations is the zero function, and therefore does not represent a linearly independent eigenfunction. In fact one can show that bound state energy levels in one-dimensional QM are non-degenerate.

- A measurement of parity can only give the results  $+1$  or  $-1$  and the state of the system then collapses to a state whose position space wave function is either even or odd. The average of parity measurements on several copies of the same state is the expectation value of parity in that state. For example, the expected value of parity in the state  $\psi = \psi_0 + \psi_1$  which is a linear combination of the ground and first excited states of the SHO is  $\langle \psi | \mathbb{P} | \psi \rangle = 0$ . This is because  $\psi_0$  has even parity while  $\psi_1$  has odd parity and they are orthogonal, but check it! The avg value of  $\mathbb{P}$  measurements in a state  $\psi$  tells us to what extent  $\psi(x)$  is even or odd. If the avg parity is one,  $\psi(x)$  must be even and if the average is  $-1$ ,  $\psi(x)$  must be odd. But everything in between is also allowed. The expectation value of parity in any state must lie in the interval  $[-1, 1]$  since it is a weighted avg of  $1$ 's and  $-1$ 's.

- Parity (in three dimensions) is an important symmetry in microscopic physics. It is a symmetry of the electromagnetic and strong interactions and therefore has important consequences for atomic and nuclear/hadronic physics. However, parity is not a symmetry of the forces governing radioactive  $\beta$  decay.

## 4 Symmetry among identical particles: bosons & fermions

### 4.1 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

$$\psi(x_1, x_2) = \sum_{a,b} c_{ab} \phi_a(x_1) \otimes \phi_b(x_2) \quad (22)$$

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

$$\psi(x_1, x_2) = e^{i\theta} \psi(x_2, x_1) \quad (23)$$

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,

$$P\psi(x_1, x_2) = \psi(x_2, x_1) = e^{-i\theta} \psi(x_1, x_2). \quad (24)$$

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

$$P^2\psi(x_1, x_2) = \psi(x_1, x_2) \quad \text{and} \quad P^2\psi(x_1, x_2) = e^{-2i\theta} \psi(x_1, x_2). \quad (25)$$

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

$$\psi(x_1, x_2) = \pm \psi(x_2, x_1) \quad (26)$$

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

$$H(x_1, p_1; x_2, p_2) = H(x_2, p_2; x_1, p_1) \quad (27)$$

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

$$\psi_S(x_1, x_2) = \phi_a(x_1)\phi_b(x_2) + \phi_a(x_2)\phi_b(x_1), \quad \psi_A(x_1, x_2) = \phi_a(x_1)\phi_b(x_2) - \phi_a(x_2)\phi_b(x_1). \quad (28)$$

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

$$\psi_A(x_1, x_2) = \det \begin{pmatrix} \phi_a(x_1) & \phi_a(x_2) \\ \phi_b(x_1) & \phi_b(x_2) \end{pmatrix} \quad (29)$$

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

$$\psi_A(x_1, x_2) = N_1 \det \begin{pmatrix} \phi_a(x_1) & \phi_a(x_2) \\ \phi_b(x_1) & \phi_b(x_2) \end{pmatrix} + N_2 \det \begin{pmatrix} \phi_c(x_1) & \phi_c(x_2) \\ \phi_d(x_1) & \phi_d(x_2) \end{pmatrix} \quad (30)$$

- 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)

$$P_{ij}\psi(\cdots, x_i, \cdots, x_j, \cdots) = \psi(\cdots, x_j, \cdots, x_i, \cdots), \quad \text{for } 1 \leq i, j \leq N. \quad (31)$$

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’)

$$\psi_A(x_1, x_2, x_3) = \det \begin{pmatrix} \phi_a(x_1) & \phi_a(x_2) & \phi_a(x_3) \\ \phi_b(x_1) & \phi_b(x_2) & \phi_b(x_3) \\ \phi_c(x_1) & \phi_c(x_2) & \phi_c(x_3) \end{pmatrix} \quad (32)$$

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.

