Permutational Symmetry

By definition a permutation operator is defined by

$$\hat{P}_k \, \psi(1, 2, \cdots, N) = \psi\left(P_k^{-1}(1, 2, \cdots N)\right)$$

For N objects (here coordinates) we have $N!$ permutations, e.g.

$$(1, 2, 3, 4) \rightarrow (4, 3, 1, 2)$$

The set of $N!$ permutations form a group: Symmetry group S_N

- $P_i P_j = P_k$ (a new permutation)
- $P_i (P_j P_k) = (P_i P_j) P_k$ (proof ?)
- identity permutation (preserve ordering)
- inverse permutation exists

To be relevant for Quantum Mechanics we also want

$\hat{P}_k$ should be Unitary

$\hat{P}_k$ should commute with $\hat{H}$.

a) $[\hat{H}, \hat{P}_k] = 0$:

For any Ψ, any $\hat{P}_k$:

$$\hat{P}_k \left[\hat{H} \Psi(1,2,\dots N) \right]$$

$$= \hat{P}_k \left[\left(\hat{h}(1) + \dots + \hat{h}(N) + \sum_{i<j} \frac{1}{r_{ij}} \right) \Psi(1,2,\dots N) \right]$$

$$= P_k^{-1} \left(\sum_i h(i) + \sum_{i<j} \frac{1}{r_{ij}} \right) \Psi(P_k^{-1}(1,2,\dots N)) \Big]$$

$$= \left(\text{reshuffled } \hat{H} \right) \Psi(P_k^{-1}(1,2,\dots N))$$

$$= \hat{H} \hat{P}_k \Psi(1,2,\dots N)$$

$$\Rightarrow \hat{P}_k \hat{H} = \hat{H} \hat{P}_k$$

The crucial part is that a permutation of the coordinates (of identical particles) in $\hat{H}$, does not change anything, since the Hamiltonian is a symmetric sum of terms. permuting only changes the order of terms in the sum, This is irrelevant.

More formally $\hat{A} + \hat{B} = \hat{B} + \hat{A}$ (operators commute under addition)

Any operator in Q.M. is always symmetric sum over terms involving identical particles.

by $\hat{P}_h$ is unitary: $\hat{P}_h^+ \hat{P}_h = \mathbb{1}$.

proof:

$$\int f^*(1,2,\dots N)\ \hat{P}^+ \hat{P}\ g(1,2,\dots N)\ d_1 \dots d_N$$

$$= \int \left(\hat{P} f(1,2,\dots N)\right)^*\ \hat{P}\, g(1,2,\dots N)\ d_1 \dots d_N$$

$$= \int f^*\left(\hat{P}^{-1}(1,\dots N)\right)\ g\left(\hat{P}^{-1}(1,\dots N)\right)\ d_1 \dots d_N$$

$$= \int f^*(1',2',\dots N')\ g(1',2',\dots N')\ P(d_1' d_2' \dots d_N')$$

Since all integration domains for each particle are the same. The permutation over integration variables is a change in the order of integration, and doesn't matter.

Hence $\Rightarrow \int f^*(1,2,\dots N)\, g(1,2,\dots N)\ d_1 \dots d_N$

$\Rightarrow \hat{P}^+ \hat{P} = 1$, for any permutation

It is important to note that permutations refer to both space and spin coordinates.

From the above it follows that eigenfunctions of $\hat{H}$ can be chosen to transform as irreducible representations of S_N. Moreover this invariance can never change over time.

Properties of permutations and their group S_N.

Consider permutations of N objects. For definiteness let us look at 4 balls. We will indicate a permutation as:

$$\begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 3 & 4 & 1 \end{pmatrix}$$

Meaning: replace ball 1 by ball 2
ball 2 by ball 3
3 4
4 1

This means we can permute vertical columns (or pairs) and this represents the same permutation

$$\begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 3 & 4 & 1 \end{pmatrix} = \begin{pmatrix} 4 & 2 & 1 & 3 \\ 1 & 3 & 2 & 4 \end{pmatrix}$$

The number of permutations is $N! = N(N-1)(N-2)\cdots 1$

$$\begin{pmatrix} 1 & 2 & 3 & 4 \\ . & . & . & . \end{pmatrix}$$

N possibilities for first ;
$N-1$ possibilities for second ;
all of them are different

