IX. Identical Particles

All electrons have identical properties, as do all protons, neutrons, dust etc. Two physical situations that differ only by the interchange of identical particles are indistinguishable. Hence the Hamiltonian for such a system must be invariant under the permutation of identical particles. For N identical particles a typical Hamiltonian describing their interaction has the form

$$H = \sum_{i=1}^{N} \left(\frac{1}{2m} \vec{P}_i^2 + U(|\vec{R}_i|) \right)$$

$$+ \sum_{\substack{i,j=1 \\ i<j}}^{N} V(|\vec{R}_i - \vec{R}_j|) .$$

The particles have the same mass, spin, charge, etc.. The first set of terms in H are the kinetic energy of each particle as well as any external potential $U(|\vec{R}_i|)$. These terms only involve the coordinates (momentum) of a single particle at a time, they are called one-body operators

Let $H_0 = \sum_{i=1}^{N} h_0(\vec{P}_i, \vec{R}_i)$

with

$$h_0(\vec{P}, \vec{R}) = \frac{1}{2m}\vec{P}^2 + U(|\vec{R}|) .$$

Assuming that we can solve the $h_0(\vec{P}, \vec{R})$ eigenvalue problem

$h_0|\varphi_\alpha\rangle = \epsilon_\alpha|\varphi_\alpha\rangle$, we have a complete set of single particle states $\{|\varphi_\alpha\rangle\}$

$$1 = \sum_\alpha |\varphi_\alpha\rangle\langle\varphi_\alpha|$$

which we take to be orthonormal.

$$\langle\varphi_\alpha|\varphi_\beta\rangle = \delta_{\alpha\beta} .$$

(For example $|\varphi_\alpha\rangle$ might be the hydrogen atom $|n,l,m\rangle$ states, or the SHO states $|n_x, n_y, n_z\rangle$ etc.)

The part of the Hamiltonian

$$H' = \sum_{i<j=1}^{N} V(|\vec{R}_i - \vec{R}_j|) = \frac{1}{2}\sum_{i,j=1}^{N} V(|\vec{R}_i - \vec{R}_j|)$$

involves pairs of particle coordinates at a time, it is referred to as a two-body operator.

The coordinates and momenta of different particles are independent, hence the canonical commutation relations have the form

$$[X_{im}, X_{jn}] = 0 = [P_{im}, P_{jn}]$$

$$[P_{im}, X_{jn}] = \delta_{ij}(-i\hbar\delta_{mn})$$

where $i,j = 1,\ldots,N$ and $m,n = x,y,z$ (or $1,2,3$).

In general the many-body state vectors can be described by the direct products of the single particle states:

$$|\psi_{\alpha_1\cdots\alpha_N}\rangle = |\psi_{\alpha_1}\rangle|\psi_{\alpha_2}\rangle\cdots|\psi_{\alpha_N}\rangle.$$

The wavefunctions for these many-body states are given by their projections onto the N-coordinate vector and spin basis states

$$|\vec{r}_1, m_{s_1}; \vec{r}_2, m_{s_2}; \ldots; \vec{r}_N, m_{s_N}\rangle = |\vec{r}_1, m_{s_1}\rangle \cdots |\vec{r}_N, m_{s_N}\rangle$$

where recall in the $\{\vec{R}, \vec{S}^2, S_z\}$ CSCO basis $|\vec{r}, m_s\rangle = |\vec{r}\rangle \otimes |s, m_s\rangle$. (page -719- and page -787-).

For spin 0 particles, the N-body wavefunction is simply

$$\varphi_{\alpha_1 \cdots \alpha_N}(\vec{r}_1, \ldots, \vec{r}_N) = \langle \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N | \varphi_{\alpha_1 \cdots \alpha_N} \rangle$$

$$= \langle \vec{r}_1 | \varphi_{\alpha_1} \rangle \langle \vec{r}_2 | \varphi_{\alpha_2} \rangle \cdots \langle \vec{r}_N | \varphi_{\alpha_N} \rangle$$

