CHAPTER 7
MULTIELECTRON ATOMS
OUTLINE

Homework Questions Attached

PART A: The Variational Principle and the Helium Atom

SECT   **TOPIC**

1.   The Variational Method

2.   Applications of the Variational Method

3.   The Helium Atom

4.   Perturbation Theory Treatment of Helium

5.   Variational Method Treatment of Helium

6.   Better Variational Wavefunctions

PART B: Electron Spin and the Pauli Principle

SECT   **TOPIC**

1.   The Energy of Ground State Helium

2.   Electron Spin and the Pauli Principle

3.   Inclusion of Spin in Helium Atom Wavefunctions

4.   Spin Angular Momentum of Ground State Helium

5.   The Wavefunctions of Excited State Helium

6.   Excited State Helium Energies: $He(1s^1 2s^1)$

PART C: Many Electron Atoms

SECT **TOPIC**

1. The Hamiltonian for Multielectron Atoms

2. Koopman's Theorem

3. Extension to Multielectron Atoms

4. Antisymmetrized Wavefunctions: Slater Determinants

5. The Hartree-Fock Method

6. Hartree-Fock Orbital Energies for Argon

7. Electron Correlation

Chapter 7 Homework

PART A: The Variational Principle and the Helium Atom

1. An approximate wavefunction for the ground state of the PIB is:
    $$\psi_{app} = Ax^2(a-x) \quad 0 \le x \le a$$

    Normalize this wavefunction and compute the expectation value for the energy, <E>. Compare your answer with the exact ground state energy ($0.125h^2/ma^2$).

2. Consider the 3 electrons in a lithium atom, which has the electron configuration: $1s^2 2s^1$.

    (a) Write the Hamiltonian for the electrons in a Lithium atom in (i) MKS (SI) units and (ii) in atomic units.

    (b) Use the "Independent Particle Model" (i.e. ignore interelectronic repulsions) to calculate the electronic energy of Lithium in atomic units. **Note:** You can use the hydrogenlike atom equation to calculate the energy:
    $$E = -\frac{Z^2}{2n^2}$$

    (c) The actual Lithium electronic energy (-7.48 a.u.) is **higher** than the approximate energy you calculated in part (b). Is this a violation of the Variational Principle? Why or why not?

3. One variational wavefunction for helium that was discussed in the chapter is:
    $$\phi = A\left[e^{-Z'(r_1+r_2)}(1+b\cdot r_{12})\right]$$

    Both Z' and b are variational parameters.

    (a) Do you expect the function above to give you a higher or lower calculated energy than the function:
    $$\phi = Ae^{-Z'(r_1+r_2)}$$
    Explain your answer.

    (b) What is the purpose of the term $(1 + br_{12})$ in the first wavefunction above?

4.   One may illustrate the Variational Principle by using a Variational trial function of the
      form below as an approximate solution to the ground state of the hydrogen atom.:

$$\psi = Ae^{-\alpha r^2}$$

where α is a vrariational parameter. It can be shown that the calculated energy
in atomic units is given by:

$$E = \frac{3\alpha}{2} - \frac{4\alpha^{1/2}}{\sqrt{2\pi}}$$

Determine the value of α that minimizes the energy and the computed energy
for this value of α. Compare your result with the exact hydrogen atom ground
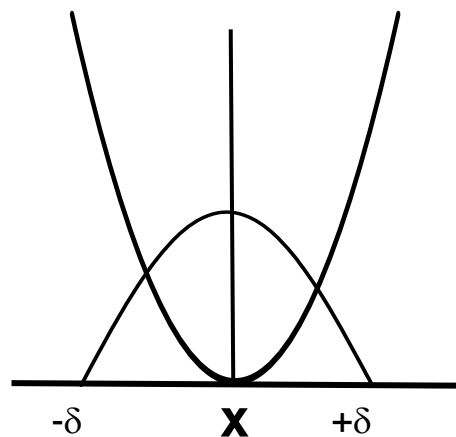state energy of -0.50 hartrees (a.u.).

5.   An approximate wavefunction for the ground state
      of the Harmonic Oscillator is:

$$\psi = A(\delta^2 - x^2) \qquad -\delta \le x \le +\delta$$

It can be shown that the expectation value for
the energy using this wavefunction is:

$$E = \frac{5\hbar^2}{4\mu\delta^2} + \frac{k\delta^2}{14} = \frac{5\hbar^2}{4\mu\Delta} + \frac{k\Delta}{14}$$

We have set $\delta^2 \equiv \Delta$ to avoid confusion in the calculations.

-δ   X   +δ

(a) Determine the value of δ^2 (i.e. Δ) which gives the lowest
     value of the energy.

(b) Use your result for part (a) to calculate the minimum energy, in units
     of $\hbar\omega$ (**Note:** Your result should be $\ge 0.5\ \hbar\omega$)

     Note: It will probably be useful to use: $\omega = \sqrt{\dfrac{k}{\mu}} \rightarrow k = \mu\omega^2$

PART B: Electron Spin and the Pauli Principle

6.   Indicate whether each of the functions is (i) symmetric, (ii) antisymmetric, or (iii) neither,
      with respect to electron exchange. **Note:** f and g are spatial functions.

