We have seen that the wavefunctions of electrons are completely anti-symmetric. By this statement we mean that under the exchange of any two particles' coordinates and spins the wavefunction changes sign. Inclusion of the spin degree of freedom complicates the matters a little bit, but the discussion is fairly simple for two electrons. When the total spin is conserved eigenfunctions of the Hamiltonian can also be chosen as the eigenfunctions of the total spin. More precisely, we can choose the energy eigenfunctions as the common eigenstates of H, S^2 and S_z. In that case the eigenfunctions will be

$$\Psi(1,2) = \phi(\mathbf{r}_1, \mathbf{r}_2)\chi_{\text{spin}}$$

where ϕ is the part of the wavefunction describing positions of the two electrons and χ_{spin} is the part that describe the "spin motion" of the electrons. Since that last part is chosen as an eigenstate of S^2 and S_z, it can be written as

$$\chi_{\text{spin}} = \mid S = 1, m_s\rangle = \begin{cases} |\uparrow\uparrow\rangle & m_s = 1, \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) & m_s = 0, \\ |\downarrow\downarrow\rangle & m_s = -1, \end{cases}$$

and

$$\chi_{\text{spin}} = \mid S = 0, m_s = 0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \qquad .$$

Since for $S = 1$ case (triplet) χ_{spin} is symmetric under the exchange of particles' spin, the space part of the wavefunction should be antisymmetric:

$$\phi_{\text{triplet}}(\mathbf{r}_1, \mathbf{r}_2) = -\phi_{\text{triplet}}(\mathbf{r}_2, \mathbf{r}_1) \qquad .$$

For the $S = 0$ case (singlet), spin part is antisymmetric and as a result the space part should be symmetric:

$$\phi_{\text{singlet}}(\mathbf{r}_1, \mathbf{r}_2) = \phi_{\text{singlet}}(\mathbf{r}_2, \mathbf{r}_1) \qquad .$$

We should add that this simplification occurs *only if* the total spin, $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$, is a conserved quantity (i.e., it commutes with the Hamiltonian). In real atoms and molecules, this is not the case due to the spin-orbit coupling. Only the total angular momentum is conserved and not the total spin. As a result, true eigenstates of realistic Hamiltonians will be a mixture of singlet and triplet states, i.e., a very complicated wavefunction where spin and space are "correlated".

For the case of three or more particles, the breakdown of the wavefunction into a space and spin part will be quite complicated, even when the total spin is conserved. You may try to see this yourself for the case of three electrons with total spin quantum number $S = 1/2$. If the complete antisymmetry of the whole wavefunction is imposed, no wavefunction can be written as a product of a space part and a spin part. This is a result of the non-commutativeness of the different exchange operators for three or more particles. As a result in some cases (e.g., when $S = 1/2$ restriction is imposed) you cannot find common eigenfunctions of all the exchange operators.

1 Slater Determinants

Therefore a general method is needed to construct electron wavefunctions which are completely antisymmetric in all cases. For this purpose, we can use the complete antisymmetry property of determinants. Since interchanging any two rows (or columns) of a determinant changes the sign of the determinant, completely antisymmetric wavefunctions can be expressed in the form of a determinant.

Let us consider the case of N electrons. Let $\varphi_1, \ldots, \varphi_N$ be some arbitrary "one-particle states" of electrons. By a "one-particle state" we mean the spin and space part of a wavefunction of single electron. So, φ_i might be $\psi_{100}(r) \left| \uparrow \right\rangle$, or $\psi_{21-1}(r, \theta, \phi)\frac{1}{\sqrt{2}}(\left| \uparrow \right\rangle - \left| \downarrow \right\rangle)$. They do not even need to be a product of spin and space parts, so $\frac{1}{\sqrt{3}}(\psi_{100}(r) \left| \uparrow \right\rangle + \sqrt{2}\psi_{211} \left| \downarrow \right\rangle)$ is possible as well.

We will also have a short-hand notation for the particle coordinates. The space and spin coordinates of the ith particle will be denoted by the single number i. We haven't been very precise in what we mean by "spin coordinate" of a particle, since it is fairly obvious. So by $\varphi_j(i)$ we mean that the ith particle's space and spin is in the one-particle state φ_j. Since exchange should change both the space coordinate and the spin coordinate, this short-hand notation is quite useful in this case.