$$= \varphi_{\alpha_1}(\vec{r}_1) \cdots \varphi_{\alpha_N}(\vec{r}_N)$$

while for spin $\frac{1}{2}$ particles, the N-body wavefunction is

$$\varphi_{\alpha_1 \cdots \alpha_N}(\vec{r}_1, m_{s_1}; \vec{r}_2, m_{s_2}; \ldots; \vec{r}_N, m_{s_N})$$

$$= \langle \vec{r}_1, m_{s_1}; \ldots; \vec{r}_N m_{s_N} | \varphi_{\alpha_1 \cdots \alpha_N} \rangle$$

$$= \langle \vec{r}_1, m_{s_1} | \varphi_{\alpha_1} \rangle \cdots \langle \vec{r}_N, m_{s_N} | \varphi_{\alpha_N} \rangle$$

$$= \varphi_{\alpha_1}(\vec{r}_1, m_{s_1}) \cdots \varphi_{\alpha_N}(\vec{r}_N, m_{s_N}).$$

As usual for each spin up or down we have a wavefunction $\varphi_\alpha(\vec{r}, \uparrow \text{or} \downarrow)$. Hence we can more economically group

these as products of 2-component spinors, So let

$$\varphi_\alpha(\vec{r}) \equiv \begin{pmatrix} \varphi_\alpha(\vec{r},+\tfrac{1}{2}) \\ \varphi_\alpha(\vec{r},-\tfrac{1}{2}) \end{pmatrix} = \begin{pmatrix} \langle \vec{r},\tfrac{+1}{2}|\varphi_\alpha\rangle \\ \langle \vec{r},-\tfrac{1}{2}|\varphi_\alpha\rangle \end{pmatrix}.$$

So the direct product space wavefunction is a multi-component spinor (direct product of N 2-component spinors is a spinor with 2^N-components)

$$\varphi_{\alpha_1\cdots\alpha_N}(\vec{r}_1,\cdots,\vec{r}_N) \equiv \varphi_{\alpha_1}(\vec{r}_1)\cdots\varphi_{\alpha_N}(\vec{r}_N).$$

(Recall that the inner product of such vectors also requires the "matrix" scalar product for the spinors i.e. $\cdots\begin{pmatrix}\cdot & \cdot \\ \cdot & \cdot\end{pmatrix}$.)

We are now in a position to determine the consequences of the indistinguishability of the identical particles. Consider just a system of two identical particles. Recall that the wavefunction $\psi(1,2)$ has the interpretation that $|\psi(1,2)|^2$ is the probability density that particle 1 is in the volume $d^3\vec{r}_1$ about $\vec{r}_1$ and

particle 2 is in the volume d^3x_2 about $\vec{r}_2$. Let P_{12} be the interchange or permutation operator so that

$P_{12}\psi(1,2) = \psi(2,1)$. P_{12} interchanges all the 1 and 2 labels of the particles in the wavefunction, i.e. spin & coordinate. If $\psi(1,2)$ is a stationary state

$H\psi(1,2) = E\psi(1,2)$, then, since H is invariant under interchange of the particles, that is $[P_{12}, H] = 0$, $\Rightarrow$

$[H, P_{12}]\psi(1,2) = 0$. Thus

$$H\underbrace{P_{12}\psi(1,2)}_{=\psi(2,1)} = P_{12}\underbrace{H\psi(1,2)}_{=E\psi(1,2)}$$

$$H\psi(2,1) = EP_{12}\psi(1,2) = E\psi(2,1).$$

Hence $\psi(1,2)$ and $\psi(2,1)$ are degenerate in energy. This is called exchange degeneracy. Consequently the linear combination

$$\Psi(1,2) \equiv A\psi(1,2) + B\psi(2,1)$$

is an eigenstate of H with eigenvalue E.

Since the particles are identical, labelling them by 1 and 2 as we have done can have no physical consequences. Hence the probability density $|\Psi(2,1)|^2$ should be the same as $|\Psi(1,2)|^2$.

