Lecture 18

Many-electron atoms

Study Goal of This Lecture

- Pauli exclusion principle

- Slater determinant

- Electron configurations and the periodic table

18.1 Preface

Now we finally reach the point of writing down the full wavefunction of a many-electron system. Weather it's atomic or molecular, the key concepts are:

- Construct many-electron wavefunctions using products of single-electron wavefunctions(orbitals)

- Pauli exclusion principle $\rightarrow$ it is necessary to use Slater determinants

18.2 Pauli Exclusion Principle

We have discussed about the spatial part and the spin part of the wavefunctions. Let's pick Helium groundstate as the example.

$$\Psi(r_1, r_2) = 1s(1)2s(2). \tag{18.1}$$

$$\sigma(s) = \begin{cases} \alpha(1)\alpha(2), \\ \beta(1)\beta(2), \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)], \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]. \end{cases} \tag{18.2}$$

What is the full wavefunction? Is $\psi(r_1, r_2)\alpha(1)\alpha(2)$ a valid wavefunction ? The answer is no, but why? It turns out that since electrons are Fermions, the valid wavefunction of a many-electron system must satisfy a certain "spin-statistics".

Pauli Exclusion Principle:

The wavefunction for any system of electrons must be antisymmetric with respect to the interchange of any two electrons.

i.e.

$$\Psi(\cdots, r_i, \cdots, r_j, \cdots) = -\Psi(\cdots, r_j, \cdots, r_i, \cdots). \tag{18.3}$$

For helium atom, the spatial part is symmetrical, so the only valid total Ψ is

$$\Psi = 1s(1)2s(2)\frac{1}{\sqrt{2}}[\alpha(1)\alpha(2) - \alpha(2)\alpha(1)],$$

$$\Psi' = 1s(2)2s(1)\frac{1}{\sqrt{2}}[\alpha(2)\alpha(1) - \alpha(1)\alpha(2)], \tag{18.4}$$

$$= -\{1s(1)2s(2)\frac{1}{\sqrt{2}}[\alpha(1)\alpha(2) - \alpha(2)\alpha(1)]\} = -\Psi.$$

This is a singlet state!(And it must be.)

It is convenient to write this in a determinantal form $\Rightarrow$ Slater determinant.

Slater determinant: a convenient way to build-in the antisymmetric property. (Obeying exclusion principle)

Consider all antisymmetric combination using the mathematics of determinant

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}, \tag{18.5}$$

"spin-orbital by columns, electron by rows" $\Rightarrow$ It can be extended to N electron system

χ: spin orbital

$$\Psi(1,2,\cdots,N) = \frac{1}{\sqrt{N}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(1) & \cdots & \cdots & \\ \chi_1(3) & \chi_2(3) & \ddots & & \\ \vdots & \vdots & & \ddots & \\ \chi_1(N) & \chi_2(N) & & & \chi_N(N) \end{vmatrix}. \tag{18.6}$$

Since the interexchange of two rows in a determinant flips the sign, it automatically satisfy the Pauli exclusion principle. In addition, a deteminant is zero if two columns in the deteminant are the same → meaning two electrons cannot occupy the same spin-orbital. This is another form of Pauli exclusion principle: No two electrons can have the same set of quantum numbers (n, l, m_l, m_s). The Pauli exclusion principle is important for chemistry ⇒ (Periodic table,⋯)

More generally, particle can be seperated into two types:

- Fermions: with half-integer spin, antisymmetric ⟶ Obey Fermi-Dirac statistics.

- Boson: with integer spin, symmetric ⟶ Obey Bose-Einstein statistics.

Actually, the very familiar "electron configuration" diagram can be directly mapped onto a Slater deteminant.
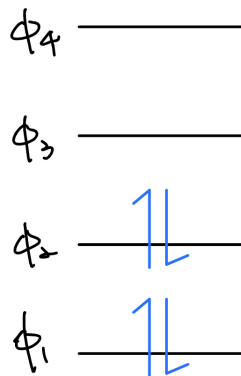
For example, given the state:

Figure 18.1: Superposition of several wave.

