

Multiple Particles

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1 Symmetrisation postulate

1.1 Schrödinger's equation for multiple particles

The Hamiltonian for a system with N particles can be written as

$$\hat{H} = - \sum_{j=1}^N \frac{\hbar^2}{2m_j} \nabla_j^2 + V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t),$$

where ∇_j^2 is the laplacian in the coordinate system \mathbf{r}_j of the j -th particle. The wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)$, satisfying the Schrödinger's equation as usual, has the statistical interpretation that

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N$$

is the probability of finding particle 1 in $d^3\mathbf{r}_1$, particle 2 in $d^3\mathbf{r}_2$, etc.

For a time-independent potential $V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, the spatial and temporal parts can be separated as usual, giving

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) &= \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) e^{iEt/\hbar}, \\ - \sum_{j=1}^N \frac{\hbar^2}{2m_j} \nabla_j^2 \psi + V\psi &= E\psi. \end{aligned} \tag{1}$$

For non-interacting particles (i.e. the system is only subject to external forces), the potential energy can be separated into $V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{j=1}^N V_j(\mathbf{r}_j)$. In this case, Eq.(1) will adopt separable solutions $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N)$, where each wavefunction will satisfy the one-particle Schrödinger's equation

$$-\frac{\hbar^2}{2m_j} \nabla_j^2 \psi_j(\mathbf{r}_j) + V_j(\mathbf{r}_j) = E_j \psi_j(\mathbf{r}_j),$$

and the energy is $E = \sum_{j=1}^N E_j$.

Here, we are effectively combining wavefunctions from different Hilbert spaces using a direct product ($|\psi_1\rangle \otimes |\psi_2\rangle$ in the Dirac notation). Solutions that can be written as a direct product of two wavefunctions from their respective Hilbert space are said to be **unentangled**, most generally

$$\psi_{\text{pure}} = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N) = \left(\sum_{i=1} a_i f_i(\mathbf{r}_1) \right) \left(\sum_{j=1} b_j g_j(\mathbf{r}_2) \right) \dots \left(\sum_{k=1} d_k h_k(\mathbf{r}_N) \right),$$

where $a_i, b_j, \dots, d_k \in \mathbb{C}$ and f_i, g_j, \dots, h_k are the eigenfunctions. More generally, any wavefunction in the new Hilbert space can be written as a linear combination of pure states, as the direct products of the eigenfunctions form a complete basis for the new Hilbert space. When the linear combination has more than one term (i.e. it cannot be expressed as a single direct product of two wavefunctions in the respective subspace), the wavefunction is said to be **entangled**. An important example is the singlet state of two spin-1/2 particles

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

In this example, the spin of one particle is completely dependent on the other particle's —though each particle can be spin up or down, once measurement of one particle's spin is done, the other particle

will automatically take the opposite spin (collapse of the wavefunction turns it into a pure state). Note also that this state has the maximum randomness in the state of each qubit: the reduced density operator (see later) of each qubit has the maximum entropy.

In the case of a two-particle system, the Schrödinger's equation Eq.(1) could also be simplified when the particles only interact with each other (i.e. $V(\mathbf{r}_1, \mathbf{r}_2) \rightarrow V(|\mathbf{r}_1 - \mathbf{r}_2|)$). This is done in a similar fashion as the effective one-body problems in classical mechanics by introducing the centre of mass and relative position

$$\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}, \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$

and converting the Schrödinger's equation into

$$-\frac{\hbar^2}{2(m_1 + m_2)} \nabla_R^2 \psi = E_R \psi, \quad -\frac{\hbar^2}{2\mu} \nabla_r^2 \psi + V(\mathbf{r})\psi = E_r \psi.$$

1.2 The symmetrisation postulate

By constructing the wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\dots\psi(\mathbf{r}_N)$, we are distinguishing the particles—particle 1 is in ψ_1 , particle 2 is in ψ_2 , and so on. This, however, is not always allowed by the inherent indeterminacy of quantum mechanics that we can never know if two particles has secretly exchanged position with each other. Following this reasoning, we are *forced* to conclude that all electrons are identical (so are other types of particles) and that $|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$ must be unchanged under interchange of any $\mathbf{r}_i \longleftrightarrow \mathbf{r}_j$. Furthermore, we **postulate** that there are only two possibilities:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = \pm \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N).$$