Using the above representation it is easy to multiply permutations

Example:

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

(left)

Have I aligned the top row by permuting columns to be identical to the bottom row (right)

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

Permutations may not commute:

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

They always have an inverse

$$\begin{pmatrix}2&3&1\\1&2&3\end{pmatrix}\begin{pmatrix}1&2&3\\2&3&1\end{pmatrix} = \begin{pmatrix}1&2&3\\1&2&3\end{pmatrix} = \mathbb{1}$$

$$\begin{pmatrix}1&2&3\\2&3&1\end{pmatrix}^{-1} = \begin{pmatrix}2&3&1\\1&2&3\end{pmatrix} = \begin{pmatrix}1&2&3\\3&1&2\end{pmatrix}$$

often $P_k^{-1} \neq P_k$.

From this it is easy to see that P_k form a group. You can verify associativity, it follows from the ability to permute columns + multiplication rule

Another very useful representation of permutations uses cycles.
Let us take an example

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 3 & 4 & 5 & 2 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 3 & 5 & 2 & 4 \\ 3 & 5 & 1 & 4 & 2 \end{pmatrix}$$
$$= (1\ 3\ 5)\ (2\ 4) = (2\ 4)(1\ 3\ 5)$$

$(1 \to 3,\ 3 \to 5,\ 5 \to 1)\ (2 \to 4)\ (4 \to 2)$

Using cycles we can see which objects are permuted into one-another. (disjoint) For this reason cycles commute~~permute~~, as they refer to different sets of objects.

We can ask the question, if I have N objects and a cycle of k-elements, how many different cycles can one make?

Answer $\binom{N}{k} \cdot k! \cdot k = \binom{N}{k} (k-1)!$

Why: ① Choose k elements from N to enter the cycle. ② The order of elements in a cycle matters. ③ But, it does not matter which element I put first:

$(a\ b\ c) = (c\ a\ b) = (b\ c\ a)$

$(a\ b\ c) \neq (a\ c\ b)$

This allows us to categorize permutations in terms of cycle structures, and to enumerate how many there are.

For example for 5 elements

cycle structure	# of permutations
$(1)^5$	1
$(2)(1)^3$	$\binom{5}{2}$ 10
$(2)^2(1)$	$\binom{5}{2}\binom{3}{2}/2$ 15
$(3)(1)^2$	$\binom{5}{3}\cdot 2!$ 20
$(3)(2)$	$\binom{5}{3}\cdot 2!$ 20
$(4)(1)$	$\binom{5}{4}\cdot 3!$ 30
(5)	$4!$ 24
	120

$(2)^2(1)$, e.g. $(12)(34)(5) = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 2 & 1 & 4 & 3 & 5 \end{pmatrix}$

for the first 2-cycle I have $\binom{5}{2}$ possibilities, for the second $\binom{3}{2}$. The order doesn't matter, so divide by $2!$

In the exercises you will do the analysis for S_6.

It can be shown that if $P_j = P_k^{-1} P_i P_k$, then

P_j and P_i have the same cycle structure, for any P_k.

In group theory $P_j = P_k^{-1} P_i P_k$ are in the same conjugacy class.
For the groups S_M the classes are identical to the cycle structures.

From group theory (or inorganic chemistry) you may recall the ~~group multiplication~~ character table. They look like this

G	class 1 ⇅	class 2	class 3	...
irrep A	χ_{A1}	χ_{A2}	χ_{A3}	
irrep B	χ_{B1}	χ_{B2}	χ_{B3}	
irrep C	χ_{C1}	χ_{C2}	χ_{C3}	

The columns refer to classes, the rows to irreps.

The χ, characters, denote the trace of the representation matrices of the irrep

Recall $T_a T_b = T_c$

$\Rightarrow \mathbb{M}(a)\,\mathbb{M}(b) = \mathbb{M}(ab) = \mathbb{M}(c)$

The matrices have the same group multiplication table (represent the groups).

$\chi^{(\alpha)} = \sum_i \mathbb{M}_{ii}(a)$ (trace)

The trace is the same for each $T_a \to \mathbb{M}(a)$ in the same class.

The possible traces are determined by so-called "orthogonality relations".

