IDENTICAL PARTICLES

MATTHEW R. HENNEFARTH

1. Spin Statistics Relations

Lets consider some system of isolated particles. Classically, we could follow the trajectories of identical particles such that the exchange of particles results in physically equivalent configuration. In quantum mechanics; however, particles are truly indistinguishable. That is to say, if we were to try and follow the path of 2 particles, labeled A and B, but then lost track of them for a split second, we would have no idea which particle was A and which was B (Fig. 1)!

That means that given the following states $|k'\rangle$ and $|k''\rangle$, the states

$$|k'\rangle|k''\rangle \text{ and } |k''\rangle|k'\rangle \tag{1}$$

are 2 distinct states only if the particles are distinguishable. However, for all normalized states

$$c_1|k'\rangle|k''\rangle + c_2|k''\rangle|k'\rangle \tag{2}$$

they all give the same eigenvalues when a measurement is made. This is called **exchange degeneracy**. Lets define a permutation operator $\hat{\mathscr{P}}_{12}$ such that

$$\hat{\mathscr{P}}_{12}|k'\rangle|k''\rangle = |k''\rangle|k'\rangle \tag{3}$$

and this can be generalized for any particles i, j of $\hat{\mathscr{P}}_{ij}$.

$$\hat{\mathscr{P}}_{ij}|k^1\rangle\ldots|k^i\rangle\ldots|k^j\rangle\ldots = |k^1\rangle\ldots|k^j\rangle\ldots|k^i\rangle\ldots \tag{4}$$

Note that

$$\hat{\mathscr{P}}_{ij}^2 = \mathbb{1} \tag{5}$$

So that $\hat{\mathscr{P}}_{ij} = \hat{\mathscr{P}}_{ij}^{-1}$. Hence the eigenvalues of $\hat{\mathscr{P}}_{ij}$ is ± 1. We can also discuss its action on operators. Suppose we have some observable $\hat{\mathcal{O}}_1$ which acts on particle 1. Then

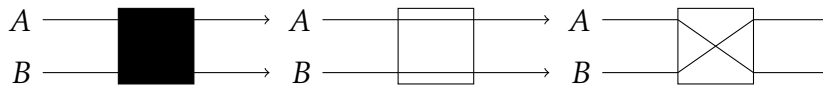$$\hat{\mathscr{P}}_{12}\hat{\mathcal{O}}_1\hat{\mathscr{P}}_{12}^{-1} = \hat{\mathcal{O}}_2 \tag{6}$$

Figure 1. Indistinguishably of particles A and B. If we were to follow there trajectories and our vision was obscured slightly, we would have no idea if particle A was on the top or not.

We can see this via (where α are some eigenstates of the operator)

$$\hat{\mathscr{P}}_{12}\hat{\mathscr{O}}_1\hat{\mathscr{P}}_{12}^{-1}\left|\alpha'\right\rangle\left|\alpha''\right\rangle = \hat{\mathscr{P}}_{12}\hat{\mathscr{O}}_1\left|\alpha''\right\rangle\left|\alpha'\right\rangle$$
$$= \alpha''\left|\alpha'\right\rangle\left|\alpha''\right\rangle \tag{7}$$

So $\hat{\mathscr{P}}_{12}\hat{\mathscr{O}}_1\hat{\mathscr{P}}_{12}^{-1}$ acts like $\hat{\mathscr{O}}_2$.

Considering the 2 particle case. We can see that the eigenstates of $\hat{\mathscr{P}}_{12}$ are

$$\frac{1}{\sqrt{2}}\left(\left|k'\right\rangle\left|k''\right\rangle \pm \left|k''\right\rangle\left|k'\right\rangle\right) \tag{8}$$

Where the + goes has an eigenvalue of +1 and − has an eigenvalue of −1. Finally, any permutation $\hat{\mathscr{P}}_{ijk}$ where $i \to j \to k \to i$ can be expressed as a product of $\hat{\mathscr{P}}_{ij}$. For example,

$$\hat{\mathscr{P}}_{123} = \hat{\mathscr{P}}_{12}\hat{\mathscr{P}}_{13} \tag{9}$$

Lets project the operator into a symmetric and antisymmetric contribution

$$\hat{S}_{12} = \frac{1}{2}\left(\mathbb{1} + \hat{\mathscr{P}}_{12}\right) \tag{10}$$

$$\hat{A}_{12} = \frac{1}{2}\left(\mathbb{1} - \hat{\mathscr{P}}_{12}\right) \tag{11}$$