(a) $f(1)f(2)\alpha_1\alpha_2$

(b) $f(1)g(2)\alpha_1\alpha_2$

(c) $f(1)f(2)[\alpha_1\beta_2 - \beta_1\alpha_2]$

(d) $[f(1)g(2) + g(1)f(2)]\beta_1\beta_2$

(e) $[f(1)g(2) - g(1)f(2)][\alpha_1\beta_2 + \beta_1\alpha_2]$

7.   Which of the following are valid wavefunctions for He? (Ignore Normalization)

(a) $1s(1)2s(2)(\alpha_1\beta_2 - \beta_1\alpha_2)$

(b) $[1s(1)2s(1) - 2s(1)1s(1)]\alpha_1\beta_2$

(c) $[1s(1)2s(2) - 2s(1)1s(2)](\alpha_1\beta_2 - \beta_1\alpha_2)$

(d) $1s(1)2s(2)\alpha_1\beta_2 - 2s(1)1s(2)\beta_1\alpha_2 + 1s(1)2s(2)\beta_1\alpha_2 - 2s(1)1s(2)\,\alpha_1\beta_2$

8.   Consider the wavefunction, $\psi = N(\alpha + c\beta)$, where N and c are constants

(a) Normalize the wavefunction, ψ (The result will contain the constant, c)

(b) Find $<s_z>$ for this wavefunction.

9.   Write down the complete expression for the Coulomb Integral $[J_{1s2p}]$ and Exchange Integral $[K_{1s2p}]$ for the repulsive and exchange interactions between electrons in 1s and 2p orbitals, respectively. Use atomic units and give your answer in (i) standard double integral notation and (ii) "Bra-Ket" notation..

10.   Consider the Helium excited state configuration $1s^1 2p^1$.

$$\psi_{Sing} = \left[\frac{1}{\sqrt{2}}\left(\phi_{1s}(\vec{r}_1)\phi_{2p}(\vec{r}_2) + \phi_{2p}(\vec{r}_1)\phi_{1s}(\vec{r}_2)\right)\right]\cdot\left[\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\right] = \psi_{spatial}\cdot\psi_{spin}$$

or

$$\psi_{Sing} = \left[\frac{1}{\sqrt{2}}\left(1s(1)2p(2) + 2p(1)1s(2)\right)\right]\cdot\left[\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\right] = \psi_{spatial}\cdot\psi_{spin}$$

(a)   Calculate the result of $\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$ operating on the spin portion of the wavefunction.

(b)   Assume that the spatial atomic orbitals, $\phi_{1s} \equiv 1s \; and \; \phi_{2p} \equiv 2p$, are orthonormal. Show that the spatial and spin wavefunctions are normalized

$$\psi_{Spatial} = \frac{1}{\sqrt{2}}\left(1s(1)2p(2) + 2p(1)1s(2)\right) \qquad \psi_{Spin} = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$$

i.e. show that: $\left\langle\psi_{Spatial}\middle|\psi_{Spatial}\right\rangle = 1$ and $\left\langle\psi_{Spin}\middle|\psi_{Spin}\right\rangle = 1$

(c)   The Helium atom Hamiltonian is:

$$H = \left[-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} \right] + \left[-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} \right] + \frac{1}{r_{12}} = H_1 + H_2 + \frac{1}{r_{12}}$$

H_1 and H_2 are the one electron He^+ ion Hamiltonians operating on the coordinates of electron 1 and 2, respectively. One can ignore the spin wavefunction when evaluating the expectation value for the energy because the Hamiltonian does not operate on the spin functions.

The expectation value for the energy is therefore:

$$\langle E \rangle = \frac{\langle \psi_{Spatial} | H | \psi_{Spatial} \rangle}{\langle \psi_{Spatial} | \psi_{Spatial} \rangle} = \langle \psi_{Spatial} | H | \psi_{Spatial} \rangle$$

Show that: $\langle E \rangle_{Sing} = \varepsilon_{1s} + \varepsilon_{2p} + J_{1s2p} + K_{1s2p}$

ε_{1s} and ε_{2p} are the energies of a He^+ ion in a 1s and 2p orbital, respectively. J_{1s2p} and K_{1s2p} are the Coulomb and Exchange Integrals, given in the last problem.

PART C: Many Electron Atoms

11.   Qualitative Questions (see PowerPoint slides and class notes for answers)

(a) What is the basic assumption behind the Hartree-Fock method?
(b) Why is it necessary to solve the Hartree-Fock equations iteratively?
(c) What is Koopman's Theorem and what approximations have been made?

12.   Evaluate the following 3x3 determinants:

(a) $\begin{vmatrix} 9 & 7 & 2 \\ 5 & 8 & 3 \\ 1 & 6 & 4 \end{vmatrix}$ (b) $\begin{vmatrix} 6 & -3 & 4 \\ 2 & 4 & -3 \\ 1 & 6 & 4 \end{vmatrix}$

13.   (a) Write the Hamiltonian for a Beryllium atom, in both SI and atomic units.