$\Rightarrow$ The class structure of a group, determines the character table.

The identity is always in a class by it self: $T_a^{-1}\,\mathbb{1}\,T_a = \mathbb{1}$

and $\mathbb{M}(\mathbb{1}) = \mathbb{1}_n$ (unit matrix)

$\Rightarrow \sum_A \chi_{A_1}$ = sum of dimensions

over all irreps = # of elements in group.

Also: # of irreps = # of classes

Let us return to permutation groups S_N:

# of irreps = # cycle structures

This is fairly small. $N!$ is very large.

For $N \geq 7$ we have the following dimensions for irreps

- Totally symmetric representation
  1-dimensional "S"
- Totally antisymmetric representation
  1-dimensional "A"
- "permutation representation"
  $N-1$ dimensional "P"
- Other irreps of dimension at least $(N-1)$

From this it is plausible that only "S" and "A" irreps are physically relevant.
For example for 100 e^-, other irrep 'P' would imply that lightstates are 99-fold degenerate.

For the wave function describing a gas of particles — $(10^{23}-1)$-fold degenerate lightstates!!

Therefore we will focus on the

(1) Totally symmetric representation.
This describes bosons.

(2) Totally antisymmetric (or sign) representation.
This describes fermions.

In Quantum Field Theory it is shown that bosons have integer spin, while Fermions have half-integer spin.
I can only make plausible that only 'S' and 'A' representations make sense.

To discuss the symmetric and antisymmetric representation, ~~now~~ it is convenient to introduce transpositions.

A transposition is an interchange of two objects, e.g

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 1 & 2 & 4 & 3 & 5 \end{pmatrix}, \text{ or } \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 4 & 2 & 3 & 1 & 5 \end{pmatrix}$$

in terms of cycles: $(a\,b)\,(c)(d)(e)\ldots$

Any k-cycle can be expressed in terms of (k-1) transpositions. Let us demonstrate this.

First:

$$(a\ b\ c\ d\ e) = (a\ e)(a\ b\ c\ d)$$

$$\begin{pmatrix} a & b & c & d & e \\ b & c & d & e & a \end{pmatrix} = \begin{pmatrix} a & b & c & d & e \\ b & c & d & a & e \end{pmatrix} \begin{pmatrix} a & b & c & d & e \\ b & c & d & a & e \end{pmatrix}$$

$$= \begin{pmatrix} b & c & d & a & e \\ b & c & d & e & a \end{pmatrix} \begin{pmatrix} a & b & c & d & e \\ b & c & d & a & e \end{pmatrix}$$

$$= \begin{pmatrix} a & b & c & d & e \\ b & c & d & e & a \end{pmatrix}$$

Evidently this can be extended to a cycle of any length.

But then, by iteration

$$\begin{aligned} (a\ b\ c\ d\ e) &= (a\ e)(a\ b\ c\ d) \\ &= (a\ e)(a\ d)(a\ b\ c) \\ &= (a\ e)(a\ d)(a\ b)(a\ c) \end{aligned}$$

a 5 cycle $\Rightarrow$ 4 transpositions

a k-cycle $\Rightarrow$ (k-1) transpositions

Since every permutation can be written in terms of cycles, it follows that every permutation can be written as a product of transpositions.

Using the above recipe we get a precise number of transpositions (the minimum). One can always 'add' more transpositions, but this has to be an even number

The parity of a permutation P_α is denoted as $(-)^{P_\alpha}$ = $(-)^{\#\text{ of transpositions}}$

The # of transpositions in a given permutation P_α is always either even or odd.

We can enumerate for S_5:

S_5	min # of T	Sign $(-)^{\#}$	# of Perm
(1)	0	1	1
$(2)(1)^3$	1	-1	10
$(2)^2(1)$	$1+1=2$	1	15
$(3)(1)^2$	2	1	20
$(3)(2)$	$2+1=3$	-1	20
$(4)(1)$	3	-1	30
(5)	4	1	24

It follows that the number of even permutations (+1) is $1+15+20+24=60$

odd permutations $10+20+30=60$

total 120

# of even = # of odd is always true. (no proof)

The use of transpositions allows us to characterize the fully symmetric and fully antisymmetric representations.

