Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 26
Nov 8th, 2013

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Objectives

- To introduce the Slater determinant as a wave-function for multi-electron system.

- To show an explicit example of Slater determinants for the ground-state configuration of Helium and Lithium.

- To show how the Slater determinant is consistent with the Pauli exclusion principle.

- To introduce the shorthand notation for Slater determinants.

- To stress that the Slater determinant is an approximate wave-function.

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Slater determinants: An example for the Helium atom

We discussed in previous lectures that a wave-function that describes multi-electron systems must be antisymmetric.

A simple way of constructing an antisymmetric wave-function for a multi-electron system is by means of the **Slater determinant**.

For Helium, for instance, its ground-state electronic configuration is $1s^2$. Thus, the Slater determinant associated with this configuration is

$$\Phi_{\text{He, g.s}}(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_{1s}(\mathbf{r}_1)\alpha(1) & \phi_{1s}(\mathbf{r}_1)\beta(1) \\ \phi_{1s}(\mathbf{r}_2)\alpha(2) & \phi_{1s}(\mathbf{r}_2)\beta(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2!}}\left[\phi_{1s}(\mathbf{r}_1)\alpha(1)\phi_{1s}(\mathbf{r}_2)\beta(2) - \phi_{1s}(\mathbf{r}_1)\beta(1)\phi_{1s}(\mathbf{r}_2)\alpha(2)\right]$$

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The Slater determinant for Lithium

Similarly, an antisymmetric wave-function for the ground state of Lithium can be constructed. The electronic configuration in this case is $1s^2 2s^1$.

The Slater determinant for this configuration is

$$\Phi_{\text{Li, g.s}}(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2;\mathbf{r}_3,\sigma_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{1s}(\mathbf{r}_1)\alpha(1) & \phi_{1s}(\mathbf{r}_1)\beta(1) & \phi_{2s}(\mathbf{r}_1)\alpha(1) \\ \phi_{1s}(\mathbf{r}_2)\alpha(2) & \phi_{1s}(\mathbf{r}_2)\beta(2) & \phi_{2s}(\mathbf{r}_2)\alpha(2) \\ \phi_{1s}(\mathbf{r}_3)\alpha(3) & \phi_{1s}(\mathbf{r}_3)\beta(3) & \phi_{2s}(\mathbf{r}_3)\alpha(3) \end{vmatrix}$$

$$= \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{1s}(\mathbf{r}_1)\alpha(1) & \phi_{1s}(\mathbf{r}_2)\alpha(2) & \phi_{1s}(\mathbf{r}_3)\alpha(3) \\ \phi_{1s}(\mathbf{r}_1)\beta(1) & \phi_{1s}(\mathbf{r}_2)\beta(2) & \phi_{1s}(\mathbf{r}_3)\beta(3) \\ \phi_{2s}(\mathbf{r}_1)\alpha(1) & \phi_{2s}(\mathbf{r}_2)\alpha(2) & \phi_{2s}(\mathbf{r}_3)\alpha(3) \end{vmatrix}$$

where we have explicitly indicated that the determinant does not change if we transpose the matrix

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Pauli exclusion principle

If in the Slater determinant for Li: $1s^2 2s^1$ we allow the "third" electron to occupy the 1s orbital with spin "up", we obtain:

$$\Phi_{\text{Li,g.s}}\left(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2;\mathbf{r}_3,\sigma_3\right)=\frac{1}{\sqrt{3!}}\begin{vmatrix} \phi_{1s}\left(\mathbf{r}_1\right)\alpha\left(1\right) & \phi_{1s}\left(\mathbf{r}_1\right)\beta\left(1\right) & \phi_{1s}\left(\mathbf{r}_1\right)\alpha\left(1\right) \\ \phi_{1s}\left(\mathbf{r}_2\right)\alpha\left(2\right) & \phi_{1s}\left(\mathbf{r}_2\right)\beta\left(2\right) & \phi_{1s}\left(\mathbf{r}_2\right)\alpha\left(2\right) \\ \phi_{1s}\left(\mathbf{r}_3\right)\alpha\left(3\right) & \phi_{1s}\left(\mathbf{r}_3\right)\beta\left(3\right) & \phi_{1s}\left(\mathbf{r}_3\right)\alpha\left(3\right) \end{vmatrix}=0$$

The determinant reduces to zero because the determinant of a matrix with two identical rows or columns is zero.

This is consistent with the **Pauli exclusion principle**:

No two electrons can have the same values for all four quantum numbers, $\left(n,l,m_l,m_s\right)$

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Pauli exclusion principle

The antisymmetry requirement is provided automatically by a Slater determinant: If two rows (or columns) of a determinant are interchanged, the sign of the determinant changes to the opposite.