(b) Write the normalized Slater Determinant for the ground state of Beryllium, which has the configuration: $1s^2 2s^2$

14. The experimental Ionization Energies of the 3 electrons in Lithium are: $IE_1=5.39$ eV, $IE_2=75.66$ eV, and $IE_3=122.43$ eV. The computed Hartree-Fock (HF) energy of Lithium is $E_{HF}(Li) = -7.432$ au (hartrees). The computed Hartree-Fock energies of Li^+ and Li^- are: $E_{HF}(Li^+)= -7.236$ au and $E_{HF}(Li^-)= -7.427$ au.

   a) Calculate the Correlation Energy of Lithium in (i) au (hartrees) and (i) kJ/mol.

   b) Calculate the Hartree-Fock values of the First Ionization Energy and the Electron Affinity of Lithium (in eV).

   Note: 1 au $= 27.21$ eV $= 2625$ kJ/mol

15. The energy of the highest Hartree-Fock occupied orbital in oxygen is $\varepsilon= -0.616$ au. Estimate the First Ionization Energy of oxygen, in kJ/mol. Why does it differ from the experimenal value of 1314 kJ/mol.

16. The Hamiltonian for a Lithium atom is:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2}\nabla_3^2 - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

$$= \left[-\frac{1}{2}\nabla_1^2 - \frac{3}{r_1}\right] + \left[-\frac{1}{2}\nabla_2^2 - \frac{3}{r_2}\right] + \left[-\frac{1}{2}\nabla_3^2 - \frac{3}{r_3}\right] + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

$$= H_1 + H_2 + H_3 + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

Consider the following simple product wavefunction (non-Antisymmetrized) for a ground-state Lithium atom ($1s^2 2s^1$):

$$\psi(1,2,3) = 1s(1)\alpha_1 1s(2)\beta_2 2s(3)\alpha_1$$
$$= [1s(1)1s(2)2s(3)][\alpha_1\beta_2\alpha_3]$$
$$= \psi_{Spat} \cdot \psi_{Spin}$$

(a) Why does the expectation value for the energy not dependent upon ψ_{Spin}?

(b) Calculate the expectation value of the energy, $\left\langle \psi_{Spat} \left| H \right| \psi_{Spat} \right\rangle$, in terms of:

   ε_{1s}: Energy of an electron in a Li^{2+} 1s orbital

   ε_{2s}: Energy of an electron in a Li^{2+} 2s orbital

   $$J_{1s1s} = \left\langle 1s(1)1s(2) \left| \frac{1}{r_{12}} \right| 1s(1)1s(2) \right\rangle$$

   $$J_{1s2s} = \left\langle 1s(1)2s(2) \left| \frac{1}{r_{12}} \right| 1s(1)2s(2) \right\rangle$$

(c) Why does the energy not depend upon the Exchange Integral, K_{1s2s}?

SOME "CONCEPT QUESTION" TOPICS

Refer to the PowerPoint presentation for explanations on these topics.

PART A: The Variational Principle and the Helium Atom

- The Independent Particle Model

- The Variational Principle

- Perturbation Theory Treatment of Helium

- Variational Treament of Helium

PART B: Electron Spin and the Pauli Principle

- The Permutation Operator

- The Pauli Antisymmetry Principle (and relation to Exclusion Principle)

- Spin Eigenfunctions (α and β)

- Symmetric and Antisymmetric Spin Wavefunctions and Spatial Wavefunctions

- The Spin Quantum Numbers (S and M_S)

- Spin and Spatial Wavefunctions of Excited State Helium

- Relative Energies of Singlet and Triplet Excited State Helium (basis for difference).

- Coulomb and Exchange Integrals

PART C: Many Electron Atoms

- The Hamiltonian for Multielectron Atoms

- The Hartree Method: Qualitative Concepts and Interpretation of Equations

- Reason for difference between total Hartree energy and sum of orbital energies

- Koopman's Theorem

- Definitions of Ionization Energy and Electron Affinity

- Antisymmetric Wavefunctions: Slater Determinants (+ shorthand notation)

- The Hartree-Fock Method: Qualitative Concepts and Interpretation of Equations (difference from Hartree Method)

- Coulomb and Exchange Integrals

- Electron Correlation

DATA

$h = 6.63 \times 10^{-34}$ J·s

$\hbar = h/2\pi = 1.05 \times 10^{-34}$ J·s

$c = 3.00 \times 10^{8}$ m/s $= 3.00 \times 10^{10}$ cm/s

$N_A = 6.02 \times 10^{23}$ mol^{-1}

$k = 1.38 \times 10^{-23}$ J/K

$R = 8.31$ J/mol-K

$R = 8.31$ Pa-m^3/mol-K

$m_e = 9.11 \times 10^{-31}$ kg (electron mass)

1 J $= 1$ kg·m^2/s^2

1 Å $= 10^{-10}$ m

$k \cdot N_A = R$

1 amu $= 1.66 \times 10^{-27}$ kg

1 atm. $= 1.013 \times 10^{5}$ Pa

1 eV $= 1.60 \times 10^{-19}$ J

1 au $= 1$ hartree (h) $= 2625$ kJ/mol

Chapter 7

Multielectron Atoms

Part A: The Variational Principle and the Helium Atom

Part B: Electron Spin and the Pauli Principle

Part C: Many Electron Atoms

**Part A: The Variational Principle
and the Helium Atom**

• **The Variational Method**

• Applications of the Variational Method

• The Helium Atom

• Perturbation Theory Treatment of Helium

• Variational Method Treatment of Helium

• Better Variational Wavefunctions

The Variational Method

In quantum mechanics, one often encounters systems for which the Schrödinger Equation cannot be solved exactly.