$|\Psi(1,2)|^2 = |\Psi(2,1)|^2$, the physics is the same. Multiplying this out yields

$$|A|^2|\psi(1,2)|^2 + |B|^2|\psi(2,1)|^2 + A^*B\psi^*(1,2)\psi(2,1) + AB^*\psi(1,2)\psi^*(2,1)$$

$$= |A|^2|\psi(2,1)|^2 + |B|^2|\psi(1,2)|^2 + A^*B\psi^*(2,1)\psi(1,2) + AB^*\psi(2,1)\psi^*(1,2).$$

Hence we find that

1) $|A|^2 = |B|^2 \Rightarrow B = Ae^{i\varphi}$ with $\varphi \in \mathbb{R}$.

2) $A^*B = AB^* \Rightarrow \frac{A^*}{A} = \frac{B^*}{B} = \frac{A^*e^{-i\varphi}}{Ae^{+i\varphi}} = \frac{A^*}{A}e^{-2i\varphi}$

So $e^{-2i\varphi} = 1 \Rightarrow \varphi = n\pi$, $n = 0, \pm 1, \pm 2, \ldots$

Putting this together $B = Ae^{in\pi} = (-1)^n A$.

Since $(-1)^n = \begin{cases} +1, & n = \text{even} \\ -1, & n = \text{odd} \end{cases}$, we have two cases

$$\psi_I(1,2) = A[\psi(1,2) \pm \psi(2,1)]$$ with A an overall normalization constant.

Note: As a consequence of the properties of relativistic quantum field theory, it can be shown that the (relative) + sign in the wavefunction is required for 2 identical integer spin particles (called bosons). The − sign can be shown to be required for 2 identical half odd integer spin particles (called fermions). The wavefunction for bosons (fermions) is symmetric (antisymmetric) under particle interchange. This is known as the spin-statistics theorem. It is shown many times to be valid experimentally

(periodic table of elements).

Hence the normalized direct product basis vectors have the form for bosons

$$\varphi_{\alpha_1\alpha_2}(1,2) = \frac{1}{\sqrt{2}}\left(\varphi_{\alpha_1}(1)\varphi_{\alpha_2}(2) + \varphi_{\alpha_2}(1)\varphi_{\alpha_1}(2)\right)$$

for $\alpha_1 \neq \alpha_2$

and

$$\varphi_{\alpha\alpha}(1,2) = \varphi_{\alpha}(1)\varphi_{\alpha}(2).$$

For fermions we have

$$\varphi_{\alpha_1\alpha_2}(1,2) = \frac{1}{\sqrt{2}}\left(\varphi_{\alpha_1}(1)\varphi_{\alpha_2}(2) - \varphi_{\alpha_2}(1)\varphi_{\alpha_1}(2)\right)$$

for $\alpha_1 \neq \alpha_2$

$$\varphi_{\alpha\alpha}(1,2) = 0.$$

This last result is an expression of the fact that we cannot construct an antisymmetric wavefunction with both fermions in the same quantum state. This is nothing but the Pauli Exclusion Principle.

The 2-fermion basis wavefunction can be written as a determinant (called a Slater determinant)

$$\varphi_{\alpha_1\alpha_2}(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{\alpha_1}(1) & \varphi_{\alpha_1}(2) \\ \varphi_{\alpha_2}(1) & \varphi_{\alpha_2}(2) \end{vmatrix}.$$

The properties of the determinant imply the antisymmetry of $\varphi_{\alpha_1\alpha_2}$ under the interchange of the 2 particles (interchange rows) and hence the Pauli exclusion principle is built in to the vector.

These results can be generalized to the N-particle system. The N-particle wavefunction which is antisymmetric under the interchange of any 2 identical fermions can be written as the Slater determinant

$$\varphi_{\alpha_1\cdots\alpha_N}(1,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(1) & \varphi_{\alpha_1}(2) & \cdots & \varphi_{\alpha_1}(N) \\ \varphi_{\alpha_2}(1) & \cdots & \cdots & \vdots \\ \vdots & \cdots & \ddots & \vdots \\ \varphi_{\alpha_N}(1) & \cdots & \cdots & \varphi_{\alpha_N}(N) \end{vmatrix}.$$

From the properties of the determinant we see that the N-fermion wavefunction has the required form.

1) To interchange 2 fermions ($\alpha_i \leftrightarrow \alpha_j$), interchange their rows $\Rightarrow$ the determinant and hence wavefunction changes sign, thus it is antisymmetric.