## 4.2 Two spin half electrons in Helium

Consider a pair of spin half fermions, whose orbital motion is not coupled to the spin degrees of freedom, e.g. if the hamiltonian operator is the identity in spin space. This is true for the two electrons in Helium in a non-relativistic treatment where the hamiltonian does not involve any spin-orbit coupling terms:

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}. \quad (33)$$

$H$  is symmetric under exchange of the degrees of freedom of the two particles. So it commutes with the exchange operator and we seek simultaneous eigenstates of  $H$  and  $P$ . We write the total wave function as a product of a spatial and a spin part<sup>2</sup>

$$\psi(x_1, m_1; x_2, m_2) = \phi(x_1, x_2)\chi(m_1, m_2) \quad (34)$$

$\phi(x_1, x_2)$  is  $\propto$  to the probability amplitude for the first particle to be at  $x_1$  and second to be at  $x_2$  irrespective of their spin states. Similarly,  $\chi(m_1, m_2)$  is  $\propto$  the probability amplitude for the spin projection of the first particle to be  $\hbar m_1$  and that of the second particle to be  $\hbar m_2$ , irrespective of their positions<sup>3</sup>. Here  $m_1$  and  $m_2$  only take the values  $\pm\frac{1}{2}$  while  $x_1, x_2$  are any points in 3d space. In general,

$$\chi = a \uparrow\uparrow + b \uparrow\downarrow + c \downarrow\uparrow + d \downarrow\downarrow \quad \text{where} \quad \chi\left(\frac{1}{2}, \frac{1}{2}\right) = a, \quad \chi\left(\frac{1}{2}, -\frac{1}{2}\right) = b, \dots \quad (35)$$

The Pauli principle of anti-symmetrization states that the total wavefunction must be anti-symmetric under exchange of both coordinate and spin degrees of freedom

$$\psi(x_1, m_1; x_2, m_2) = -\psi(x_2, m_2; x_1, m_1) \quad (36)$$

Now let us look for other operators that commute with both  $H$  and  $P$ .  $H \propto I$  in spin space, so it commutes with the combined spin operators of the two particles  $S^2$  and  $S_z$  as well as with  $S_1^2$  and  $S_2^2$  which are each proportional to the identity. All these four spin observables also commute with  $P$ . On the other hand,  $S_{1z}$  commutes with  $H$  but not with  $P$ . So in particular,  $P$  is *not* diagonal in the uncoupled basis of spin states, but it is diagonal in the coupled basis.

- So we look for energy eigenstates that are simultaneous eigenstates of  $P$ ,  $S^2$  and  $S_z$ . Then there are only two ways to make  $\psi$  anti-symmetric:  $\phi$  and  $\chi$  are symmetric and anti-symmetric respectively or vice-versa.

$${}^1\psi = \phi_S(x_1, x_2)\chi_A(m_1, m_2) \quad \text{or} \quad {}^3\psi = \phi_A(x_1, x_2)\chi_S(m_1, m_2) \quad (37)$$

We have seen that there is only one anti-symmetric 2 particle spin state, the singlet  $\chi_A = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$  while there are a triplet of symmetric spin states  $\chi_S$ . In the case of Helium, the

<sup>2</sup>If the orbital and spin degrees of freedom were coupled, we would need linear combinations of such product wave functions

<sup>3</sup>If the spin and coordinate degrees of freedom were coupled, the amplitudes for spin projections could depend on position.

spin singlet states are called parahelium and the spin triplet ones orthohelium. Orthohelium states are triply degenerate since the hamiltonian is diagonal in spin space.

- Often we may approximate  $\phi$  by an (anti-)symmetrized combination of single particle wave functions  $\phi_1$  and  $\phi_2$  (in general we will need linear combinations of these):

$$\phi_A(x_1, x_2) = \frac{1}{\sqrt{2}} (\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)) \quad \text{and} \quad \phi_S(x_1, x_2) = \frac{1}{\sqrt{2}} (\phi_1(x_1)\phi_2(x_2) + \phi_1(x_2)\phi_2(x_1))$$

In the Helium atom, these two single particle wave functions  $\phi_1, \phi_2$  could be taken as two stationary state wavefunctions of a Hydrogenic atom with nuclear charge  $Z = 2$ <sup>4</sup>. By making different choices for  $\phi_1$  and  $\phi_2$  we may search for a state  $\psi$  which minimizes the expectation value of the Helium hamiltonian. It turns out that the ground state of the Helium atom is a spin singlet (parahelium) state  $\phi_S\chi_A$  where  $\phi_1$  and  $\phi_2$  are both approximately ground state wave functions of hydrogenic atoms. This is why we say Helium has the electronic configuration  $1s^2$ . The first excited state is a triplet of degenerate orthohelium states etc. To find the eigenfunctions (only  $\phi(r_1, r_2)$  remains to be found) we must solve the Schrodinger eigenvalue problem. This is quite hard and one resorts to approximations such as perturbation theory and the variational method. In both approaches, one needs to calculate the expectation value of the the helium hamiltonian. The variational principle states that the ground state energy is the minimal value of  $\langle \psi | H | \psi \rangle$  among all unit norm states.

