which can be interpreted as the expectation value of Coulomb energy when the first particle is in the state φ_i and the second particle is in the state φ_j. On the other hand, the exchange term,

$$\langle \varphi_j \varphi_i \mid A \mid \varphi_i \varphi_j \rangle = \int \int \varphi_i(\mathbf{r}_1)^* \varphi_i(\mathbf{r}_2) \varphi_j(\mathbf{r}_2)^* \varphi_j(\mathbf{r}_1) \frac{e^2}{\mid \mathbf{r}_1 - \mathbf{r}_2 \mid} d\mathbf{r}_1 d\mathbf{r}_2 \qquad ,$$

is something else. We cannot give a nice physical meaning to it immediately. However, the exchange terms have a contribution to the Coulomb energy of two particles in the N particle system. Where did this term come from? Basic interpretation goes something like this: The Coulomb interaction between the particles can cause the particles to exchange their places. (Is this physically meaningful?) This issue does not arise for distinguishable particles. Only for identical particles such a path is open. Presence of such an exchange processes, then, affects the expectation values of two-particle observables. The meaning of this last interpretation is left to the reader. But, mathematically, exchange terms are present and we have to use them to obtain the physically relevant results.

1.5   The question of independence

We say that two statistical quantities A and B are *uncorrelated* if the statistical properties of A and B are independent of each other. (Distribution of A is not dependent on which value we find for B.) In terms of averages this implies that $\langle AB \rangle = \langle A \rangle \langle B \rangle$. That property should be valid for any property of A and B, so we should have $\langle f(A)g(B) \rangle = \langle f(A) \rangle \langle g(B) \rangle$ for all functions f and g. For the case of particles, we say that two particles are independent (or they are uncorrelated) if $\langle A(1)B(2) \rangle = \langle A(1) \rangle \langle B(2) \rangle$ for all observables A and B. This is only possible if the wavefunction of the whole system is a product of the wavefunctions of two particles:

$$\Psi(1, 2) = \varphi_1(1)\varphi_2(2) \qquad .$$

Only in that case we can say that any property of particle-1 can be measured by disregarding particle-2. Any property of particle-1 is independent of what the second particle is doing.

In classical mechanics we will have independent particles if the particles are not interacting either directly or indirectly. (If 1 interacts with 3 and 2 interacts with 3, then 1 and 2 interacts indirectly although there may not be

a direct interaction between them.) In quantum mechanics, the absence of the interaction is not enough. You also need to have a wavefunction which is uncorrelated.

Independence issue may also arise in the investigation of an isolated system. In that case, we expect that any property of the system is independent of what is going on in the rest of the universe. In such a case, what we mean by independence, in terms of wavefunctions, is, $\Psi_{\text{Universe}} = \psi_{\text{system}} \psi_{\text{rest}}$. As a result, any property of the isolated system, evaluated in the full wavefunction of the universe, Ψ_{Universe}, will be the same as the one calculated in the wavefunction of the system only (ψ_{system}), ignoring the rest of the universe. This is what we have been doing when we were solving the Hydrogen atom problem. In principle, though, we might have correlations between the particular hydrogen atom and the rest of the universe.

Now, for the case of identical fermions, the wavefunctions of many-particle systems cannot be written as a simple product. The best we can do is to write them in Slater determinants. As a result, *identical particles can never be independent by the definition given above.* This is actually troublesome, since if we want to investigate the behavior of an electron in a particular hydrogen atom, we cannot claim that this electron is behaving *independently* from what the electrons on the Moon are doing!

It is important that we settle the questions that arise in the paragraph above. When we claim "independence" we have to separate the (direct or indirect) interaction effects from the effects arising from indistinguishability. You can claim that your electron is independent of the other electrons in the Moon because the Coulomb potentials of the Moon's electrons are negligible at the location of your hydrogen atom. This is OK. On the other hand, the most troublesome is the effects caused by identicalness. In that case, it seems that the relevant concept that has to to used is the "exchange effects". Since the probability of your electron exchanging places with one of the electrons on the Moon is small, the "exchange processes" cause a negligible change in what you are measuring.