These operators, when acting on general linear combinations of $\left|k'\right\rangle\left|k''\right\rangle$ result in necessarily symmetric/antisymmetric states.

$$\hat{S}_{12}\left(c_1\left|k'\right\rangle\left|k''\right\rangle + c_2\left|k''\right\rangle\left|k'\right\rangle\right) = \frac{1}{2}\left(c_1\left|k'\right\rangle\left|k''\right\rangle + c_2\left|k''\right\rangle\left|k'\right\rangle\right) + \frac{1}{2}\left(c_1\left|k''\right\rangle\left|k'\right\rangle + c_2\left|k'\right\rangle\left|k''\right\rangle\right)$$
$$= \frac{c_1 + c_2}{2}\left(\left|k'\right\rangle\left|k''\right\rangle + \left|k''\right\rangle\left|k'\right\rangle\right) \tag{12}$$

$$\hat{A}_{12}\left(c_1\left|k'\right\rangle\left|k''\right\rangle + c_2\left|k''\right\rangle\left|k'\right\rangle\right) = \frac{c_1 - c_2}{2}\left(\left|k'\right\rangle\left|k''\right\rangle - \left|k''\right\rangle\left|k'\right\rangle\right) \tag{13}$$

Now, the question is, does nature take advantage of the totally symmetric/antisymmetric states? It turns out that Bosons (particles with integer spin, $0, 1, 2, \ldots$) satisfy Bose-Einstein statistics. That is

$$\hat{\mathscr{P}}_{ij}\left|N\text{-identical}\right\rangle = +\left|N\text{-identical}\right\rangle \tag{14}$$

The wave function must be completely symmetric. Hence, Bosonic states are eigenstates of $\hat{S}_{ij}$. On the other hand, it is known that Fermions (particles with half-integer spin, $\frac{1}{2}, \frac{3}{2}, \ldots$) satisfy Fermi-Dirac statistics. Which is that

$$\hat{\mathscr{P}}_{ij}\left|N\text{-identical}\right\rangle = -\left|N\text{-identical}\right\rangle \tag{15}$$

The wave function must be **antisymmetric** with the exchange of any 2 particles! Hence, they are eigenstates of $\hat{A}_{ij}$. Note that these results are also applicable to composite systems (recall total spin states)!

A fundamental consequence of the fact that Fermions are completely antisymmetric is the **Pauli Exclusion Principle**. Note this is a result of Fermions being antisymmetric, not the other way around.

Theorem 1 (Pauli Exclusion Principle). No two Fermions can occupy the same exact state.

Proof. We proceed with a proof by contradiction. Suppose that two Fermions were in the same quantum state. That is $|\psi\rangle|\psi\rangle$. Then, Fermions are eigenstates of $\hat{A}_{12}$ (it should act like the identity). Therefore,

$$\hat{A}_{12}|\psi\rangle|\psi\rangle = \frac{1}{2}\left(\mathbb{1} - \hat{\mathscr{P}}_{12}\right)|\psi\rangle|\psi\rangle = 0 \tag{16}$$

So in fact, it is impossible! □

Lets consider further the difference between bosons and fermions. For a system of two fermions, there is only one possibility for the state:

$$\frac{1}{\sqrt{2}}\left(|k'\rangle|k''\rangle - |k''\rangle|k'\rangle\right) \tag{17}$$

On the other hand, bosons can be in 3 possible states:

$$|k'\rangle|k'\rangle, \; |k''\rangle|k''\rangle, \; \frac{1}{\sqrt{2}}\left(|k'\rangle|k''\rangle + |k''\rangle|k'\rangle\right) \tag{18}$$

This differs from the classical particles which have no restriction on symmetrc and can be in any 4 independent states. Note the observation of bosons differing from fermions is most dramatic at low temperature where it is possible for all bosons to energy the ground state, and this is known as **Bose-Einstein condensation**, this feature is impossible for fermions.