### 4.3 Coulomb and exchange interactions

To find the ground state of helium, we need to minimize the expectation value of  $H$  among all anti-symmetric two particle states. The symmetry /antisymmetry of  $\phi_{S,A}$  imply some interesting qualitative features for the expectation value of the interaction energy arising from electrostatic repulsion of electrons. The interaction part of the helium hamiltonian can be written

$$V_I = G(r_1 - r_2) = \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|} \quad (38)$$

Since electrons are identical,  $G(r_1 - r_2) = G(r_2 - r_1)$ . As discussed in the last section, we are interested in spatial wave functions that are built from a pair of (normalized) one-particle wave functions

$$\phi_{S,A} = \frac{1}{\sqrt{2}} [\phi_a(r_1)\phi_b(r_2) \pm \phi_a(r_2)\phi_b(r_1)] \quad (39)$$

Let us calculate the expectation value of  $V_I$  in the states  $\phi_{S,A}$  Show that you get

$$\langle V_I \rangle = \int d^3r_1 d^3r_2 G(r_1 - r_2) [|\phi_a(r_1)|^2|\phi_b(r_2)|^2 \pm \Re \phi_a^*(r_1)\phi_b^*(r_2)\phi_a(r_2)\phi_b(r_1)] = V_C \pm V_E \quad (40)$$

The first term  $V_C$  is called the Coulomb (or direct) interaction energy while the second term  $V_E$  is the exchange interaction energy. Of course, both arise from the Coulomb repulsion of electrons. While the direct Coulomb interaction can be classically interpreted as the energy of a pair of charge clouds, the exchange term has no such simple classical interpretation. Indeed, it is a quantum mechanical effect due to the identical nature of particles and (anti-)symmetry of wave functions. Moreover, the exchange interaction contributes with a different sign according

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<sup>4</sup>If we ignore the electron-electron repulsion, each electron is in a hydrogenic atom with  $Z = 2$ .

as the spatial wave function is symmetric or anti-symmetric (spin singlet or spin triplet state). The Coulomb energy  $V_C$  is clearly positive. In cases where the exchange term is also positive  $V_E \geq 0$  (as is the case for Helium) we can conclude that the interaction energy  $\langle V_I \rangle$  is greater for  $\phi_S$  than for  $\phi_A$ . So (other things being equal) the spin singlet states  $^1\chi_A$  will have a higher energy than the spin triplet states  $^3\chi_S$ . This is seen in Helium, where typically the spin triplet orthohelium states have a lower energy than the corresponding spin singlet parahelium states constructed from the same pair of single particle states  $\phi_a, \phi_b$ . There is one notable exception to this rule: the ground state of helium is a spin singlet parahelium state with  $\phi_a = \phi_b$ . There is no anti-symmetric wave function that can be constructed if  $\phi_a = \phi_b$ .

#### 4.4 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

$$H = \sum_{i=1}^N \left( \frac{p_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_i|} \right) + \sum_{1 \leq i < j \leq N} \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} \quad (41)$$

To 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.,

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = A \det \begin{pmatrix} \phi_1(r_1) & \phi_1(r_2) & \phi_1(r_3) \\ \phi_2(r_1) & \phi_2(r_2) & \phi_2(r_3) \\ \phi_3(r_1) & \phi_3(r_2) & \phi_3(r_3) \end{pmatrix} \quad (42)$$

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.

$$\phi_1(r) = \langle r | n = 1, l = 0, m_l = 0, s = \frac{1}{2}, m_s = \frac{1}{2} \rangle \propto e^{-r/a_0} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (43)$$

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

$$\psi = \phi_{n=1, l=0, m=0}(r_1)\phi_{n=1, l=0, m=0}(r_2) \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \sim e^{-(r_1+r_2)/a}(\uparrow\downarrow - \downarrow\uparrow). \quad (44)$$

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 Ne  $4s^1$  and magnesium Ne  $4s^2$  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.