For the state where these N electrons are in these N one-particle states,

the wavefunction of the whole system can be written as

$$\Psi(1, 2, \ldots, N) = \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \ldots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \ldots & \varphi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(1) & \varphi_N(2) & \ldots & \varphi_N(N) \end{vmatrix}$$

where we have ignored the normalization factor. This expression is called as the Slater determinant of N states $\varphi_1, \ldots, \varphi_N$. As can be seen, exchanging the coordinates of ith and j^{th} particles' coordinates is equivalent to interchanging i^{th} and j^{th} columns of the determinant. As a result, exchange of any two particles' coordinates changes the sign of the wavefunction of the system Ψ. We have managed to obtain a totally anti-symmetric wavefunction. Although the equation does not show us well, there is a price that we pay for this: Ψ may not be chosen as an eigenstate of some operators (like S^2). For the time being, we will postpone the discussion of the physical meaning of the state Ψ.

We should also note that, since the determinant is also totally antisymmetric rowwise, interchanging the places of any two one-particle states will change the sign of Ψ. One implication of this property is that when you have chosen a set $\varphi_1, \ldots, \varphi_N$ such that two states are the same, e.g., $\varphi_i = \varphi_j$, then the wavefunction of the system is identically zero. This is because, when you interchange the positions of ith and j^{th} states, Ψ should remain the same since the one-particle-state set is unchanged. On the other hand, it should change sign because of the antisymmetry of the determinant. Last two sentences are consistent only if Ψ is identically zero. Since an identically zero wavefunction is not possible in quantum mechanics, we should have distinct one-particle states in the set $\varphi_1, \ldots, \varphi_N$. This is the famous "Pauli exclusion principle". No two electrons in a system can be in the same one-particle state. Although we have shown this only for Slater determinants, we can extend this statement for other types of system wavefunctions as well. Note that in the statement "one-particle state" refers to both space and spin parts.

1.1 Choosing one-particle states

We have said that if two one-particle states are the same, the determinant is identically zero, since in that case two rows in the determinant will be exactly identical for all possible values of the particle coordinates. There

are other properties of the determinants which will enable us to do further simplifications. For example, multiplying a row by a constant and adding to another row will not change the value of a determinant. As a result, for example we can replace the one-particle state φ_1 with $\varphi_1 + a\varphi_2$ and the system's wavefunction Ψ will remain the same. Since, only the system's wavefunction is relevant for the physical properties of the system, we have some freedom in choosing one-particle states.

First of all we can extend the "Pauli exclusion principle" a little bit. If the one-particle state set $\varphi_1, \ldots, \varphi_N$ is linearly dependent (that means one state can be written as a linear combination of others, e.g., $\varphi_1 = a\varphi_2 + b\varphi_3$) the Ψ is identically zero. We have to make sure that the set $\varphi_1, \ldots, \varphi_N$ is formed by N independent one-particle states. Their being distinct is not enough. Linear independence of the N one-particle states is enough to guarantee that Ψ is not identically zero. Proof of this statement is left to the reader.

There is still some freedom in choosing the one-particle states, and it is convenient to take advantage of this. First of all, we need to explore how much freedom we have. We claim that for a given set of one-particle states $\varphi_1, \ldots, \varphi_N$, by taking any linear combinations of this set and forming any other N linearly independent states, say $\varphi'_1, \ldots, \varphi'_N$, we won't change Ψ. Let us be a little bit more specific. Let us define the new one-particle states φ'_i as

$$\varphi'_i = \sum_{j=1}^{N} A_{ij} \varphi_j \qquad , \tag{1}$$

where A_{ij} are some complex numbers. The new set φ'_i is linearly independent only if the determinant of the matrix A is non-zero. In this case the old set can be written in terms of the new set as well.