Particles that take the plus sign are called **bosons** while those with the minus sign are **fermions**. From the **spin statistics theorem**, bosons have integral spins while fermions have half-integral spins. Noting that this “exchange operator” \hat{P} between identical particles would leave the system's Hamiltonian unchanged, $\langle \hat{P} \rangle$ is a constant of motion—bosons will stay bosons and fermions will stay fermions.

Furthermore, since \hat{P} commutes with any operator, it can be shown that a fully symmetric wavefunction must be composed of fully symmetric eigenfunctions and measurement does not change the symmetry.

In the case of a two-particle systems, we can easily construct wavefunctions for fermions and bosons from the distinguishable wavefunction $\psi_d(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$:

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)),$$

where bosons take the plus sign and fermions take the minus sign, as usual. Failing to be unentangled, this no longer has the distinguishable interpretation “particle 1 is in ψ_1 while particle 2 is in ψ_2 .” Instead, either of the two particle can be in ψ_1 or ψ_2 . However, we can still claim that *one* particle is in ψ_1 while *the other* is in ψ_2 . Noting that the fermions' wavefunction would be zero if $\psi_1 = \psi_2$, we arrive at the **Pauli exclusion principle** for all fermions that the *total wavefunction* (which may not only have the spatial dependence) of two identical particles must be different.

For a more complete description, though, we need to incorporate spins into the picture by constructing the total wavefunction $\Psi = \psi(\mathbf{r}_1, \mathbf{r}_2)\chi(1, 2)$, where $\chi(1, 2)$ is the general spinor. In this sense, the antisymmetric requirement becomes

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\chi(1, 2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)\chi(2, 1),$$

giving the possibilities of an antisymmetric wavefunction combined with a symmetric spinor (the triplets) or a symmetric wavefunction combined with an antisymmetric spinor (singlet). This allows two fermions to have the same spatial wavefunction, as long as they have opposite spins.

When the system has more than two states, the symmetrisation may not be as trivial. Luckily, for non-interacting systems, we could always find separable solutions to the Schrödinger's equations, thus concluding (for a three-particle system) that one particle is in ψ_1 , one other in ψ_2 , and the other in ψ_3 . The antisymmetric wavefunction can be constructed from the **Slater determinant**

$$\begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \psi_3(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \psi_3(\mathbf{r}_2) \\ \psi_1(\mathbf{r}_3) & \psi_2(\mathbf{r}_3) & \psi_3(\mathbf{r}_3) \end{vmatrix}$$

while the symmetric wavefunction can be constructed in a similar fashion by replacing the determinant by a permanent (no minus sign). It should be noted that a non-zero determinant requires $\psi_1 \neq \psi_2 \neq \psi_3$ (generalised exclusion principle). Therefore, it is not possible to form an antisymmetric spinor $\chi(1, 2, 3)$ in this way. This sometimes implies that we could form a wavefunction by symmetrising ψ and χ individually. Instead, we could construct an antisymmetric wavefunction by

$$\Psi = \begin{vmatrix} \psi_1(\mathbf{r}_1) |\uparrow\rangle_1 & \psi_1(\mathbf{r}_1) |\downarrow\rangle_1 & \psi_2(\mathbf{r}_1) |\uparrow\rangle_1 \\ \psi_1(\mathbf{r}_2) |\uparrow\rangle_2 & \psi_1(\mathbf{r}_3) |\downarrow\rangle_2 & \psi_2(\mathbf{r}_2) |\uparrow\rangle_2 \\ \psi_1(\mathbf{r}_3) |\uparrow\rangle_2 & \psi_1(\mathbf{r}_3) |\downarrow\rangle_2 & \psi_2(\mathbf{r}_3) |\uparrow\rangle_3 \end{vmatrix}.$$

When the particles are interacting with each other, the time-independent Schrödinger's equation may not be separable. In this case, it may not be possible to express any state by a single Slater determinant. Instead, a linear combination of Slater determinant might be needed. This means that the interpretation “one particle is in ψ_1 while the other is in ψ_2 ” loses its meaning as well.