## 5 Time reversal

### 5.1 Time reversal in classical mechanics

Newton's law of motion is time-reversal invariant. What we mean by this is that if  $x(t)$  is a solution of

$$m \frac{d^2 x(t)}{dt^2} = F(x(t)), \quad (45)$$

then  $x(-t)$  is also a solution. Indeed let  $y(t) = x(-t) = x(t')$  where  $t' = -t$ . Then

$$\frac{dy(t)}{dt} = \frac{dx(-t)}{dt} = -\frac{dx(t')}{dt'} \Rightarrow \frac{d^2 y(t)}{dt^2} = \frac{d^2 x(t')}{dt'^2}. \quad (46)$$

But we know that  $m \frac{d^2 x(t')}{dt'^2} = F(x(t'))$  which implies that

$$m \frac{d^2 y(t)}{dt^2} = F(y(t)) \quad (47)$$

So  $x(-t)$  satisfies Newton's equation whenever  $x(t)$  does. More precisely, if  $x(t)$  is a solution of Newton's equation with initial conditions  $x(t_1) = x_1$  and  $\dot{x}(t_1) = v_1$  and ending up at  $x(t_2) = x_2$  with  $\dot{x}(t_2) = v_2$ , then  $y(t) = x(-t)$  is also a solution with initial conditions  $y(-t_2) = x_2$ ,  $\dot{y}(-t_2) = -v_2$  and ending up at  $y(-t_1) = x_1$ ,  $\dot{y}(-t_1) = -v_1$ . So the final state for  $x$  becomes the initial state for  $y$  after reversing the sign of velocities and vice versa. A movie of the trajectory described by  $y$  would look like the movie of  $x$  run backwards. The main point is that this backwards movie is also a legitimate solution of Newton's equation. For example, a ball thrown up decelerates and comes to rest at a maximum height. The time reversed trajectory

is a ball at rest that falls down and accelerates. One is a solution of Newton's equation if and only if the other is. We may plot this in an  $x-t$  diagram.

- Note what this is *not* saying. Suppose a mango is seen to fall (from rest) from a tree 27 minutes after the birth of the nation and hit the ground with velocity 1 m/s, 28 minutes after the birth of the nation. It certainly does not mean that a mango rose up from the ground 28 minutes before the birth of the nation and reached the tree 27 minutes before the birth of the nation. Rather, what it means is that one could (at a time of one's choosing, say 50 min after the birth of the nation) throw a mango up with a velocity of 1 m/s from the point of impact on the ground, and it would follow the reversed path as the earlier mango and reach (with zero instantaneous velocity) the same point on the tree one minute later.

- We say that time reversal is implemented in classical mechanics by reversing the sign of the time variable wherever it appears. As a consequence, velocities and momenta change sign under time reversal, though accelerations do not change sign. Since  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ , angular momentum too changes sign under time reversal.

- There are situations where the time reversed trajectory is *not* a solution of Newton's equation. This is the case if the force is not time-reversal invariant. An example of such a force is friction. Another example of such a force is the magnetic part of the Lorentz force  $\vec{F} = e\vec{v} \times \vec{B}$ . The time-reversed trajectory of a charged particle moving in a *fixed external* magnetic field is in general *not* a solution of Newton's equation  $m\ddot{\vec{r}} = e\dot{\vec{r}} \times \vec{B}$ .

## 5.2 Time reversal in quantum mechanics

- We need to understand how time-reversal  $T$  is implemented in the quantum theory. We would like to promote the time reversal invariance of the classical theory of a free particle or a particle in a potential  $V(x)$  to the quantum theory. Whatever  $T$  is, we wish to find that for a free particle,  $T\psi$  is a solution of the SE whenever  $\psi$  is a solution.

- For instance, consider a stationary solution of the free particle SE  $\psi(x, t) = \sin(kx)e^{-iEt/\hbar}$  where  $E = \hbar^2 k^2 / 2m$ . Unfortunately,  $\psi(x, -t) = \sin(kx)e^{iEt/\hbar}$  is *not* a solution of the SE, as one checks. This means reversal of sign of  $t$  is not a symmetry of the SE. But interestingly  $\psi^*(x, -t)$  (which happens to be equal to  $\psi(x, t)$  in this case), is a solution of the SE! We will exploit this observation soon.