$$\varphi_i = \sum_{j=1}^{N} (A^{-1})_{ij} \varphi'_j \qquad .$$

Now, what happens when we form the Slater determinant from the new set φ'_i? To see this clearly, we need to re-express Eq. (1) in matrix notation:

$$\begin{bmatrix} \varphi'_1 \\ \varphi'_2 \\ \vdots \\ \varphi'_N \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & \ldots & A_{1N} \\ A_{21} & A_{22} & \ldots & A_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ A_{N1} & A_{N2} & \ldots & A_{NN} \end{bmatrix} \begin{bmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_N \end{bmatrix} \qquad .$$

It is fairly straightforward to change this relationship to a relationship between Slater determinants. First, in matrix form

$$
\begin{bmatrix}
\varphi_1'(1) & \ldots & \varphi_1'(N) \\
\varphi_2'(1) & \ldots & \varphi_2'(N) \\
\vdots & \ddots & \vdots \\
\varphi_N'(1) & \ldots & \varphi_N'(N)
\end{bmatrix}
=
\begin{bmatrix}
A_{11} \ldots & A_{1N} \\
A_{21} \ldots & A_{2N} \\
\vdots \ddots & \vdots \\
A_{N1} \ldots & A_{NN}
\end{bmatrix}
\begin{bmatrix}
\varphi_1(1) & \ldots & \varphi_1(N) \\
\varphi_2(1) & \ldots & \varphi_2(N) \\
\vdots & \ddots & \vdots \\
\varphi_N(1) & \ldots & \varphi_N(N)
\end{bmatrix}
$$

Since the determinant of a product of matrices is equal to the product of determinants we have

$$
\Psi'(1, 2, \ldots, N) = \det(A)\Psi(1, 2, \ldots, N) \qquad ,
$$

where Ψ' is the wavefunction of the system prepared by the new set of one-particle states $\varphi_1', \ldots, \varphi_N'$ and Ψ is the one that is prepared by the old set $\varphi_1, \ldots, \varphi_N$. Therefore the wavefunctions of the system prepared by the two sets differ only by a normalization factor. Since, that means the same expectation values for physical observables (if proper normalization is carried out), we claim that the "same" wavefunction is obtained in both cases.

As a result, we see that in the choice of the one-particle states $\varphi_1, \ldots, \varphi_N$, neither order nor the particular linear combination is important. As a concrete example, a Slater determinant constructed from the states 1s-spin-up and 1s-spin-down is not different than the one constructed from 1s-spin-x-up and 1s-spin-x-down. There is no physical way of distinguishing the way the determinant is constructed.

Because of this, we choose the one-particle states as an orthonormal set. Gram-Schmidt process enables us to do this for any independent set of N states. As a result we will assume that the relations

$$
\langle \varphi_i \mid \varphi_j \rangle = \delta_{ij}, \qquad i, j = 1, \ldots, N
$$

are satisfied. This orthonormality property that we require will be very useful in evaluating expectation values of observables. Even with that restriction, there is some arbitrariness in the choice of the particular states of the set. We can still take linear combinations

$$
\varphi_i' = \sum_{j=1}^{N} A_{ij}\varphi_j \qquad ,
$$

and if the matrix-A is unitary, the new set will be orthonormal as well. This kind of arbitrariness cannot be eliminated further. At this point, the user should decide which particular linear combinations are useful. So, if the two electron system mentioned above is in a magnetic field along x-axis, then you may want to choose your states as 1s-spin-x-up and 1s-spin-x-down.

1.2 Normalization

Before going further we need to normalize the system's wavefunction. We need to keep in mind that in evaluating $\langle \Psi \mid \Psi \rangle$ integrals over particles' coordinates should be unlimited. This is a choice that we have made at the beginning when we were discussing the wavefunctions of identical particles. For the case of a Slater determinant formed by N orthonormal one-particle states, it is useful to have an expanded form of the determinants. Expanding the determinant is easy for $N = 2$ and perhaps for $N = 3$, but for larger N values, it becomes increasingly cumbersome to write the expansion. For this reason we need a shortened way of representing the determinant.