Lets return to our 2 electron system (ie 2 spin 1/2 particles). Furthermore, lets suppose that $\left[\hat{H}, \hat{\mathscr{S}}^2\right] = 0$ so that we can write our eigenfunctions of $\hat{H}$ as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \phi(\mathbf{r}_1, \mathbf{r}_2)\sigma(\omega_1, \omega_2) \tag{19}$$

Furthermore, they must also be eigenfunction of $\hat{\mathscr{S}}^2$, hence they can either be in the triplet manifold

$$\sigma(\omega_1, \omega_2) = \begin{cases} \alpha(\omega_1)\alpha(\omega_2) \\ \frac{1}{\sqrt{2}}(\alpha(\omega_1)\beta(\omega_2) + \beta(\omega_1)\alpha(\omega_2)) \\ \beta(\omega_1)\beta(\omega_2) \end{cases} \tag{20}$$

or singlet manifold

$$\sigma(\omega_1, \omega_2) = \frac{1}{\sqrt{2}}(\alpha(\omega_1)\beta(\omega_2) - \beta(\omega_1)\alpha(\omega_2)) \tag{21}$$

Fermi-Dirac statistics requires that

$$\phi(\mathbf{r}_1, \mathbf{r}_2)\sigma(\omega_1, \omega_2) = -\phi(\mathbf{r}_2, \mathbf{r}_1)\sigma(\omega_2, \omega_1) \tag{22}$$

Hence, the permutation operator $\hat{\mathscr{P}}_{12}$ can be decomposed into

$$\hat{\mathscr{P}}_{12} = \hat{\mathscr{P}}_{12}^{(\text{space})} \otimes \hat{\mathscr{P}}_{12}^{(\text{spin})} \tag{23}$$

where $\hat{\mathscr{P}}_{12}^{(\text{space})}$ only interchanges the position coordinate and $\hat{\mathscr{P}}_{12}^{(\text{spin})}$ interchanges the spin coordinate. This necessarily implies that either $\hat{\mathscr{P}}_{12}^{(\text{space})}$ or $\hat{\mathscr{P}}_{12}^{(\text{spin})}$ must be antisymmetric for $\hat{\mathscr{P}}_{12}$ to be antisymmetric. But both cannot be antisymmetric or both being symmetric. If σ is a triple, then it must be that ϕ is antisymmetric. If σ is a singlet, then ϕ must be symmetric!

Now, lets suppose that our Hamiltonian commutes with the spin operators and is separable such that

$$\hat{H} = \hat{h}(1) + \hat{h}(2) \tag{24}$$

where $|\phi_A\rangle, |\phi_B\rangle$ are two spatial eigenfunctions. Then we know the spatial portion of the wave function must look something like

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \pm \phi_B(\mathbf{r}_1)\phi_A(\mathbf{r}_2)) \tag{25}$$

where the + combination goes with the spin singlet and − combination goes with the spin triplet. Note that the − combination cannot have that $A = B$, but for the + combination, $A = B$ is allowed. All we need is for the spatial portion to be symmetric/antisymmetric respectively.

Lets assume that in general $A \neq B$. We can then ask the question, what is the probability of finding an electron near $\mathbf{r}_1$ and an electron near $\mathbf{r}_2$. Well, we have

$$
\begin{aligned}
P(\mathbf{r}_1, \mathbf{r}_2) &= |\phi|^2 \\
&= \frac{1}{2}\left(|\phi_A(\mathbf{r}_1)|^2|\phi_B(\mathbf{r}_2)|^2 + |\phi_A(\mathbf{r}_2)|^2|\phi_B(\mathbf{r}_1)|^2 \pm \mathrm{Re}\left(\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2)\phi_A^*(\mathbf{r}_2)\phi_B^*(\mathbf{r}_1)\right)\right)
\end{aligned}
\tag{26}
$$

The cross term is called the **exchange density**. In the event that we had a spin triplet, then there was a minus sign and $P(\mathbf{r}_1 = \mathbf{r}_2) = 0$. The electrons are hence avoiding each other! However, for the spin singlet, $P(\mathbf{r}_1 = \mathbf{r}_2)$ is actually enhanced (that is the exchange density contributes)! We might be a bit worries since classically, we don't see exchange effects at all, they are purely a quantum phenomena. And in fact, we are fine since for localized wave functions ϕ_A, ϕ_B that are fairly far from each other, then there overlap is small and the exchange density is consequently small. Hence the exchange density is only important when the spatial wave functions are relatively close or delocalized. More precisely, we don't have to worry about antisymmetrizing Fermions which are far apart from each other, but in the case of molecules, we do.