(1) $\hat{T}_a |\psi^{(S)}\rangle = |\psi^{(S)}(T_a(1,2,\cdots N))\rangle$

$= + |\psi^{(S)}\rangle \quad \forall T_a$

The symmetric functions are the same under interchange of 2 coordinates.

(2) $\hat{T}_a |\psi^{(A)}\rangle = \psi^{(A)}(T_a(1,2,\cdots N))$

$= - |\psi^{(A)}\rangle$

antisymmetric functions change sign under interchange of two coordinates: $\psi(3,2,1) = -\psi(1,2,3)$

Since any permutation is a product of transpositions

$\hat{P}_u |\psi^{(S)}\rangle = + |\psi^{(S)}\rangle$

$\hat{P}_u (|\psi^{(A)}\rangle) = (-)^{\#\text{ of Transp}} |\psi^{(A)}\rangle$

$= (-)^{P_u} |\psi^{(A)}\rangle$

One can argue that one can expect this behaviour, by examining eigenfunctions of $\hat{T}$

Recall $\hat{T} = \hat{T}^{-1} = \hat{T}^{+}$

$\hat{T}$ is Hermitean and its own inverse.

$\Rightarrow$ eigenfunctions of $\hat{T}$:

$$\hat{T}\,|\psi\rangle = \lambda\,|\psi\rangle$$
$$\hat{T}\,\hat{T}\,|\psi\rangle = \lambda^2\,|\psi\rangle = |\psi\rangle \qquad (T^2 = \mathbb{1})$$

$$\Rightarrow \lambda^2 = 1 \qquad \lambda = 1 \quad \text{or} \quad \lambda = -1$$

So since $\hat{T}_a$ commutes with $\hat{H}$, $\hat{T}_a\,|\psi\rangle$ can be chosen either to change sign or stay the same.

In principle I can make a set of commuting $\hat{T}_{12}, \hat{T}_{34}, \hat{T}_{56}$

and demand that ψ is eigenstate of $\hat{H}$ and selected $\hat{T}$.

Then, one could choose some T_a to have $\lambda_a = +1$ and some $\hat{T}_a$ to have $\lambda_a = -1$.

Such eigenfunctions do exist.

However for $|\psi^{(S)}\rangle$ $\hat{T}_a\,|\psi^{(S)}\rangle = +\,|\psi^{(S)}\rangle$ $\forall\ \hat{T}_a$, whilst for $|\psi^{(A)}\rangle$

$\hat{T}_a\,|\psi^{(A)}\rangle = -\,|\psi^{(A)}\rangle$,

These are the only 1-dimensional irreps of the permutation group.

To describe fully symmetric or antisymmetric wave functions projectors are useful.

For a projector: $P^2 = P$

$P^+ = P$

Eigenfunctions of a projector

$$P|\psi\rangle = \lambda|\psi\rangle$$

$$P^2|\psi\rangle = PP|\psi\rangle = \lambda^2|\psi\rangle$$
$$= P|\psi\rangle = \lambda|\psi\rangle$$

$$\Rightarrow (\lambda^2 - \lambda)|\psi\rangle = 0$$
$$\lambda = 1, \text{ or } \lambda = 0$$

$\hat{P}|\psi\rangle = |\psi\rangle$: $|\psi\rangle$ is in the subspace defined by $\hat{P}$

$\hat{P}|\psi\rangle = 0$ $\Rightarrow$ $|\psi\rangle$ is orthogonal to subspace defined by $\hat{P}$.

$$\hat{P} = \sum_{\lambda \in \text{subspace}} |\phi_\lambda\rangle\langle\phi_\lambda|$$

with $\langle\phi_\lambda|\phi_\mu\rangle = \delta_{\lambda,\mu}$.

Here we define projectors on the symmetric and antisymmetric subspaces.

$$\hat{S} = \frac{1}{N!} \sum_{k=1}^{N!} \hat{P}_k$$

$$\hat{A} = \frac{1}{N!} \sum_{k=1}^{N!} (-)^{P_k} \hat{P}_k$$

In the exercises you will prove that $\hat{S}$, $\hat{A}$ are Hermitean and that they satisfy $\hat{S}^2 = \hat{S}$; $\hat{A}^2 = \hat{A}$. $\hat{\rho}^2 = \hat{\rho}$ is called idempotent.