First we note that the determinant will be a sum of terms that are obtained by multiplying N elements of the matrix coming from different rows and different columns. As a result, the first few terms in the expansion of Ψ will be

$$\Psi(1, 2, \ldots, N) = \quad \varphi_1(1)\varphi_2(2)\varphi_3(3) \cdots \varphi_N(N)$$
$$-\varphi_1(2)\varphi_2(1)\varphi_3(3) \cdots \varphi_N(N) \quad + \ldots$$

There will be $N!$ terms in the expansion which will be formed by terms like

$$\pm \varphi_{i_1}(1)\varphi_{i_2}(2) \cdots \varphi_{i_N}(N)$$

where $i_1, i_2, \ldots, i_N$ are distinct numbers from the set $1, 2, \ldots, N$. We say that $i_1, i_2, \ldots, i_N$ is a *permutation* of $1, 2, \ldots, N$. Since there are $N!$ different permutations of an N element set, we have $N!$ terms in the expansion of the determinant. The only problem is to decide whether the term should have a $+$ or $-$ sign.

A property that we should keep in mind is that when we have a permutation and we exchange the places of two labels, the new permutation should have the opposite sign. Since the "identity" permutation $12 \ldots N$ should have $+$ sign, you can find the sign of any permutation starting from the identity permutation. As a definition, a permutation which can be obtained

from the identity permutation by an even number of exchanges is called an *even permutation* and should have $+$ sign. On the other hand, a permutation which can be obtained from the identity permutation by an odd number of exchanges is called an *odd permutation* and should have $-$ sign.

There is a faster way of finding the sign of a permutation which might be useful. When you write down the permuted labels, you count the number of the pairs which are out of order. Or, in other words, for each label in the list you count the number of labels which came before but was larger than the particular label you are considering. If the sum of all of these numbers are even, then the permutation is even and similarly for the odd case. For example in the permutation 143265 of six labels, the sum of the numbers mentioned above is $0 + 0 + 1 + 2 + 0 + 1 = 4$, as a result the permutation is even.

Denoting a permutation by P, its labels by $P1, P2, \ldots, PN$ and its sign by $(-)^P$ we can express the Slater determinant as:

$$\Psi(1, 2, \ldots, N) = \sum_P (-)^P \varphi_{P1}(1) \varphi_{P2}(2) \cdots \varphi_{PN}(N) \qquad .$$

Note that each term in this summation is normalized and any two different terms are orthogonal. This is because the inner product of the term with permutation P and the one with permutation Q is

$$(-)^P (-)^Q \langle \varphi_{P1}(1) \cdots \varphi_{PN}(N) \mid \varphi_{Q1}(1) \cdots \varphi_{QN}(N) \rangle =$$
$$(-)^P (-)^Q \delta_{P1,Q1} \cdots \delta_{PN,QN} \qquad .$$

Since the Slater determinant is a sum of $N!$ orthonormal terms, the inner product of Ψ with itself is simly

$$\langle \Psi \mid \Psi \rangle = N! \qquad .$$

Hence, including the normalization, the Slater determinant of N orthonormal one-particle states can be written as

$$\Psi(1, 2, \ldots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \ldots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \ldots & \varphi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(1) & \varphi_N(2) & \ldots & \varphi_N(N) \end{vmatrix} \qquad (2)$$

This is the form that we will use when evaluating the expectation values.

1.3 Expectation values single-particle observables

We start with the expectation values of single-particle observables. Consider an arbitrary operator A which expresses a property of only one particle. For example, A might be a component of position (x), of momentum (p_y) or of spin (S_z). We will use the notation $A(i)$ to show that the operator depends on i^{th} particle's properties. So, if $A(1) = x_1$, then $A(2) = x_2$, etc. Since the wavefunction of the system Ψ is quite complicated, we need to find a simple expression for the expectation value of $A(i)$.

The first thing that we should note is that the expectation value of A for particle-1 should not be different from the expectation value of A for any other particle. i.e.,

$$\langle A(1) \rangle = \langle \Psi \mid A(1) \mid \Psi \rangle = \langle A(2) \rangle = \ldots = \langle A(N) \rangle \qquad .$$

This is not a result of the particular properties of the Slater determinants. It is due to the identicalness of the electrons. Same relations should hold for an arbitrary totally antisymmetric wavefunction as well. It just expresses the fact that there is no physical way of distinguishing particles in your system.