Example 2 (The Helium Atom). Recall our example from earlier on the Helium atom. We first assumed that we could ignore electron-electron interactions so that we could write the ground-state wave function as

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) \tag{27}$$

We then found that we could include the electron-electron interaction by using ψ as a trial wave function and variationally optimizing the Z parameter (effective nuclear charge) so as to minimize the energy. We found $Z_0 = 2 - \frac{5}{16}$ gave the optimal result.

$$\xi_0(\mathbf{r}_1, \mathbf{r}_2, Z_0) = \left(\frac{Z_0^3}{\pi}\right)e^{-Z_0(r_1 + r_2)} \tag{28}$$

Ah, but we neglected basically everything we just talked about (namely indistinguishably and spin!). Lets add spin into this formulation. We know the ground state of Helium should have 2 electrons in the 1s orbital. And we can take ξ to be the spatial part of our wave function which is symmetric with respect to exchange of the electron coordinates.

FIGURE 2. Schematic of the energy level splitting in the excited state of Helium.
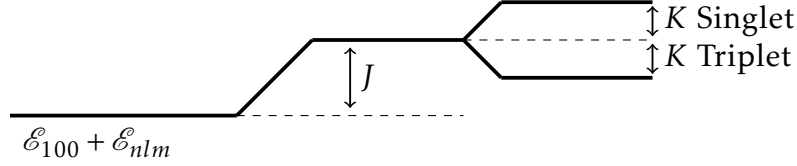
Hence, we should multiply by an antisymmetric spin component (in this case, the singlet spin) so that our final wave function is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \xi_0(\mathbf{r}_1, \mathbf{r}_2, Z_0)(\alpha(\omega_1)\beta(\omega_2) - \beta(\omega_1)\alpha(\omega_2)) \tag{29}$$

Note that by adding in spin, we have not changed the energy for the wave function, nor have we altered the optimal value of Z_0! This is because our Hamiltonian does not depend on spin, and so spin can always be dealt with later!

Example 3 (Helium Atom Excited State). Lets also consider the excited states of Helium. Lets consider one electron in the 1s orbital and the other in the nl orbital. In general, we could write the energy for the state as

$$\mathscr{E} = \mathscr{E}_{100} + \mathscr{E}_{nlm} + \Delta\mathscr{E} \tag{30}$$

where the $\Delta\mathscr{E}$ comes from the electron-electron interaction. The excited state singlet state will have a symmetric spatial wave function and the triplet state will have an antisymmetric spatial wave function. In first-order perturbation theory, we can evaluate $\Delta\mathscr{E}$ as the expectation value of e^2/r_{12} so that

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = J \pm K \tag{31}$$

where J and K are known as the Coulomb and exchange integrals respectively.

$$J = \int \left|\psi_{100}(\mathbf{x}_1)\right|^2 \left|\psi_{nlm}(\mathbf{x}_2)\right|^2 \frac{e^2}{r_{12}} \tag{32}$$

$$K = \int \psi_{100}(\mathbf{x}_1)\psi_{nlm}^*(\mathbf{x}_1)\psi_{100}^*(\mathbf{x}_2)\psi_{nlm}(\mathbf{x}_2) \frac{e^2}{r_{12}} \tag{33}$$

The upper/lower signs go with the spin singlet/triplet respectively. Both J and K are positive valued so it can be seen that the spin singlet is higher in energy than the corresponding spin triplet (Fig. 2). What is particularly interesting is that the Hamiltonian commutes with spin, so there should not be any particular preference for singlet or triplet spin states to have higher or lower energy. But this spin effect is due to the Fermi-Dirac statistics of fermions!

2. Hartree Product and Slater Determinants

2.1. **Spin and Spatial Molecular Orbitals.** Lets return to our discussion on the electronic Hamiltonian. We know that it is in general non-separable due to the electron-electron interactions. Lets, for the moment, neglect all of the electron-electron interaction

terms such that the Hamiltonian for an N electron system is given by

$$\hat{H} = \sum_{i}^{N} \hat{h}(i) \tag{34}$$

where $\hat{h}(i)$ is ith electron operator which consists of just the electron kinetic energy and nuclear-electron interaction terms. Let suppose we knew what the exact eigenstate of the individual $\hat{h}(i)$ (and they should actually be all the same!), and enumerate them as $\left|\phi_p\right\rangle$. That is,

$$\hat{h}\left|\phi_p\right\rangle = \varepsilon_p\left|\phi_p\right\rangle \tag{35}$$

In general, we won't be able to exactly solve these one-electron operators, but we can use the LCAO approach from earlier to get a set of approximate MOs generated from a basis set of AOs.