There are several methods by which the Equation can be solved approximately, to whatever degree of accuracy desired.

One of these methods is **Perturbation Theory**, which was introduced in Chapter 5.

A second method is the **Variational Method**, which is developed here, and will be applied to the Helium atom Schrödinger Equation.

The Variational Theorem

This theorem states that if one chooses an *approximate* wavefunction, ϕ, then the Expectation Value for the energy is greater than or equal to the exact ground state energy, E_0.

$$< E >= E_{trial} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} = \frac{\int \varphi * H \varphi d\tau}{\int \varphi * \varphi d\tau} \geq E_0$$

Note: I will outline the proof, but you are responsible only for the result and its applications.

Proof: $< E > - E_0 = \dfrac{\int \varphi * H \varphi d\tau}{\int \varphi * \varphi d\tau} - E_0 \dfrac{\int \varphi * \varphi d\tau}{\int \varphi * \varphi d\tau} \geq 0$

$$< E > - E_0 = \frac{\int \varphi * (H - E_0) \varphi d\tau}{\int \varphi * \varphi d\tau}$$

Assume that we know the exact solutions, ψ_n: $H\psi_n = E_n \psi_n$

In Chapter 2, it was discussed that the set of eigenfunctions, ψ_n, of the Hamiltonian form a **complete set**. of orthonormal functions.

That is, any arbitrary function with the same boundary conditions can be expanded as a linear combination (an infinite number of terms) of eigenfunctions.

$$\varphi = \sum_{n=0}^{\infty} c_n \psi_n = \sum_n c_n \psi_n$$

This can be substituted into the expression for <E> to get:

$$<E> -E_0 = \frac{\int \varphi^* (H - E_0) \varphi d\tau}{\int \varphi^* \varphi d\tau} = \frac{\int \left(\sum_m c_m \psi_m \right)^* (H - E_0) \left(\sum_n c_n \psi_n \right) d\tau}{\int \left(\sum_m c_m \psi_m \right)^* \sum_n c_n \psi_n d\tau}$$

$$<E> -E_0 = \frac{\int \left(\sum_m c_m \psi_m \right)^* \left(\sum_n c_n (H - E_0) \psi_n \right) d\tau}{\int \left(\sum_m c_m \psi_m \right)^* \sum_n c_n \psi_n d\tau}$$

$$<E> -E_0 = \frac{\int \left(\sum_m c_m \psi_m \right)^* \left(\sum_n c_n (E_n - E_0) \psi_n \right) d\tau}{\int \left(\sum_m c_m \psi_m \right)^* \sum_n c_n \psi_n \varphi^* \varphi d\tau} = \frac{\sum_m \sum_n c_m^* c_n (E_n - E_0) \int \psi_m^* \psi_n d\tau}{\sum_m \sum_n c_m^* c_n \int \psi_m^* \psi_n d\tau}$$

$$<E> -E_0 = \frac{\sum_m \sum_n c_m^* c_n (E_n - E_0) \delta_{mn}}{\sum_m \sum_n c_m^* c_n \delta_{mn}} \quad \text{because} \quad \int \psi_m^* \psi_n d\tau = \delta_{mn}$$

ψ orthonormality

$$<E> -E_0 = \frac{\sum_n c_n^* c_n (E_n - E_0)}{\sum_n c_n^* c_n} \geq 0 \quad \text{because} \quad \begin{array}{c} c_n^* c_n \geq 0 \\ E_n - E_0 \geq 0 \end{array}$$

Therefore: $\boxed{<E> = E_{trial} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} \geq E_0}$

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Part A: The Variational Principle and the Helium Atom

- The Variational Method

- **Applications of the Variational Method**

- The Helium Atom

- Perturbation Theory Treatment of Helium

- Variational Method Treatment of Helium

- Better Variational Wavefunctions

Applications of the Variational Method

The Particle in a Box

In Chapter 3, we learned that, for a PIB:

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

$$E_n = \frac{n^2 h^2}{8ma^2}$$

$$\xrightarrow[\text{State}]{\text{Ground}}$$

$$\psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

$$E_1 = \frac{h^2}{8ma^2} = 0.125 \frac{h^2}{ma^2}$$

In a Chapter 2 HW problem (#S5), you were asked to show that for the approximate PIB wavefunction $\psi_{app} = Ax(a-x)$

The expectation value for <p²> is $\left\langle p^2 \right\rangle = \frac{10\hbar^2}{a^2}$

Let's calculate <E>: $\left\langle E \right\rangle = \left\langle \frac{p^2}{2m} \right\rangle = \frac{\left\langle p^2 \right\rangle}{2m} = \frac{10\hbar^2}{2ma^2} = \frac{5h^2}{4\pi^2 ma^2} = 0.12665 \frac{h^2}{ma^2}$
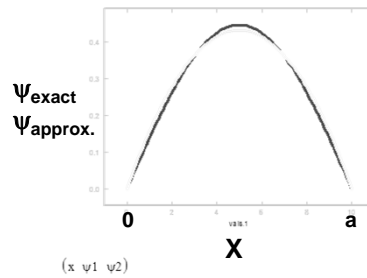
Exact GS Energy: $E_1 = 0.125 \dfrac{h^2}{ma^2}$ using $\psi_1 = \sqrt{\dfrac{2}{a}} \sin\left(\dfrac{\pi x}{a}\right)$

Approx. GS Energy: $E_{app} = 0.12665 \dfrac{h^2}{ma^2}$ using $\psi_{app} = Ax(a-x)$

The approximate wavefunction gives a ground state energy that is only 1.3% too high.