1.3 Exchange interactions

The symmetrisation (in one dimension)

$$\psi_{\pm} = \frac{1}{\sqrt{2}} (\psi_a(x_1)\psi_b(x_2) \pm \psi_a(x_2)\psi_b(x_1))$$

could impact the expected distance

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 x_2 \rangle$$

between the two particles of interest due to the difference in $\langle x_1 x_2 \rangle$.

For distinguishable particles, this simply separates and gives

$$\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b.$$

For identical particles, the cross terms are more complicated with

$$\langle x_1 x_2 \rangle = \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2,$$

where

$$\boxed{\langle x \rangle_{ab} = \int x \psi_a(x)^* \psi_b(x) dx} \quad (2)$$

is the overlap integral, giving

$$\boxed{\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2 |\langle x \rangle_{ab}|^2.}$$

Therefore, identical particles with symmetric spatial wavefunctions are closer to each others while those with antisymmetric spatial wavefunctions are further from each other compared to distinguishable particles. This geometrical result is called the **exchange interaction**, which are only related to the spatial wavefunctions and are not necessarily associated with either fermions or bosons.

2 Entanglement and density operators

2.1 Entanglement

Suppose we know all the possible state of two particles $\{|\phi_1^i\rangle\} \in V_1$ and $\{|\phi_2^j\rangle\} \in V_2$, then the most complete information we have about the composite system is the **direct product** state

$$\psi = \sum_{n,m} c_{n,m} |\phi_1^n\rangle |\phi_2^m\rangle \in V_1 \oplus V_2. \quad (3)$$

When this direct product state cannot be separated into $|\psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle$, as shown in section 1.1, the state is said to be in entanglement. Such entanglement can be used to teleport quantum states in quantum information systems. The degree of entanglement is not an observable and is mathematically defined using the density operator discussed below.

2.2 Density operator

The most information we have about a system is its wavefunction, often expressed as a superposition of eigenstates $|\psi\rangle = \sum_i c_i |\phi_i\rangle$, giving the phase relations between composite states. This, however, is not always possible or useful, and we are often just concerned about the probability of different states the system can be in $\{p_i\}$. This is called a “classical ensemble of quantum states,” where only the moduli of probability amplitudes are known and often occurs when a system is somehow coupled to the surrounding. In this case, we could instead choose to form a density matrix

$$\hat{\rho} = \sum_i p_i |\phi_i\rangle \langle \phi_i|, \quad (4)$$

evolving in time as

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}].$$

The expectation value of an operator in this ensemble is

$$\langle \hat{A} \rangle = \text{Tr}[\hat{A} \hat{\rho}],$$

where the trace of an operator is $\text{Tr}[\hat{O}] = \sum_i \langle \phi_i | \hat{O} | \phi_i \rangle$. The trace of $\hat{\rho}$ is, by definition, unity. For example, the density operator of a quantum system in a heat bath (boltzmann distribution) is

$$\rho = \frac{\exp(-\hat{H}/k_B T)}{\text{Tr}[\exp(-\hat{H}/k_B T)]}.$$

If there only one possible state, $\rho = |\psi\rangle \langle \psi|$ and the ensemble is said to be **pure**, and $\hat{\rho}$ simply becomes the projection operator. In this case, it must be the case that

$$\text{Tr}[\rho^2] = 1.$$

The density operator is completely determined by its eigenvalues p_i , as it is diagonal. We could extend the classical idea of entropy to become

$$S = -\text{Tr}[\hat{\rho} \ln \hat{\rho}] = -\sum_i p_i \ln p_i,$$

which is 0 for a pure state and $\ln N$ for a random state (its classical value, c.f. equipartition theorem)

The definition of density operator in Eq.(4) looks suspiciously like the direct product state in Eq.(3), but they are two different things: probability is superposed in ρ while amplitude is superposed in ψ . Mathematically, $\hat{\rho}$ is an operator in V while ψ is a state in $V_1 \oplus V_2$. Moreover, entanglement, to some extent, reflects the cross-talk between states of different particles while the density operator only has diagonal terms. In particular, the phase relations are definitive in an entangled state, so an entangled state is pure and thus has zero entropy.