When you try to calculate the expectation value of $A(1)$, you will find the expression

$$\langle A(1) \rangle = \frac{1}{N!} \sum_{P,Q} (-)^P (-)^Q \langle \varphi_{P1}(1) \mid A(1) \mid \varphi_{Q1}(1) \rangle \delta_{P2,Q2} \cdots \delta_{PN,QN}$$

It is not difficult to see that in the summation the permutations P and Q need to be same if a non-zero result should be found. Nor it is difficult to sum over most of the terms. The final result for the expectation value is:

$$\langle \Psi \mid A(1) \mid \Psi \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle \varphi_i(1) \mid A(1) \mid \varphi_i(1) \rangle$$

In the terms within the summation we have expectation values of A in each of the N one-particle states. In here, there is no need to keep the label-1, which denotes space and spin coordinates of the first particle. As a result, we can rewrite the last expression as

$$\langle \Psi \mid A(1) \mid \Psi \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle \varphi_i \mid A \mid \varphi_i \rangle$$

In these kinds of expressions, care is needed to distinguish in which state the expectation value is taken. On the left, we have the expectation value in the state of the system (the physically relevant ones), and on the right we have the expectation values in the one-particle states used to prepare the Slater determinant (physically inaccessible ones).

The last expression can be utilized to calculate the expectation values of single-particle operators. But it has a clear physical meaning as well. It just expresses the fact that the particle-1 sees an equal probability of occupying each of the N states. As a result, property-A of the particle-1 will be the arithmetic average of the properties in each state.

Finally, one is rarely interested in a property of a single particle in an N-particle system. For example, consider the case where $A(1)$ denotes the electric field created by particle-1 at a certain point in space. Obviously, electric field at that certain point will not be created by the first particle only. So, for that physical quantity we should be interested in $A(1) + A(2) + \ldots + A(N)$ as the electric field created by all of the N electrons. This is a general property of systems composed of identical particles. Any physically relevant observables should remain the same under particle exchanges. Although you can form observables (operators) which does not have this property (like $A(1)$), and evaluate their expectation values, they cannot be measured by a physical apparatus. Now the expectation value of $A(1) + A(2) + \ldots + A(N)$ can be expressed as

$$\langle \Psi \mid \{A(1) + A(2) + \ldots + A(N)\} \mid \Psi \rangle =$$

$$\langle \varphi_1 \mid A \mid \varphi_1 \rangle + \langle \varphi_2 \mid A \mid \varphi_2 \rangle + \ldots + \langle \varphi_N \mid A \mid \varphi_N \rangle$$

So, the sum of a property over particles is equal to the sum of the same property over one-particle states.

1.4 Expectation values of two-particle observables

The simplification obtained above is not present for observables depending on two particles. Such a property might be the Coulomb interaction potential between electrons

$$A(1, 2) = \frac{e^2}{\mid \mathbf{r}_1 - \mathbf{r}_2 \mid} \qquad ,$$

(which is usually the case) or it might be operators like $A(1, 2) = x_1 p_{y2} + x_2 p_{y1}$. You should make sure that the operator is symmetric under the ex-

change of two coordinates since they have to be physically relevant. [In principle you may evaluate the expectation values of the operators like $A(1,2) = x_1 p_{y2}$, but such operators will never arise in actual problems. You need to extend the expression given below to deal with those kinds of operators.]

Now, the expectation value of $A(1,2)$ can be expressed as,

$$\langle \Psi \mid A(1,2) \mid \Psi \rangle = \frac{1}{N!} \sum_{P,Q} (-)^P (-)^Q \langle \varphi_{P1} \varphi_{P2} \mid A \mid \varphi_{Q1} \varphi_{Q2} \rangle \delta_{P3,Q3} \cdots \delta_{PN,QN}.$$

In this case, if a term in the summation is nonzero, either P and Q should be the same, or they should differ by an exchange of first and second labels. Because of this, the expectation value can be expressed as

$$\langle \Psi \mid A(1,2) \mid \Psi \rangle = \frac{2}{N(N-1)} \sum_{i<j} \langle \varphi_i \varphi_j \mid A \mid \varphi_i \varphi_j \rangle - \langle \varphi_j \varphi_i \mid A \mid \varphi_i \varphi_j \rangle. \quad (3)$$