Another mathematical property of determinants is that if two rows (or columns) are identical, the determinant vanishes. That is, if any two electrons occupy the same spin-orbital $\varphi_{nml}\alpha$ or $\varphi_{nml}\beta$, then the wave function vanishes, meaning that the probability of this event is zero.

An equivalent way of stating this result in a way that is directly relevant to chemistry is to say that no two electrons in an atom may have the same quantum numbers n, l, m_l, and m_s. This statement if known as the **Pauli exclusion principle**.

The Pauli exclusion principle and the antisymmetry requirement are in fact two equivalent ways of expressing the same physical law of nature. This is why the names "Pauli exclusion principle" and "antisymmetry requirement" may be used interchangeably.

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Fermions and bosons

It turns out that particles with half-integer spin ($s = 1/2, 3/2, ...$) all require antisymmetric wave functions. Indistinguishable particles that are described with antisymmetric wave functions are referred to as **fermions** because they must obey a kind of statistics called Fermi–Dirac statistics.

Particles with integer spin ($s = 0, 1, 2, ...$) all require symmetric wave functions. Indistinguishable particles that are described with symmetric wave functions are referred to as **bosons** because they follow a different statistical law called Bose–Einstein statistics.

The periodic table has the form it does because electrons are fermions. If electrons were distinguishable or if a system of electrons could be symmetric with respect to interchange of any two electrons, then there would be an entirely different set of chemical elements.

The periodic table as we know it can be rationalized only if we accept that electrons are indistinguishable and that many-electron wave functions are antisymmetric.

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The N-electron Slater determinant

In general, the Slater determinant for an N-electron system is therefore given by

$$\Phi\left(\boldsymbol{r}_1, \sigma(1); \ldots; \boldsymbol{r}_N, \sigma(N)\right) \equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\boldsymbol{r}_1)\sigma_1(1) & \psi_2(\boldsymbol{r}_1)\sigma_2(1) & \cdots & \psi_N(\boldsymbol{r}_1)\sigma_N(1) \\ \psi_1(\boldsymbol{r}_2)\sigma_1(2) & \psi_2(\boldsymbol{r}_2)\sigma_2(2) & \cdots & \psi_N(\boldsymbol{r}_2)\sigma_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\boldsymbol{r}_N)\sigma_1(N) & \psi_2(\boldsymbol{r}_N)\sigma_2(N) & \cdots & \psi_N(\boldsymbol{r}_N)\sigma_N(N) \end{vmatrix}$$

In order to avoid lengthy writing a **shorthand notation for the Slater determinant** can be introduced

$$\Phi \equiv \begin{vmatrix} \psi_1\sigma_1 & \psi_2\sigma_2 & \cdots & \psi_N\sigma_N \end{vmatrix}.$$

For instance, the Slater determinant for the Lithium atom can be written as

$$\Phi_{\text{Li, g.s}} = \begin{vmatrix} \phi_{1s}\alpha & \phi_{1s}\beta & \phi_{2s}\alpha \end{vmatrix}$$

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The Slater determinant is an approximate wave-function of an N-electron system

In an N-electron system there are two main effects that must be considered: **exchange** and **correlation** effects.

Exchange effects are the ones associated with the spin of electrons in the system. The way electrons spin interact through spin is described by the **Pauli exclusion principle** (see slides 5 and 6).

Correlation effects are the ones associated with the **Coulomb repulsion** that electrons experience. In other word, they avoid to each other. Such repulsion is described by the **Coulomb potential**, which is considered in the Hamiltonian of the system (see slide 3 of lecture 25).

The Slater determinant for an N-electron system describes correctly exchange effects. Correlation effects, however, are much more difficult to model and are not captured at all by the Slated determinant. **9**

Appendix: Determinants of 3x3 matrices

The determinant of a 3 X 3 matrix can be computed as the sum of three 2 X 2 determinants

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a\begin{vmatrix} e & f \\ h & i \end{vmatrix} - b\begin{vmatrix} d & f \\ g & i \end{vmatrix} + c\begin{vmatrix} d & e \\ g & h \end{vmatrix}$$

$$= a(ei - fh) - b(di - fg) + c(dh - eg)$$
$$= aei + bfg + cdh - ceg - bdi - afh.$$

This procedure can be extended for higher order determinants. For instance, a 4 X 4 determinant can be expanded as the sum of four 3 X 3 determinants. In general:

An N X N determinant can be expanded as the sum of N (N-1) X (N-1) determinants.

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