The occupied spin orbitals are

$$\phi_1(r)\alpha(s), \ \phi_1(r)\beta(s), \ \phi_2(r)\alpha(s), \ \phi_2(r)\beta(s). \tag{18.7}$$

From these we can construct a direct product state:

$$\Psi = \phi_1(1)\alpha(1) \cdot \phi_1(2)\beta(2) \cdot \phi_2(3)\alpha(3) \cdot \phi_2(4)\beta(4). \tag{18.8}$$

This wavefunction does not satisfy the Pauli exclusion principle. We need to use Slater deteminant. (But it is easy, just put occupied spin orbitals as columns and vary electron indices by rows)

Slater determinant:

$$\Rightarrow \frac{1}{\sqrt{4!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \cdots & \cdots \\ \phi_1(3)\alpha(3) & \vdots & \ddots & \\ \phi_1(4)\alpha(4) & \vdots & & \phi_2(4)\beta(4) \end{vmatrix} \tag{18.9}$$

This is the valid electron configuration. The construction of a Slater deteminant guarantees:

- Electrons are indistinguishable

- Total wavefunctions is antisymmetric (exchange rows)

- Two different electrons cannot occupy the same spin orbital

Note that a many-electron wavefunction needs not to be in a product form, nor does it requires to be representable as a single Slater deteminant. ⇒ The determinant wavefunction is an approximation.(good one for general groundstate.)

Now, let's we summarize the content in this lecture: A Slater determinant represents a many-electron state, note that in a Slater determinant wavefunction, the many-electron state is constructed by "products" of orbitals. So, in a single-determinant limit, the electrons are still "uncorrlated"(In the sense of independent product distributions.)

Electron ⟷ Slater determinant

If we use orbitals with variational parameters to construct a single Slater determinant and use the variational principle to yield the "optimized" wavefunction ⇒ Hartree-Fock Method!

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18.3 Slater Determinant for Lithium Atom

Now, we use Slater deteminant to consider the "electron configuration" of Li atom. Li atom has one more electron than the Helium atom. (Li:$1s^2 2s^1$) If the additional electron is in $1s$ orbital:

$$|\Psi\rangle = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)\alpha(3) \end{vmatrix} = 0, \qquad (18.10)$$

the wavefunction is zero $\Rightarrow$ the additional electron can't be filled in the $1s$ orbital. The correct one is:

$$|\Psi\rangle = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}, \qquad (18.11)$$

note that if the electron is filled in $2s(3)\beta(3)$, the energy will be the same, the ground state of the lithium atom is doubly degenerate $\Rightarrow$ doublet. Following the variational procedure that we discussed on previous lecture with effective charge for $1s$ and $2s$ orbitals respectively. With

$$\phi_{1s}(Z_1) = \frac{1}{\sqrt{\pi}} \left(\frac{Z_1}{a_0} \right)^{\frac{3}{2}} \cdot e^{-\frac{Z_1}{a_0} r}, \qquad (18.12)$$

and

$$\phi_{2s}(Z_2) = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z_2}{a_0} \right)^{\frac{3}{2}} \cdot \left(2 - \frac{Z_2 r}{a_0} \right) e^{-\frac{Z_2}{2a_0} r}, \qquad (18.13)$$

we minimize $\langle \Psi | \hat{H} | \Psi \rangle$ with respect to Z_1, Z_2 to find out:

$$Z_1 = 2.69,$$

$$Z_2 = 1.78,$$

and variational energy $E_{min} = -201.2 eV$, the experimental energy $= -203.48 eV$. Note that the more outside the orbital, the smaller the effective charge because of more screening. For the same shell:

$$\langle r \rangle_d > \langle r \rangle_p > \langle r \rangle_s,$$

therefore, energy changes for many electron system:

$$E_{nd} > E_{np} > E_{ns}.$$

This is not the same as the Hydrogen-like atom. (For single electron, there is no screening, therefore the energy for s, p, d, f orbitals are the same.)

Remark: Notice of notation

Up to now, we have introduced many kind of wavefunctions. The careful reader should notice that we utilizs different notations to represent different kind of wavefunctions. We will adapt this notation system for the following courses. The below table is the summary. Students should carefully distinguish those wavefunctions too!

Notation for different wavefunctions		
Term	**Meaning**	**Symbol**
Atomic spatial orbital	Single electron wavefunction for atom without spin states	ϕ
Atomic spin orbital	Single electron wavefunction for atom with spin state	χ
Atomic spatial wavefunction	Many electron wavefunction for atom without spin states	Φ
Atomic spin wavefunction	Many electron wavefunction for atom with spin states	X
Molecular wavefunction	Many electron wavefunction for molecule	Ψ
Molecular orbital	Single electron wavefunction for molecule	ψ