- More generally, consider the SE for a particle in a real potential  $V(x)$  with initial condition  $\psi(x, t_0) = \psi_0(x)$

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x)\psi(x, t). \quad (48)$$

Merely changing the sign of  $t$ , unfortunately produces an equation different from the SE.  $\psi(x, -t)$  satisfies the equation

$$-i\hbar \frac{\partial \psi(x, -t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, -t)}{\partial x^2} + V(x)\psi(x, -t). \quad (49)$$

Due to the first order time derivative in the SE, it is not-invariant if we simply let  $t \rightarrow -t$ . This is in contrast to Newton's equation that is second order in time and invariant under  $t \rightarrow -t$ .

- What is more, we found that classically  $p \rightarrow -p$  under time reversal. But simply changing the sign of  $t$  does not affect  $p = -i\hbar \frac{\partial}{\partial x}$  in the quantum theory. So time reversal in quantum mechanics must involve more than just reversing the sign of time.

- However, notice that the above equation is in fact the SE for the complex conjugate wave function. This suggests how to implement time reversal: we must not only reverse the sign of  $t$  but also replace the wave function by its complex conjugate. This combined operation is a symmetry of the SE and is defined as the time-reversal operation in quantum mechanics.
- So let  $\phi(x, t) = \psi^*(x, -t) = \psi^*(x, t')$  where  $t' = -t$ . We will show that  $\phi(x, t)$  is a solution of the SE whenever  $\psi(x, t)$  is. To see this, note that

$$\frac{\partial \phi(x, t)}{\partial t} = -\frac{\partial \psi^*(x, t')}{\partial t'}, \quad \text{and} \quad \frac{\partial^2 \phi(x, t)}{\partial x^2} = \frac{\partial^2 \psi^*(x, t')}{\partial x^2}. \quad (50)$$

Thus the SE for  $\psi(x, t')$  implies the following equation for  $\phi(x, t)$

$$-i\hbar \frac{\partial \phi^*(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \phi^*(x, t)}{\partial x^2} + V(x)\phi^*(x, t). \quad (51)$$

Taking the complex conjugate of this equation we find that  $\phi(x, t)$  also solves the SE. So  $\psi^*(x, -t)$  is a solution of SE with final state  $\psi^*(x, -t_0) = \psi_0^*$  whenever  $\psi(x, t)$  is a solution of SE with initial state  $\psi_0$ .

- We say that time-reversal is implemented in quantum theory by reversing the sign of the time variable (wherever it appears) and by taking the complex conjugate of the wave function:

$$(T\psi)(x, t) = \psi^*(x, -t) \quad (52)$$

- Notice that time reversal is an anti-linear operator

$$T(\psi + \phi) = T\psi + T\phi, \quad \text{but} \quad T(\lambda\psi(t)) = \lambda^*\psi^*(-t) = \lambda^*T\psi(t). \quad (53)$$

- As a consequence,  $Tp\psi = T(-i\hbar\psi'(x, t)) = i\hbar\frac{\partial}{\partial x}T\psi = -pT\psi$ . So  $TpT^{-1} = -p$ , which is the quantum mechanical version of the reversal of sign of momentum under time reversal. For this 'reversal of sign' of  $p$ , it was crucial that  $T$  involves complex conjugation.

- In fact, the time-reversal operator  $T$  is an anti-unitary operator on solutions of the SE. A unitary operator is one which satisfies  $\langle U\phi|U\psi\rangle = \langle\phi|\psi\rangle$  for all states  $\phi, \psi$ . On the other hand,

$$\langle T\phi(t)|T\psi(t)\rangle = \langle\phi^*(-t)|\psi^*(-t)\rangle = \langle\phi(-t)|\psi(-t)\rangle^* = \langle\phi(t)|\psi(t)\rangle^* \quad (54)$$

The last equality follows since Schrödinger evolution preserves inner products. Thus  $\langle T\phi(t)|T\psi(t)\rangle = \langle\phi(t)|\psi(t)\rangle^*$  for any pair of states  $\phi, \psi$ . Such an operator is called anti-unitary. Thus time-reversal symmetry of the Schrodinger equation is implemented by an anti-unitary operator (unlike other symmetries like parity, space and time translation or rotation invariance, which are implemented by unitary operators  $\mathbb{P}, e^{ipx/\hbar}, e^{-iHt/\hbar}$  and  $e^{i\vec{L}\cdot\vec{\phi}/\hbar}$ ).