This is because the approximate wavefunction is a good one.

Ψ_{exact}
$\Psi_{\text{approx.}}$

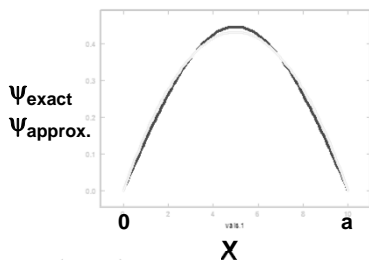0   X   a

$(x \ \psi 1 \ \psi 2)$

PIB: A Second Trial Wavefunction

If one considers a second trial wavefunction: $\psi_{app} = Ax^2(a-x)^2$
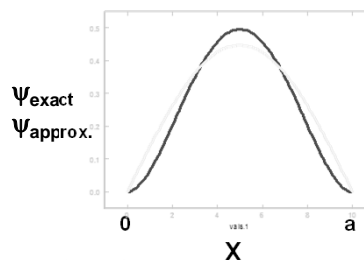
It can be shown (with a considerable amount of algebra) that:

$$E_{app} = \frac{6\hbar^2}{ma^2} = \frac{6h^2}{4\pi^2}\frac{1}{ma^2} = 0.152\frac{h^2}{ma^2} \quad 21.6\% \text{ Error}$$

The much larger error using this second trial wavefunction is not surprising if one compares plots of the two approximate functions.

Ψ_{exact}
$\Psi_{\text{approx.}}$

0   X   a

$(x \ \psi 1 \ \psi 2)$

$\psi_{app} = Ax(a-x)$ $E_{app} = 0.12665\dfrac{h^2}{ma^2}$

Ψ_{exact}
$\Psi_{\text{approx.}}$

0   X   a

$(x \ \psi 3 \ \psi 1)$

$\psi_{app} = Ax^2(a-x)^2$ $E_{app} = 0.152\dfrac{h^2}{ma^2}$

PIB: A Linear Combination of Combined Trial Wavefunctions

Let's try a trial wavefunction consisting of a linear combination
of the two approximate functions which have been used:

$$\psi_{app} = Ax(a-x) + Bx^2(a-x)^2$$

$$\text{or} \quad \psi_{app} = A\left[x(a-x) + Rx^2(a-x)^2\right] \quad \text{where} \quad R = \frac{B}{A}$$

Because the Variational Theorem states that the approximate
energy cannot be lower than the exact Ground State energy, one can
vary the ratio of the two functions, R, to find the value that minimizes
the approximate energy.

This can be done using a method (solving a Secular Determinant) that
we will learn later in the course. The result is:[a]

$$R = \frac{B}{A} = \frac{1.133}{a^2} \quad \text{and} \quad E_{app} = 0.1250018\frac{h^2}{ma^2} \quad \begin{array}{l}0.0015\% \text{ Error} \\ \text{Not bad!!}\end{array}$$

a) Quantum Chemistry, 5th Ed., by I. N. Levine, pg. 226

Ψ_{exact}
$\Psi_{approx.}$

0   X   a

$(x \; \psi1 \; \psi4)$
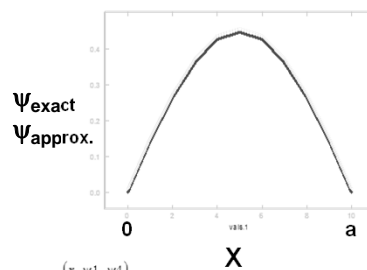
$$\psi_{app} = A\left[x(a-x) + Rx^2(a-x)^2\right]$$

$$E_{app} = 0.1250018\frac{h^2}{ma^2}$$

The agreement of $\psi_{approx.}$ with ψ_{exact} is actually even better than it looks.

The two plots were perfectly superimposed and I had to add on a small

constant to ψ_{exact} so that you could see the two curves.

An Approximate Harmonic Oscillator Wavefunction

Exact HO Ground State: $H = -\dfrac{\hbar^2}{2\mu}\dfrac{d^2}{dx^2} + \dfrac{1}{2}kx^2$ $\psi_0 = Ae^{-\alpha x^2/2}$

$$E_0 = \dfrac{1}{2}\hbar\omega = 0.5\hbar\omega$$

Let's try an approximate wavefunction: $\psi_{app} = A\cos(\lambda x)$ $-\dfrac{\pi}{2\lambda} \le x \le \dfrac{\pi}{2\lambda}$

Ψ_{exact}
$\Psi_{approx.}$

0
X

$(x \; \psi1 \; V \; \psi2)$
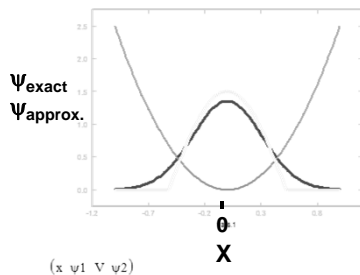
λ is a variational parameter, which can be adjusted to give the lowest, i.e. the best energy.