Here we needed to use a short-hand notation for the two-particle integrals on the left hand side. This notation is quite widely used. When the one-particle states do not include the spin degree of freedom, the definition is

$$\langle \phi \psi \mid A \mid \chi \xi \rangle = \int \int \phi(\mathbf{r}_1)^* \psi(\mathbf{r}_2)^* A(1,2) \chi(\mathbf{r}_1) \xi(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \qquad .$$

We don't dare to write the right hand side when the spin is included, especially when $A(1,2)$ includes spin operators. But how the spin part is handled should be obvious. In $\langle \phi \psi \mid A \mid \chi \xi \rangle$, the first states on the bra and ket sides (ϕ and χ) have the same particle's coordinate. And similarly for the second states.

In the first term in the summation of Eq. (3), the states on the bra and the ket sides are the same and they are in the same order. Thus, this first term is the same thing as what we mean by "expectation value". However, in the second term, $\langle \varphi_j \varphi_i \mid A \mid \varphi_i \varphi_j \rangle$, the order of the states are different in the bra and ket sides. For this reason, these terms (and similar terms that will arise later) are called *exchange* terms. Exchange terms do not have a classical counterpart. To see why, consider the case where A is the Coulomb potential energy of two electrons. In this case, the first terms give (ignoring again the spin parts)

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

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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

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

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

$$h\varphi_i = \epsilon_i \varphi_i \qquad ,$$

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

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

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If V_{ee} term is ignored this state will have the energy eigenvalue $-2Z^2$ Rydbergs. Now, the addition of the V_{ee} term will definitely increase this value, since V_{ee} is a positive operator. So, at this point, we know that the ground state energy of the Helium atom is larger than $-2Z^2 = -8$ Rydbergs.

We can use the variational theory to come up with a good value of the ground state energy. The only thing that we know about the exact ground state wavefunction is that it is of the form

$$\Psi(1,2) = \phi(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)$$

where $\phi(\mathbf{r}_1, \mathbf{r}_2)$ is a symmetric function. It should also have the s-symmetry under rotations. We just need to come up with a good wavefunction having same properties.

In here we will use

$$\Psi(1,2) = \phi(r_1)\phi(r_2) \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)$$

where $\phi(r) = N \exp(-\beta r)$ as a trial wavefunction. We have chosen ϕ as a 1s-like wavefunction with a variable parameter β. At this point we need to calculate the expectation value of H, and choose the best possible value of β. You have to convince yourselves that, Ψ is antisymmetric, has total spin 0, and has the s-symmetry. Verify the following

$$N = \frac{\beta^{3/2}}{\sqrt{\pi}} \quad ,$$

$$\langle T(1) + T(2) \rangle = 2\langle \phi \mid T \mid \phi \rangle = 2\frac{\hbar^2 \beta^2}{2m} \quad ,$$

$$\langle V(1) + V(2) \rangle = 2\langle \phi \mid V \mid \phi \rangle = -2Ze^2\beta \quad .$$

Now the main problem is the calculation of $\langle V_{ee} \rangle$. Just note that spin parts are nicely eliminated and therefore there is no exchange term in here. The integral that we need to evaluate is

$$\langle V_{ee} \rangle = N^4 \int \int \frac{e^2}{\mid \mathbf{r}_1 - \mathbf{r}_2 \mid} e^{-2\beta(r_1 + r_2)} d^3\mathbf{r}_1 d^3\mathbf{r}_2.$$

As a first step, we divide the integral into two parts, one over regions $r_1 < r_2$ and the other over regions $r_1 > r_2$. Since, the integrals over both regions

should be the same, we just need to multiply the integral over the $r_1 < r_2$ region by 2.