In any case, we need a separate definition of independence for identical particles. Since the Slater determinant is the simplest expression for the many-body wavefunction of many fermions, we will say that the fermions are *independent* if their wavefunction is a Slater determinant. There is a good reason for this definition. If the N particles in a system are not interacting,

then the Hamiltonian of the system can be written as

$$H = h(1) + h(2) + \ldots + h(N)$$

where h is a one-particle hermitian operator that can be called as one-particle Hamiltonian. For the case of N non-interacting electrons in an atom, h is

$$h(i) = \frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} \quad ,$$

ignoring also the spin-orbit coupling. Now, if φ_i are the eigenstates of h with eigenvalue ϵ_i, i.e.,

$$h\varphi_i = \epsilon_i \varphi_i \quad ,$$

then the complete set of eigenstates of H are the Slater determinants of any N distinct subsets of φ:

$$\Psi_{i_1,i_2,\ldots,i_N} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{i_1}(1) & \ldots & \varphi_{i_1}(N) \\ \vdots & \ddots & \vdots \\ \varphi_{i_N}(1) & \ldots & \varphi_{i_N}(N) \end{vmatrix}$$

$$H\Psi_{i_1,i_2,\ldots,i_N} = E_{i_1,i_2,\ldots,i_N} \Psi_{i_1,i_2,\ldots,i_N} = (\epsilon_{i_1} + \ldots + \epsilon_{i_N})\Psi_{i_1,i_2,\ldots,i_N}.$$

Since, the eigenfunctions of a noninteracting system of identical particles is of the form of a Slater determinant, and since noninteracting means independent (at least classically), then all Slater determinants describe independent identical particles.

A Slater determinant is the most independent wavefunction possible for identical particles. We obviously do not have $\langle A(1)B(2)\rangle = \langle A(1)\rangle\langle B(2)\rangle$ for Slater determinants. Hence the particles are always correlated. And this is the minimum amount of correlation that you will get for identical particles.

When the particles are interacting, eigenfunctions of the Hamiltonian will not be of the form of Slater determinants. Hence, writing down an expression for the eigenstates of the Hamiltonian will be quite difficult. In those cases, we might take linear combinations of different Slater determinants. Even in this case, there will be too many possible wavefunctions that will make the life difficult for you. As an example, consider the Lithium atom with three electrons. You may want to use only the 1s, 2s and the 2p states to write down a wavefunction which will have a "dependent" electron character. That implies that there are two 1s, two 2s and six 2p states which will be available

in forming possible Slater determinants. Three element subsets of these ten one-particle states can be formed in 120 possible ways. Hence if you don't have a way of radically cutting down this number to reasonable levels (for example by using conservation of S_z and L_z) then you will have too many terms to deal with. This is the main difficulty in many-particle problems. There are too many possible states for the wavefunction of the system (which grows exponentially with the size of the system). As a result, you cannot form wavefunctions where the state is sufficiently far away from independent particle case. Even if you do form, you cannot evaluate expectation values.

2 Ground State of Helium

Now we pass on to realistic problems. Consider the states of the Helium atom. Ignoring the spin-orbit coupling, the Hamiltonian will be

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_1} + \frac{e^2}{\mid \mathbf{r}_1 - \mathbf{r}_2 \mid},$$

where Z is the number of protons in the nucleus ($Z = 2$ for Helium). We can use the shorthand to write this Hamiltonian

$$H = T(1) + T(2) + V(1) + V(2) + V_{ee}(1,2) \qquad,$$

where T denotes the kinetic energy operator, V denotes the Coulomb interaction energy with the nucleus and V_{ee} is the electron-electron interaction energy. This last term is the one that makes this problem unsolvable. With the use of variational theory and heavy use of computers, the energy levels of the Helium atom can be calculated with high accuracy. In here, we just want to obtain a suitable approximate expression for the ground state.

Since the total spin is conserved, we can label the eigenstates of H as spin-singlet and spin-triplets. The ground state is a spin singlet state. As a simple first approximation we can ignore the V_{ee} term in the Hamiltonian and write the energy eigenfunctions as Slater determinants. Presence of spin creates some minor problems in here but at least for the ground state we have

$$
\begin{aligned}
\Psi(1,2) &= \psi_{100}(r_1)\psi_{100}(r_2)\frac{1}{\sqrt{2}}\left(\mid\uparrow\downarrow\rangle - \mid\downarrow\uparrow\rangle\right) \\
&= \frac{1}{\sqrt{2!}}\begin{vmatrix} \psi_{100}(r_1)\mid\uparrow\rangle_1 & \psi_{100}(r_2)\mid\uparrow\rangle_2 \\ \psi_{100}(r_1)\mid\downarrow\rangle_1 & \psi_{100}(r_2)\mid\downarrow\rangle_2 \end{vmatrix}
\end{aligned}
$$