One can use ψ_{app} to calculate an estimate to the Ground State energy by:

$$E_{app} = \langle E \rangle = \dfrac{\langle \psi_{app}|H|\psi_{app}\rangle}{\langle \psi_{app}|\psi_{app}\rangle} = \dfrac{\langle A\cos(\lambda x)| -\dfrac{\hbar^2}{2\mu}\dfrac{d^2}{dx^2} + \dfrac{1}{2}kx^2 |A\cos(\lambda x)\rangle}{\langle A\cos(\lambda x)|A\cos(\lambda x)\rangle}$$

It can be shown that, when this expression is evaluated, one gets:

$$E_{app} = \dfrac{\hbar^2\lambda^2}{2\mu} + \left(\dfrac{\pi^2}{24} - \dfrac{1}{4}\right)\dfrac{k}{\lambda^2} = \dfrac{\hbar^2\Delta}{2\mu} + C\dfrac{k}{\Delta}$$ where $\Delta = \lambda^2$

$C = \dfrac{\pi^2}{24} - \dfrac{1}{4} = 0.1612$

Note: $\sqrt{2C} = 0.568$ (will be needed later in the calculation).

Because E_{app} is a function of λ^2 (rather than λ), it is more convenient to consider the variational parameter to be $\Delta = \lambda^2$.

$$E_{app} = \frac{\hbar^2 \Delta}{2\mu} + C\frac{k}{\Delta} \qquad \text{where} \qquad \Delta = \lambda^2$$

$$C = \frac{\pi^2}{24} - \frac{1}{4} = 0.1612$$

Note: $\sqrt{2C} = 0.568$ (will be needed later in the calculation).

The approximate GS energy is a function of the variational parameter, Δ

One "could" find the best value of Δ, which minimizes E_{app}, by trial and error.

But there must be a better way!!!

E_app
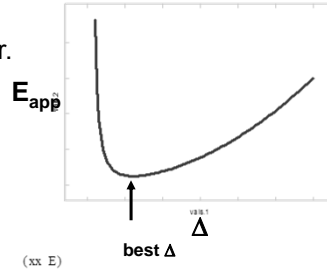

best Δ

Δ

(xx E)

$$E_{app} = \frac{\hbar^2 \Delta}{2\mu} + C\frac{k}{\Delta} \qquad \text{where} \qquad \Delta = \lambda^2 \quad C = \frac{\pi^2}{24} - \frac{1}{4} = 0.1612 \quad \sqrt{2C} = 0.568$$
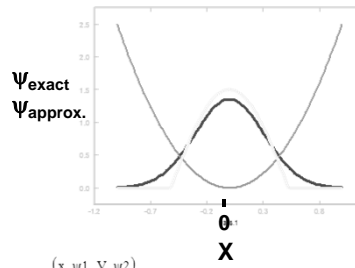
Sure!! At the minimum in E_{app} vs. Δ, one has: $\dfrac{dE_{app}}{d\Delta} = 0$

$$\frac{d\left[\frac{\hbar^2 \Delta}{2\mu} + C\frac{k}{\Delta}\right]}{d\Delta} = 0$$

On Board

$$\Delta_{best} = \sqrt{2C}\frac{\sqrt{k\mu}}{\hbar} = 0.568\frac{\sqrt{k\mu}}{\hbar}$$

On Board

$$\Delta_{best} = 0.284\hbar\omega + 0.284\hbar\omega = 0.568\hbar\omega$$

Ψ_{exact}
$\Psi_{approx.}$

X

(x ψ1 V ψ2)

13.6% error (compared to E_0 = 0.5 ħω)

It wasn't that great a wavefunction in the first place.

Note: We will use: $\dfrac{\sqrt{k\mu}}{\mu} = \sqrt{\dfrac{k}{\mu}} = \omega \quad and \quad \dfrac{k}{\sqrt{k\mu}} = \sqrt{\dfrac{k}{\mu}} = \omega$

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The Helium Atom Schrödinger Equation

The Hamiltonian

$$H = \frac{\hat{p}_1^2(\vec{r}_1)}{2m} + \frac{\hat{p}_2^2(\vec{r}_2)}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

KE(1) **KE(2)** **PE(1)** **PE(2)** **PE(12)**
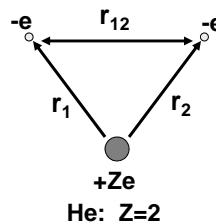
-e ⟷ r_{12} -e

r_1 r_2

+Ze

He: Z=2

$$H = -\frac{\hbar^2}{2m}\nabla_1^2(\vec{r}_1) - \frac{\hbar^2}{2m}\nabla_2^2(\vec{r}_2) - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

Atomic Units: $\hbar = m = e = 4\pi\varepsilon_0 = 1$

$$\boxed{H = -\frac{1}{2}\nabla_1^2(\vec{r}_1) - \frac{1}{2}\nabla_2^2(\vec{r}_2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}}$$

$$\nabla_1^2(\vec{r}_1) = \frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r_1^2\sin^2\theta_1}\frac{\partial}{\partial\theta_1}\left(\sin\theta_1\frac{\partial}{\partial\theta_1}\right) + \frac{1}{r_1^2\sin^2\theta_1}\frac{\partial^2}{\partial\varphi_1^2}$$

$$\nabla_2^2(\vec{r}_2) = \frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right) + \frac{1}{r_2^2\sin^2\theta_2}\frac{\partial}{\partial\theta_2}\left(\sin\theta_2\frac{\partial}{\partial\theta_2}\right) + \frac{1}{r_2^2\sin^2\theta_2}\frac{\partial^2}{\partial\varphi_2^2}$$