2) To interchange 2 coordinates $i \leftrightarrow j$, interchange their columns $\Rightarrow$ the determinant and hence wavefunction changes sign, again it is antisymmetric.

3) If the quantum numbers of any 2 fermions are equal $\alpha_i = \alpha_j$, then 2 rows are identical and the determinant and hence wavefunction vanishes $\Rightarrow$ this is the Pauli Exclusion Principle.

So the basis wavefunctions are given by Slater determinants.

The determinant can be written as a sum over all permutations of the identical particles' labels,

$$\varphi_{\alpha_1 \cdots \alpha_N}(1, \cdots, N) = \left[\frac{1}{\sqrt{N!}} \sum_P (-1)^P P\right] \prod_{i=1}^{N} \varphi_{\alpha_i}(i).$$

In this equation we have that

$$\Pi \equiv \prod_{i=1}^{N} \varphi_{\alpha_i}(i) \equiv \varphi_{\alpha_1}(1)\, \varphi_{\alpha_2}(2) \cdots \varphi_{\alpha_N}(N)$$

is called the normal sequence. P is an operator that permutes the particles' labels. There are $N!$ such permutations for N-identical particles. P acts on the labels $\alpha_1 \cdots \alpha_N$. As well, $(-1)^P$ is the signature of the permutation

$$(-1)^P = (-1)^{\text{number of interchanges from normal sequence.}}$$

Finally $\sum_P$ is the sum over all possible $(N!)$ permutations.

For example, in the case of 3-identical fermions we have:

$$\sum_P (-1)^P P = 1 - P_{12} - P_{13} - P_{23} + P_{13}P_{12} + P_{13}P_{23}$$

$$\begin{pmatrix}1&2&3\\1&2&3\end{pmatrix} \quad \begin{pmatrix}1&2&3\\2&1&3\end{pmatrix} \quad \begin{pmatrix}1&2&3\\3&2&1\end{pmatrix} \quad \begin{pmatrix}1&2&3\\1&3&2\end{pmatrix} \quad \begin{pmatrix}1&2&3\\2&3&1\end{pmatrix} \quad \begin{pmatrix}1&2&3\\3&1&2\end{pmatrix}$$

the identity

So acting on the normal sequence of labels $(1\,2\,3)$ we get

$$\sum_P (-1)^P P\,(1\,2\,3) = (1\,2\,3) - (2\,1\,3) - (3\,2\,1) - (1\,3\,2) + (2\,3\,1) + (3\,1\,2).$$

As required the RHS is antisymmetric under the interchange of any pair of labels. We can prove this in general, $\sum_P (-1)^P P$ always produces this pairwise interchange antisymmetry. To see this consider

$$P_{ij} \sum_P (-1)^P P = \sum_P (-1)^P (P_{ij} P).$$

But $P_{ij}P$ is itself one of the permutations, denote it P' since this set of $N!$ permutations form a group the permutation group

$$P' = P_{ij} P.$$

Now since we are summing over all possible P, the product P' runs over all possible permutations as well. The signature of P' is (a single interchange)

$$(-1)^{P'} = (-1)^{P_{ij}} (-1)^{P} = (-1)\cdot(-1)^{P}.$$

Thus

$$P_{ij} \sum_P (-1)^P P = \sum_P (-1)^P (P_{ij} P)$$
$$= -\sum_{P'} (-1)^{P'} P'$$

and we obtain the required antisymmetry property.

We can now evaluate matrix elements of operators in the Slater determinant basis. Consider the operator A which is totally symmetric under identical particle interchange (no physical consequences of exchange of identical particles). Hence

$$[A, P] = 0.$$

We already have examples of such operators, the one-body KE

$\sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2$ or the 2-body potential $\frac{1}{2}\sum_{i,j=1}^{N} V(|\vec{r}_i - \vec{r}_j|)$. So using the Slater determinant wavefunction the expectation value of A have the form

$$\langle A \rangle = \int (d\tau)\, \varphi^*(\tau) A \varphi(\tau)$$

where $(d\tau) = d^3x_1 \cdots d^3x_N$ is the total volume. Thus this means

$$\langle A \rangle = \int (d\tau) \underbrace{\left(\frac{1}{\sqrt{N!}} \sum_P (-1)^P P \Pi^* \right)}_{= \varphi^*(\tau)} A \underbrace{\left(\frac{1}{\sqrt{N!}} \sum_{P'} (-1)^{P'} P' \Pi \right)}_{= \varphi(\tau)}$$

$$\langle A \rangle = \frac{1}{N!} \sum_P \sum_{P'} (-1)^{P+P'} \int (d\tau) (P\Pi^*) A (P'\Pi)$$

We now see that each term in the $\sum_P$ yields the same contribution.