An entangled state is also intricately related to the density operator, illustrated in the example below: suppose we want to study a system $\{i\}$ weakly coupled to the environment $\{j\}$. The direct product state of the *universe* is

$$|\psi\rangle = \sum_{i,j} \psi_{i,j} |i\rangle |j\rangle$$

with a pure density operator $|\psi\rangle \langle \psi|$, which is in no way known. The most we can do is to form the partial trace over the surrounding to give a reduced density matrix of the system

$$\rho = \text{Tr}_j[|\psi\rangle \langle \psi|] = \sum_{i,i'} \rho_{i,i'} |i\rangle \langle i'|.$$

This makes the system manifestly mixed and thus has a non-zero entropy.

3 Atoms

The Hamiltonian for a neutral atom with atomic number Z is

$$\hat{H} = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|},$$

where the nucleus is assumed to be stationary. This is, in general, not solvable due to the electron-electron interaction. Dropping the second term, we could arrive at a separable Hamiltonian, which is identical in form to that of the hydrogen atom, except that the effective Bohr radius becomes $\frac{a_0}{Z}$. Similarly, the total energy of the system becomes

$$E = Z^2 \sum_{i=1}^N E_i,$$

where E_i is the corresponding energy level for hydrogen. The wavefunction, as usual, can be symmetrised from the pure state $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2)$.

It should be noted that the energy levels are indifferent to the azimuthal quantum number l (and of course, m as well) for a hydrogen atom. The degeneracy on l disappears, though, after introduction of electron-electron repulsions and states with lower l have lower energy.

4 Solids

In the solid state, a large number of atoms are put together, making it practically impossible to solve for the Schrödinger's equation by combining all the atoms. Instead, we treat as if some **valence electrons** furthest from the nucleus become free of any coulomb interaction. Instead, they are subject to a combined potential stemming from the crystalline nature and filled to the “energy bands” according to Pauli's exclusion principle.

4.1 The free electron gas

The most elementary approach to confine the electrons into a solid with dimensions l_x, l_y, l_z is the 3D infinite potential well

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < l_x, 0 < y < l_y, 0 < z < l_z; \\ \infty, & \text{otherwise.} \end{cases}$$

The normalised stationary solutions and the associated energies are

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right),$$

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \equiv \frac{\hbar^2 |\mathbf{k}|^2}{2m},$$

where n_x, n_y , and n_z are independent positive integers and \mathbf{k} is the wave-vector. The allowed wave-vectors \mathbf{k} form a rectangular grid in the first octant of the k -space (reciprocal space) and the contour plot of the energy is (one eighth of) a sphere.

In accordance with Pauli's exclusion principle, each state will be filled by two electrons, with increasing energy. Due to the large number of states, the spherical surface is well approximated by the rectangular grids, giving the position of the surface separating the occupied and unoccupied states for a solid with N atoms, each contributing d valence electrons, as

$$k_F = (3\rho\pi^2)^{1/3}, \rho = \frac{Nd}{V}, \implies E_F = \frac{\hbar^2}{2m} (3\rho\pi^2)^{2/3}.$$

where E_F is called the **Fermi energy**. Integrating the energy up to the Fermi states then gives the total energy

$$E_{tot} = \frac{\hbar^2 (e\pi^2 Nd)^{5/3}}{10\pi^2 m} V^{-2/3} = \frac{3}{5} E_F Nd.$$

This gives a degeneracy pressure of

$$P \equiv -\frac{dE_{tot}}{dV} = \frac{2}{3} \frac{E_{tot}}{V},$$

which partly explains why a solid does not collapse spontaneously.

4.2 Periodic delta spikes