The Schrödinger Equation

$$H = -\frac{1}{2}\nabla_1^2(\vec{r}_1) - \frac{1}{2}\nabla_2^2(\vec{r}_2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

$$\longrightarrow \quad H\Psi(\vec{r}_1,\vec{r}_2) = E\Psi(\vec{r}_1,\vec{r}_2)$$

Ψ depends upon the coordinates of both electrons

$$H = \left[-\frac{1}{2}\nabla_1^2(\vec{r}_1) - \frac{Z}{r_1}\right] + \left[-\frac{1}{2}\nabla_2^2(\vec{r}_2) - \frac{Z}{r_2}\right] + \frac{1}{r_{12}}$$

$$H = H_1(\vec{r}_1) + H_2(\vec{r}_2) + \frac{1}{r_{12}}$$

Can we separate variables?

$$\Psi(\vec{r}_1,\vec{r}_2) = \psi_1(\vec{r}_1)\cdot\psi_2(\vec{r}_2) \quad ??$$

Electron Repulsion

Nope!! The last term in the Hamiltonian messes us up.

The Experimental Electronic Energy of He

Energy

$He^{2+} + 2e^-$ —— **0**

IE_2 = **54.42 eV**
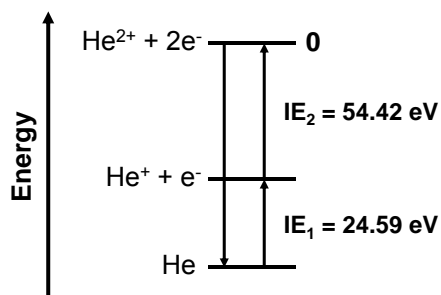
Reference State

By definition, the QM reference state (for which E=0) for atoms and molecules is when all nuclei and electrons are at infinite separation.

$He^+ + e^-$

IE_1 = **24.59 eV**

He

E_{He} = -[IE_1 + IE_2]

E_{He} = -[24.59 eV + 54.42 eV]

E_{He} = -79.01 eV

or E_{He} = -2.9037 au (hartrees)

The Independent Particle Model

$$H = \left[-\frac{1}{2}\nabla_1^2(\vec{r_1}) - \frac{Z}{r_1} \right] + \left[-\frac{1}{2}\nabla_2^2(\vec{r_2}) - \frac{Z}{r_2} \right] + \cancel{\frac{1}{r_{12}}}$$

If the $1/r_{12}$ term is causing all the problems, just throw it out.

$$H = \left[-\frac{1}{2}\nabla_1^2(\vec{r_1}) - \frac{Z}{r_1} \right] + \left[-\frac{1}{2}\nabla_2^2(\vec{r_2}) - \frac{Z}{r_2} \right] = H_1(\vec{r_1}) + H_2(\vec{r_2})$$

Separation of Variables: Assume that $\quad \Psi(\vec{r_1},\vec{r_2}) = \psi_1(\vec{r_1}) \cdot \psi_2(\vec{r_2})$

$$\left[H_1(\vec{r_1}) + H_2(\vec{r_2}) \right] \psi_1(\vec{r_1}) \cdot \psi_2(\vec{r_2}) = E\psi_1(\vec{r}) \cdot \psi_2(\vec{r_2})$$

$$\psi_2(\vec{r_2})H_1(\vec{r_1})\psi_1(\vec{r_1}) + \psi_1(\vec{r_1})H_2(\vec{r_2})\psi_2(\vec{r_2}) = E\psi_1(\vec{r_1}) \cdot \psi_2(\vec{r_2})$$

$$\underbrace{\frac{1}{\psi_1(\vec{r_1})}H_1(\vec{r_1})\psi_1(\vec{r_1})}_{E_1} + \underbrace{\frac{1}{\psi_2(\vec{r_2})}H_2(\vec{r_2})\psi_2(\vec{r_2})}_{E_2} = E$$

$$H_1(\vec{r_1})\psi_1(\vec{r_1}) = E\psi_1(\vec{r_1}) \qquad \text{and} \qquad H_2(\vec{r_2})\psi_2(\vec{r_2}) = E\psi_2(\vec{r_2})$$

$$\left[-\frac{1}{2}\nabla_1^2(\vec{r_1}) - \frac{Z}{r_1} \right]\psi_1(\vec{r_1}) = E_1\psi_1(\vec{r_1}) \qquad \left[-\frac{1}{2}\nabla_2^2(\vec{r_2}) - \frac{Z}{r_2} \right]\psi_2(\vec{r_2}) = E_2\psi_2(\vec{r_2})$$

Hey!!! These are just the one electron Schrödinger Equations for "hydrogenlike" atoms. For Z=2, we have He$^+$.

We already solved this problem in Chapter 6.