- While states transform via  $\psi \rightarrow T\psi$ , under time-reversal, an operator  $A$  must transform to  $TAT^{-1}$ . For position and momentum we found that  $T\mathbf{r}T^{-1} = \mathbf{r}$  and  $T\mathbf{p}T^{-1} = -\mathbf{p}$ . This is also consistent with the requirements of the correspondence principle (in the Heisenberg picture) and the classical result that under time reversal,  $x(t)$  and  $p(t)$  go to  $x(-t)$  and  $-p(-t)$ . On the other hand, For orbital angular momentum and spin we must have  $T\mathbf{L}T^{-1} = -\mathbf{L}$  and  $T\vec{\sigma}T^{-1} = -\vec{\sigma}$ . Show that when acting on Pauli matrices,  $T$  can be taken as  $C\sigma_2$  where  $C$  implements complex conjugation  $CzC^{-1} = z^*$ . Though  $\sigma_2$  is unitary,  $C$  makes  $T$  anti-unitary.



- We can formalize our earlier observations. The Schrödinger equation is time-reversal invariant provided the hamiltonian commutes with  $T$ . To see this, apply  $T$  to the SE  $i\hbar\frac{\partial\psi}{\partial t} = H\psi$ , assume  $TH = HT$  and use anti-linearity of  $T$  to get

$$T\left(i\hbar\frac{\partial\psi}{\partial t}\right) = TH\psi \quad \Rightarrow \quad -i\hbar T\left(\frac{\partial\psi}{\partial t}\right) = H(T\psi). \quad (55)$$

Now by definition  $T\left(\frac{\partial\psi}{\partial t}\right) = -\frac{\partial T\psi}{\partial t}$  since the sign of time is reversed. So we get

$$i\hbar\frac{\partial(T\psi)}{\partial t} = H(T\psi) \quad (56)$$

In other words, if  $\psi$  is a solution of the SE, then so is  $T\psi$  provided  $[H, T] = 0$ . This brings time-reversal invariance on par with the other symmetries of the SE. E.g. for parity we found that if  $\psi$  is a solution and  $[H, \mathbb{P}] = 0$ , then  $\mathbb{P}\psi(x) = \psi(-x)$  is also a solution.

- Now let us characterize the (time-independent) hamiltonians  $H = \frac{1}{2m}p^2 + V(x)$  that commute with  $T$ . First we use  $pT = -Tp$  to find  $[p^2, T] = ppT - Tpp = -pTp - Tpp = Tpp - Tpp = 0$ . So  $T$  commutes with the kinetic energy. As for the potential term,

$$[T, V]\psi = T(V\psi) - VT\psi = V^*T\psi - VT\psi \quad (57)$$

So  $[T, V] = 0$  iff  $V(x) = V^*(x)$ . So  $H = \frac{p^2}{2m} + V(x)$  commutes with time reversal iff the potential is real.

- In particular, if  $H$  is a hermitian hamiltonian that commutes with  $T$  and  $\psi_n(x)$  is an energy- $E_n$  eigenstate of  $H$ , then  $T\psi_n(x) = \psi_n(x)^*$  is also an eigenstate with the same energy  $E_n$ :

$$H(T\psi_n) = T(H\psi_n) = T(E_n\psi_n) = E_n(T\psi_n). \quad (58)$$

If  $\psi(x)$  is real  $T\psi(x) = \psi^*(x)$ , isn't a linearly independent eigenstate. But if  $\psi(x)$  is complex, it is linearly independent. Scattering states in 1d which behave asymptotically like  $e^{ikx}$  are complex wave functions representing particles moving rightward at  $x = \infty$ . The corresponding time-reversed state describes left moving particles of the same energy.