Consider

$$\sum_{P'}{}' (-1)^{P+P'} \int (dz)\, (P\pi^*)\, A\, (P'\pi) .$$

Since the indices are dummy variables we can make a change of variables which is equivalent to making the permutation P^{-1}. The Jacobian of a permutation is 1, hence we get

$$= \sum_{P'}{}' (-1)^{P+P'} \int (dz)\, \pi^* P^{-1} (A P' \pi)$$

$$= \sum_{P'}{}' (-1)^{P+P'} \int (dz)\, \pi^* A\, (P^{-1} P' \pi)$$

since $[A, P^{-1}] = 0$. But by the group property $P'' = P^{-1}P'$ and as P' runs over all permutations so does P''. Since $(-1)^{P+P'} = (-1)^{P+P'} = (-1)^{P''}$, we find

$$= \sum_{P''}{}' (-1)^{P''} \int (dz)\, \pi^* A\, (P''\pi) ,$$

which is independent of P. So we get

$$\langle A \rangle = \frac{1}{N!} \underbrace{\sum_P}_{=N!} \sum_{P''} (-1)^{P''} \int (d\tau)\, \pi^* A (P'' \pi)$$

$$= \sum_P (-1)^P \int (d\tau)\, \pi^* A (P\pi)$$

where we re-labelled $P'' \to P$.

$$= \int (d\tau)\, \pi^* A \Big(\underbrace{\sum_P (-1)^P P \pi}_{\sqrt{N!}\,\varphi(\tau)} \Big)$$

↖ the Slater determinant.

Hence

$$\boxed{\langle A \rangle = \int (d\tau)\, \pi^* A \left(\sqrt{N!}\, \varphi(\tau) \right)} \quad .$$

We can apply this to some simple cases.

1) $A = \underline{1}$, the identity operator

$$\langle 1 \rangle = \int (dx)\, \Pi^* \sqrt{N!}\, \varphi(x)$$

$$= \int (dx)\, \Pi^* \sum_P{}' (-1)^P P \Pi$$

$$= \int d^3x_1 \cdots d^3x_N\, \varphi^\dagger_{\alpha_1}(1) \cdots \varphi^\dagger_{\alpha_N}(N) \times$$

$$\times \sum_P{}' (-1)^P P \left[\varphi_{\alpha_1}(1) \cdots \varphi_{\alpha_N}(N) \right] .$$

But recall the single particle basis vectors are orthonormal, only the identity permutation gives non-zero result i.e.

$$\int d^3x\, \varphi^\dagger_{\alpha_i}(\vec{r})\, \varphi_{\alpha_j}(\vec{r}) = \delta_{ij} ,$$

So

$$\langle 1 \rangle = \left(\int d^3x_1\, \varphi^\dagger_{\alpha_1}(1) \varphi_{\alpha_1}(1) \right) \cdots \left(\int d^3x_N\, \varphi^\dagger_{\alpha_N}(N) \varphi_{\alpha_N}(N) \right)$$

$$= 1^N = 1 .$$

2) $A = T \equiv \sum_{i=1}^{N} t(i)$ a one-body operator

$$\langle T \rangle = \sum_{i=1}^{N} \int (dx)\, \Pi^* t(i) \sqrt{N!}\, \varphi(x)$$

$$= \sum_{i=1}^{N} \int (dx)\, \Pi^* t(i) \sum_{P} (-1)^P P\Pi$$

$$= \sum_{i=1}^{N} \int d^3x_1 \cdots d^3x_N\, \varphi^+_{\alpha_1}(1) \cdots \varphi^+_{\alpha_N}(N)\, t(i) \times$$

$$\times \sum_{P} (-1)^P P\left[\varphi_{\alpha_1}(1) \cdots \varphi_{\alpha_N}(N)\right].$$