Let us prove that $\hat{A}|\psi\rangle$ is fully antisymmetric, irrespective of $|\psi\rangle$.

$$\hat{T}_a \hat{A}|\psi\rangle = \hat{T}_a \frac{1}{N!} \sum_{k=1}^{N!} (-)^{P_k} \hat{P}_k |\psi\rangle$$

$$= \frac{1}{N!} \sum_{k=1}^{N!} (-)(-)^{P_k+1} (\hat{T}_a \hat{P}_k) |\psi\rangle$$

Now $\hat{T}_a \hat{P}_k = \hat{P}_e$, with parity $(-)^{P_k+1} = (-)^{P_e}$

Moreover $\hat{T}_a \hat{P}_k$ runs over all permutations again, hence

$$\hat{T}_a \hat{A}|\psi\rangle = (-) \frac{1}{N!} \sum_{e=1}^{N!} (-)^{P_e} \hat{P}_e |\psi\rangle = -\hat{A}|\psi\rangle.$$

$\forall \hat{T}_a$

If one applies the antisymmetrizer $\hat{A}$ to a product of orbitals one gets

$$\hat{A}\left(\phi_a(1)\,\phi_b(2)\cdots\phi_z(N)\right)$$

$$= \frac{1}{N!}\sum_{k=1}^{N!}(-)^{P_k}\hat{P}_k\left(\phi_a(1)\cdots\phi_z(N)\right)$$

$$= \frac{1}{N!}\,|\phi_a\,\phi_b\cdots\phi_z|$$

$\sim$ to the Slater determinant

$\Rightarrow$ The antisymmetrizer provides a generalization to the Slater determinant concept as it can be applied to any function $\Psi(1,2,\cdots N)$ not only to a product of orbitals.

$\leftarrow$ In chapter 2 S&O we use $\hat{A}$ with a different normalization

$$\hat{A}' = \sum_{k=1}^{N!}(-)^{P_k}\hat{P}_k.$$

then, since $\frac{1}{N!}A'\cdot\frac{1}{N!}A' = \frac{1}{N!}A'$ it follows

$$A'A' = N!\,A'$$

A' is no longer a projector (but simpler to use).

In Summary:

$$[\hat{H}, \hat{P}_k] = 0 \qquad \hat{P}_k^+ \hat{P}_k = 1$$

$\hat{P}_k$ form a group. S_N, $k = 1 \ldots N!$

This implies that eigenfunctions of $\hat{H}$ can be chosen to transform as irreducible representations of the permutation group.

The irrep would never change as all operators in $\hat{O}, \hat{H}$ and any 'perturbation' have the property $[\hat{O}, \hat{P}_k] = 0$ (symmetric in particle labels).

Hence the irrep would never change.

The only low-dimensional irreps (for many particles) are the fully symmetric and fully antisymmetric representation. They ~~allow~~ are 1-dimensional irreps and allow non-degenerate eigenstates. For such states particles are indistinguishable

$$|\psi(1, 2, \ldots N)|^2 = |\psi(P_k(1, 2 \ldots N))|^2$$

probabilities are unaffected under permutation

From the spin-statistics theorem in Quantum-Field theory:

half-integer-spin particles are Fermions ; antisymmetric irrep.

integer-spin particles are bosons ; symmetric irrep.

For systems like ^4He, Rb atoms, atomic nuclei (made of protons and neutrons, or quarks) one speaks of bosons made from composite fermions.

In my opinion these are effective theories: The true wavefunction in terms of elementary particles is anti-symmetric. We can treat the composite particle as a strongly correlated system and this gives rise to effective boson symmetry.

(No good first-principles understanding it seems in the literature)

Other irreps than the fully symmetric or fully antisymmetric irreps do play a role!

Two examples:

In NMR, and ESR one only considers spin degrees of freedom.
⇒ all irreps of $\hat{S}_N$ occur
They correspond to spin-eigenstates

Spin-eigenstates ⟺ Symmetric group.

Also in conventional Quantum Chemistry, spin can be integrated out ($\hat{H}$ spin-independent)
Then, for spatial Wfn's all irreps of S_N play a rôle.