In $r_1 < r_2$ region, we evaluate first the $\mathbf{r}_2$ integral, than the $\mathbf{r}_1$ integral. When evaluating the $\mathbf{r}_2$ integral we choose the spherical coordinates such that $\theta_2 = 0$ corresponds to the direction of the first particle. (In other words, z axis for the second particle is chosen as the direction of $\mathbf{r}_1$.) The advantage of this choice is that the distance between particles can be expressed simply as:

$$\mid \mathbf{r}_1 - \mathbf{r}_2 \mid = \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}.$$

Hence, we have

$$\langle V_{ee} \rangle = 2N^4 e^2 \int d^3\mathbf{r}_1 e^{-2\beta r_1} \int \frac{e^{-2\beta r_2}}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}} r_2^2 \sin\theta_2 dr_2 d\theta_2 d\varphi_2.$$

where r_2 is integrated from 0 to r_1. Now, φ_2 and θ_2 integrals can be evaluated quite easily,

$$\langle V_{ee} \rangle = 8\pi N^4 e^2 \int d^3\mathbf{r}_1 e^{-2\beta r_1} \int_0^{r_1} e^{-2\beta r_2} \frac{r_2^2}{r_1} dr_2.$$

Angular integrals of $\mathbf{r}_1$ brings another factor of 4π. As a result we have

$$\langle V_{ee} \rangle = 32\pi^2 N^4 e^2 \int_0^\infty dr_1 \int_0^{r_1} dr_2\ r_1 r_2^2 e^{-2\beta(r_1+r_2)}.$$

This last integral is easily evaluated if the orders of r_1 and r_2 integrations are interchanged. The final expression is

$$\langle V_{ee} \rangle = \frac{5}{8} e^2 \beta$$

Finally we have the expression for the expectation value of the Hamiltonian.

$$\langle H \rangle = 2 \left(\frac{\hbar^2 \beta^2}{2m} - (Z - \frac{5}{16})e^2\beta \right).$$

By denoting $Z - \frac{5}{16}$ as Z_{eff}, we have

$$\beta = \frac{Z_{\text{eff}}}{a_0}$$

as the best value of β and $\langle H \rangle = -2Z_{\text{eff}}^2$ Rydbergs as the minimum energy.

Now, the interpretation. We have chosen the trial wavefunction on purpose. On the one hand, we want to see how well an independent electron picture describes at least the ground state of the Helium atom. On the other hand, we want to see how the electron electron interaction alters the electron orbitals. We see that, when the interaction is not present, the 1s orbitals are

$$\phi(r) = \psi_{100}(r) = \frac{Z^{3/2}}{\sqrt{\pi}a_0^{3/2}}e^{-Zr/a_0} \quad ,$$

but when the interaction is present, the 1s orbital changes to

$$\phi(r) = \frac{Z_{\text{eff}}^{3/2}}{\sqrt{\pi}a_0^{3/2}}e^{-Z_{\text{eff}}r/a_0} \quad .$$

where $Z_{\text{eff}} = Z - 5/16$. That means, the interaction effectively decreases the nuclear charge by $5e/16$. This is the screening effect of the other electron. So, the interpretation is simple: When the electron is moving around the nucleus, it sees the effect of the other electron. The electrons will see a reduced nuclear charge, and the reduction will be a quantity between 0 and e. If one of the electrons were in higher levels, than probably this one would see a nuclear charge close to $(Z-1)e$, but the one in 1s orbital would see something close to Ze.

How good is this approximation? To be able to answer this question, we need to see how close we are to the exact energy. The exact calculations show that the exact ground state energy of the Helium atom is $E_{\text{exact}} = -78.975$ eV≈ -5.81 Rydbergs. Now, our approximation gives $\langle H \rangle \approx -5.69$ Rydbergs. These are fairly close. Obviously, the physical effects that you are looking for important in deciding whether your approximation is good or not. If, what you need is a mere qualitative picture of the eigenstates of the Helium atom, than even the Slater determinants prepared from Hydrogen-like states will be enough. If the physical processes you are interested in involves subtle many-body effects, than you have to go further than Slater determinants.

In the variation calculation above, we have chosen the electron orbital, $\phi(r)$ to be a 1s state (with arbitrary Z). It is of interest to see how we can improve on this. Obviously, $\phi(r)$ should be an s-state (it should depend only on r), but it may have a complicated variation with r. What is the best possible ϕ function? To answer this question, we should vary ϕ at all points. This whole procedure is known as Hartree-Fock theory.

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