Now $t(i)$ only acts on the i^{th} coordinates but any permutation other than the identity interchanges at least 2 labels. Hence the orthogonality of the single particle states $\Rightarrow$ zero contribution. Only the identity permutation survives

$$\langle T \rangle = \sum_{i=1}^{N} \int d^3x_1 \cdots d^3x_i \cdots d^3x_N \times$$

$$\times \varphi^+_{\alpha_1}(1) \cdots \varphi^+_{\alpha_i}(i) \cdots \varphi^+_{\alpha_N}(N)\, t(i)\, \varphi_{\alpha_1}(1) \cdots \varphi_{x_i}(i) \cdots \varphi_{\alpha_N}(N)$$

only the i-variable is non-trivial, all other integrations are the norm $=1$,

$$\langle T \rangle = \sum_{i=1}^{N} \int d^3x_i \, \varphi_{\alpha_i}^{\dagger}(i) \, t(i) \, \varphi_{\alpha_i}(i)$$

$$= \sum_{i=1}^{N} \langle \varphi_{\alpha_i} | t | \varphi_{\alpha_i} \rangle .$$

Now recall that the Pauli exclusion principle implied that only one fermion particle can be in the state $|\varphi_{\alpha_i}\rangle$, hence α_i can occur only once in φ. This allows us to replace the sum over the number of particles by a sum over the occupied particle states. So

$$T = \sum_{\alpha}' \langle \varphi_\alpha | t | \varphi_\alpha \rangle$$

$\uparrow$ sum over occupied single particle states.

So the expectation value of a one-body operator is just the sum over the expectation values of the single particle states.

3) $A = V = \frac{1}{2}\sum_{i,j=1}^{N} V(i,j)$ the 2-body operator.

$$\langle V \rangle = \frac{1}{2}\sum_{i,j=1}^{N} \int (d\tau)\, \Pi^* V(i,j) \left[\sum_P (-1)^P P \Pi\right]$$

$$= \frac{1}{2}\sum_{i,j=1}^{N} \int d^3x_1 \cdots d^3x_N\, \varphi^+_{\alpha_1}(1) \cdots \varphi^+_{\alpha_N}(N)\, V(i,j) \sum_P (-1)^P P\{\varphi_{\alpha_1}(1) \cdots \varphi_{\alpha_N}(N)\}$$

Now there are 2 different permutations that can give rise to non-trivial contributions. Of course one is the identity permutation. The other interchanges the coordinate labels $i \leftrightarrow j$ only. All other permutations give zero due to orthogonality of the single particle wavefunctions. Recalling the (-1) for a single interchange we get

$$\langle V \rangle = \frac{1}{2} \sum_{i,j=1}^{N_t} \int d^3x_i \, d^3x_j \, \varphi^{\dagger}_{\alpha_i}(i) \varphi_{\alpha_j}(j) V(i,j) \times$$

$$\times \left[\varphi_{\alpha_i}(i) \varphi_{\alpha_j}(j) - \varphi_{\alpha_i}(j) \varphi_{\alpha_j}(i) \right]$$

$$= \frac{1}{2} \sum_{i,j=1}^{N_t} \left[\langle \varphi_{\alpha_i \alpha_j} | V(i,j) | \varphi_{\alpha_i \alpha_j} \rangle \right.$$

$$\left. - \langle \varphi_{\alpha_i \alpha_j} | V(i,j) | \varphi_{\alpha_j \alpha_i} \rangle \right]$$

Appealing to the Pauli principle, the sum over particles can be replaced by a sum over the occupied single particle states

$$\langle V \rangle = \frac{1}{2} \sum_{\alpha,\beta}^{} \left[\langle \varphi_{\alpha,\beta} | V | \varphi_{\alpha\beta} \rangle \right.$$

$$\left. - \langle \varphi_{\alpha,\beta} | V | \varphi_{\beta,\alpha} \rangle \right]$$

Sum over all occupied states

and note when $\alpha = \beta$, there is no contribution due to Pauli exclusion principle.