The group theory of S_N is very well understood:
Young Tableaus, Young diagrams, etc.

Also group theory is a very rich and well-developed subject.
references on website ...

Interlude : Antisymmetric wave functions.

The Antisymmetry principle says that electrons are described by antisymmetric wavefunctions.

In principle this is true for all electrons, e.g. in two distant atoms

Why stop there : All electrons in the Universe should be described by one antisymmetric wavefunction.

How can we calculate anything ?

Let us analyse, and simplify. Consider 2 electrons in distant orbitals

The wavefunction is given by

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left(\varphi_a(\vec{r}_1)\, \varphi_b(\vec{r}_2) - \varphi_a(\vec{r}_2)\, \varphi_b(\vec{r}_1) \right)$$

if $\vec{r}_1$ is in 'domain' of φ_a, and $\vec{r}_2$ is in 'domain' of φ_b
Then only the first term contributes.

The 'exchange' term S is
zero, exponentially.
This means if orbitals decay sufficiently fast I do not need to worry about exchange terms.

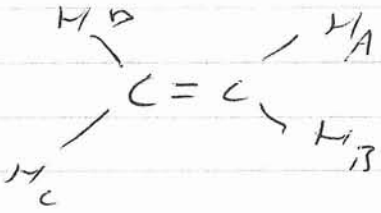
Extension: many-electron atoms
A and B

$\Psi_{AB}(\vec{r}_A, \vec{r}_B)$ fully antisymmetric

$\Psi_{AB}(\vec{r}_A, \vec{r}_B) \approx \Psi_A(\vec{r}_A)\,\Psi_B(\vec{r}_B)$

Electrons act as distinguishable particles. The coordinates that enter Ψ_A are effectively limited to the "domain" of A.

This explains also that for nuclear wave functions we usually do not worry about the Pauli principle.
Each 'normal mode' is like a separate particle.
Or use basis functions localized on atom:



Each of the four protons can be described by orbitals that are completely non-overlapping.

$$\rightarrow \quad \Psi_A(\vec{R}_A)\ \Psi_B(\vec{R}_B)\ \cdots\ \Psi_D(\vec{R}_D)$$

No need to antisymmetrize.

This is no longer true if atoms are not well separated, e.g. in the liquid. (research P.H. Roy)

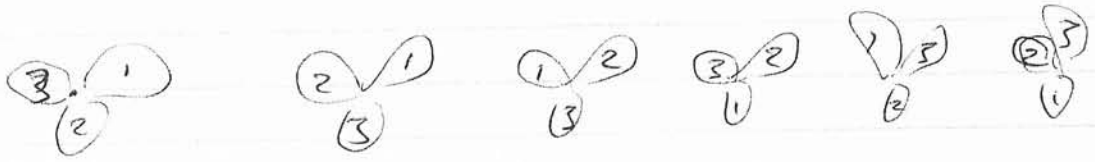
Here I argued that we do not need to worry about antisymmetry between distant parts.

Is there a consequence of antisymmetry that we do need to worry about? In another context?

Yes: antisymmetric or symmetric
Fermion Bosons

plays a crucial role in
Statistical mechanics.

Say I have 3 electrons in 3 orbitals



$\psi_a(r_1)\ \psi_b(r_2)\ \psi_c(r_3)$

for indistinguishable particles
there would be 6 different
wavefunctions associated with this
(give 1, 2, 3 colors to
see this for example)

Because of antisymmetric requirement
this collapses to only one
possibility.

$|\psi_a\ \psi_b\ \psi_c|$ Slater determinant

For N particles:
→ Count the number of
product states
→ divide by N!

(roughly)
{ For fermions we cannot double count
For bosons special counting.

⇒ consequence for partition function

$$Q \rightarrow \frac{(q)^N}{N!}$$ (Boltzmann approximation)

From Independent particles have functions
+ Antisymmetry / Symmetry,

So the Pauli Principle does have a repercussion for "all the electrons in Universe".

Nuclei: H — H

the effect of antisymmetry is delicate for nuclei
→ famous example para / ortho Hydrogen, heat capacity

From elementary statmech one introduces symmetry factor to account for equivalent nuclei. This all goes back to the requirement of antisymmetry, including also the effects of nuclear spin.
Too much to discuss here.