We know that to properly describe an electron, however, is that we must also include spin. Spin orbitals are formed by adding an appropriate α or β spin function.

$$\chi(\mathbf{x}) = \begin{cases} \phi(\mathbf{r})\alpha(\omega) \\ \phi(\mathbf{r})\beta(\omega) \end{cases} \tag{36}$$

Given some set of K spatial orbitals, we can form a set of $2K$ spin orbitals as

$$\left|\chi_{p\alpha}\right\rangle = \left|\phi_p, \alpha\right\rangle \tag{37a}$$

$$\left|\chi_{p\beta}\right\rangle = \left|\phi_p, \beta\right\rangle \tag{37b}$$

These spin orbitals are exactly single particle states (this is the translation from physics to chemistry actually). We can then form a many-electron wave function through the direct product of single particle wave functions. The simplest form is

$$|\mathrm{HP}\rangle = |\chi_P\rangle\left|\chi_Q\right\rangle\cdots|\chi_R\rangle \tag{38}$$

A wave function of this form is called a Hartree product. The particles described by a Hartree product are uncorrelated. That is the probability of finding one electron at some point in space is independent of the position of the other electrons. But more importantly, it does not take into account the indistinguishably of electrons. As such it violates the antisymmetry principle and is not a good form for our many-electron wave function

More importantly, the set of all possible Hartree products is exactly the direct product basis for the total Hilbert space describing the N electron wave function. Hence, our actual electronic wave function must be some linear combination of the Hartree products! However, in the next section we will consider an alternative basis which removes the issue of antisymmetry and indistinguishably reducing the amount of redundant parameters.

2.2. Slater Determinant.

One can correct the Hartree product by forming an antisymmetrized Hartree product. As an example, lets take a 2 electron system were the electrons occupy the spin orbitals $|\chi_P\rangle, |\chi_Q\rangle$. The Hartree product would be

$$\left|\mathrm{HP}^{1,2}\right\rangle = |\chi_P\rangle\left|\chi_Q\right\rangle \tag{39}$$

But if we didn't want to distinguish between which electron was in which orbital we could have written

$$\left|\text{HP}^{2,1}\right\rangle = \left|\chi_Q\right\rangle\left|\chi_P\right\rangle \tag{40}$$

Both do not take into consideration the antisymmetry principle. But if we take an appropriate linear combination

$$\left|\Psi\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\chi_P\right\rangle\left|\chi_Q\right\rangle - \left|\chi_Q\right\rangle\left|\chi_P\right\rangle\right) \tag{41}$$

We get a wave function which satisfies the antisymmetry principle (note the normalization factor)! This can also be written as a determinant in spin coordinates as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_P(\mathbf{x}_1) & \chi_Q(\mathbf{x}_1) \\ \chi_P(\mathbf{x}_2) & \chi_Q(\mathbf{x}_2) \end{vmatrix} \tag{42}$$

This is called a Slater determinant. The generalization for an N-electron wave function is

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_P(\mathbf{x}_1) & \chi_Q(\mathbf{x}_1) & \cdots & \chi_R(\mathbf{x}_1) \\ \chi_P(\mathbf{x}_2) & \chi_Q(\mathbf{x}_2) & \cdots & \chi_R(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_P(\mathbf{x}_N) & \chi_Q(\mathbf{x}_N) & \cdots & \chi_R(\mathbf{x}_N) \end{vmatrix} \tag{43}$$

We will use the following as a short hand

$$\left|\Psi\right\rangle = \left|\chi_P\chi_Q\cdots\chi_R\right\rangle \tag{44}$$

to represent the Slater determinant formed from the spin orbitals $\chi_P, \chi_Q, \dots \chi_R$.

Electrons which are described by a Slater determinant are no longer independent of one another. The antisymmetrization of the Hartree product introduces exchange effects (which have already seen). In particular the motion of electrons with different spins are uncorrelated, but for electrons with the same spin, it is correlated.

We can now characterize two different types of Slater determinants/sets of spin orbitals.

Definition 4. If a Slater determinant is composed of spin orbitals where the alpha and beta spin orbitals have the same spatial forms (such as in the form Eq. (37)), we call this a **restricted** Slater determinant. If the alpha and beta spin orbitals differ in at least one spatial component, then they form an **unrestricted** Slater determinant.