- Let us remark on time-dependent hamiltonians  $H = \frac{p^2}{2m} + V(x, t)$  that are time-reversal invariant. By our earlier argument, such a time dependent potential will preserve the T-invariance of Schrodinger's equation iff  $[H, T] = 0$ . We already know that  $[T, p^2] = 0$ , so we just need to characterize potentials  $V(x, t)$  that commute with  $T$ .

$$([T, V]\psi)(x, t) = V^*(x, -t)T\psi - V(x, t)T\psi \quad (59)$$

So  $[T, V] = 0$  iff  $V(x, t) = V^*(x, -t)$ , i.e., the potential itself must be time-reversal invariant.

- The simplest and most common examples of such potentials are real time-independent potentials, a class we have already encountered. But there are other interesting possibilities, such as a real potential that is even under  $t \rightarrow -t$ . For example,

$$V(\vec{r}, t) = -e\vec{r} \cdot \vec{E}_o \cos \omega t \quad (60)$$

is a time-reversal invariant time-dependent potential. It describes the electric dipole interaction energy between the electron in an atom and the oscillating electric field of light shone on it.

- Let us illustrate how quantum  $T$ -invariance reduces to classical time reversal invariance in a simple example. The gaussian wave packet with initial width  $a = \sqrt{\langle x^2 \rangle_{\psi(t=0)} - \langle x \rangle_{\psi(t=0)}^2}$  is

$$\psi(x, t) = \frac{1}{(2\pi)^{1/4} \sqrt{a} \sqrt{1 + \frac{i\hbar t}{2ma^2}}} \exp \left\{ -\frac{(x - p_o t/m)^2}{4a^2 \left(1 + \frac{i\hbar t}{2ma^2}\right)} \right\} \quad (61)$$

is a solution of the free particle SE. In this state  $\langle p \rangle = p_o$  and  $\langle x \rangle = \frac{p_o t}{m}$ . The time reversed wavefunction

$$(T\psi)(x, t) = \psi^*(x, -t) = \frac{1}{(2\pi)^{1/4} \sqrt{a + \frac{i\hbar t}{2ma}}} \exp \left\{ -\frac{(x + p_o t/m)^2}{4 \left(a^2 + \frac{i\hbar t}{2m}\right)} \right\} \quad (62)$$

too is a solution of the free particle SE. Interestingly, we notice that the time-reversed wave function differs from  $\psi$  merely by a reversal of the sign of  $p_o$ , which is the mean momentum of the state.

- To understand the classical limits of these solutions, we form the coordinate probability densities. Denoting  $a(t) = a \sqrt{1 + \frac{t^2 \hbar^2}{4m^2 a^4}}$  we find

$$|\psi(x, t)|^2 = \frac{1}{\sqrt{2\pi} a(t)} e^{-\frac{(x - \frac{p_o t}{m})^2}{2a(t)^2}} \quad \text{and} \quad |(T\psi)(x, t)|^2 = \frac{1}{\sqrt{2\pi} a(t)} e^{-\frac{(x + \frac{p_o t}{m})^2}{2a(t)^2}} \quad (63)$$

In the classical limit (to be studied more carefully in the next section), these represent particles which are located where the gaussian probability densities are peaked. We see that in the classical limit,  $\psi$  represents a particle which is moving with trajectory  $x(t) = \frac{p_o t}{m}$  while  $T\psi$  represents a particle with trajectory  $x(t) = -\frac{p_o t}{m}$ . These two trajectories are both solutions of the free particle Newton equation  $m\ddot{x} = 0$  and are related by classical time reversal  $t \rightarrow -t$ !

- As in classical mechanics, there are situations in which the Schrödinger equation is not time reversal invariant. This happens when  $[H, T] \neq 0$ . For a particle in a potential  $V(x)$ , this can happen only if  $V(x)$  is not real. Complex potentials can be used to describe damping, a quantum mechanical analogue of friction. The SE for a charge in a fixed external magnetic field is also not  $T$ -invariant.

- Despite the name, time reversal is not concerned with the possibility of traveling backwards in time or with ‘time travel’. However, it does say that the time-reversed Newton equation is the same as the Newton equation (for a wide range of forces) and the same is true of the Schrödinger equation in a real potential. This fact allows us to produce new solutions of these equations from known ones. This is already quite valuable. Based on the knowledge that certain processes occur,  $T$ -invariance can be used to predict that certain reversed-processes must also occur.