Wavefunctions

$$\psi_1^{n_1 l_1 m_1}(\vec{r_1}) = A \cdot R_{n_1 l_1}(r_1) \cdot Y_{l_1 m_1}(\theta_1,\varphi_1) \qquad \psi_2^{n_2 l_2 m_2}(\vec{r_2}) = A \cdot R_{n_2 l_2}(r_2) \cdot Y_{l_2 m_2}(\theta_2,\varphi_2)$$

Ground State Wavefunctions
(1s: n=1,l=0,m=0)

$$\psi_1^{100}(\vec{r_1}) = A \cdot e^{-Zr_1} \qquad \psi_2^{100}(\vec{r_2}) = A \cdot e^{-Zr_2}$$

Remember that in atomic units, a_0 = 1 bohr

Energies

$$E_1 = -\frac{Z^2}{2n_1^2} \qquad\qquad E_2 = -\frac{Z^2}{2n_2^2}$$

$$E = E_1 + E_2 = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2}$$

Ground State Energy
($n_1 = n_2 = 1$)

$$E = E_1 + E_2 = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 = -4 \; a.u. \,(hartrees)$$
$$Z = 2 \text{ for He}$$

$$E_{exp} = -2.9037 \; a.u. \,(hartrees)$$

Our calculated Ground State Energy is 38% lower than experiment.

This is because, by throwing out the $1/r_{12}$ term in the Hamiltonian, we ignored the electron-electron repulsive energy, which is positive.

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Perturbation Theory Treatment of Helium

$$H = \left[-\frac{1}{2}\nabla_1^2(\vec{r}_1) - \frac{Z}{r_1} \right] + \left[-\frac{1}{2}\nabla_2^2(\vec{r}_2) - \frac{Z}{r_2} \right] + \frac{1}{r_{12}}$$

The Helium Hamiltonian can be rewritten as:

$$H = H^{(0)} + H^{(1)}$$

where $H^{(0)} = \left[-\frac{1}{2}\nabla_1^2(\vec{r}_1) - \frac{Z}{r_1} \right] + \left[-\frac{1}{2}\nabla_2^2(\vec{r}_2) - \frac{Z}{r_2} \right]$

$$H^{(1)} = +\frac{1}{r_{12}}$$

$H^{(0)}$ is exactly solvable, as we just showed in the independent particle method.

$H^{(1)}$ is a small perturbation to the exactly solvable Hamiltonian. The energy due to $H^{(1)}$ can be estimated by First Order Perturbation Theory.

Zeroth Order Energy and Wavefunction

$$H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$

The "Zeroth Order" Ground State energy is:

$$E = E_1 + E_2 = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 \, a.u. = -4.00 a.u.$$

The "Zeroth Order" wavefunction is the product of He$^+$ 1s wavefunctions for electrons 1 and 2

$$\psi^{(0)} = \psi_1^{100}(\vec{r}_1) \cdot \psi_2^{100}(\vec{r}_2) = \left[\left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr_1} \right] \cdot \left[\left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr_2} \right]$$

$$\psi^{(0)} = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} = A e^{-Z(r_1+r_2)}$$

First Order Perturbation Theory Correction to the Energy

In Chapter 5, we learned that the correction to the energy,
ΔE [or $E^{(1)}$] is:

$$\Delta E = E^{(1)} = \int \psi^{(0)} * H^{(1)} \psi^{(0)} d\tau$$

For the He atom: $H^{(1)} = +\dfrac{1}{r_{12}}$ and $\psi^{(0)} = \dfrac{Z^3}{\pi} e^{-Z(r_1 + r_2)} = A e^{-Z(r_1 + r_2)}$

Therefore: $\Delta E = A^2 \int d\vec{r}_1 \int d\vec{r}_2 e^{-2Z_1} e^{-2Z_2} \dfrac{1}{r_{12}}$ where $d\vec{r}_1 \equiv r_1^2 \sin(\theta_1) dr_1 d\theta_1 d\varphi_1$

$d\vec{r}_2 \equiv r_2^2 \sin(\theta_2) dr_2 d\theta_2 d\varphi_2$

The evaluation of this integral is rather difficult, and in outlined
in several texts.

$$\Delta E = \dfrac{5}{8} Z$$

e.g. Introduction to Quantum Mechanics in Chemistry, by M. A. Ratner
and G. C. Schatz, Appendix B.

Therefore, using First Order Perturbation Theory, the total electronic
energy of the Helium atom is:

$$E = E^{(0)} + \Delta E = -\dfrac{Z^2}{2} - \dfrac{Z^2}{2} + \dfrac{5}{8} Z = -2^2 + \dfrac{5}{8} \cdot 2 = -2.75 \ a.u.$$

This result is 5.3% above (less negative) the experimental
energy of -2.9037 a.u.

However, remember that we made only the ***First Order*** Perturbation
Theory correction to the energy.

Order	Energy	% Error
0	-4.0 a. u.	-38%
1	-2.75	+5
2	-2.91	-0.2
13	-2.9037	~0

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Variational Method Treatment of Helium

Recall that we proved earlier in this Chapter that, if one has an approximate "trial" wavefunction, ϕ, then the expectation value for the energy must be either higher than or equal to the true ground state energy. It cannot be lower!!

$$< E >= E_{trial} = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} = \frac{\int \varphi^* H \varphi d\tau}{\int \varphi^* \varphi d\tau} \geq E_0$$

This provides us with a very simple "recipe" for improving the energy. The lower the better!!

When we calculated the He atom energy using the "Independent Particle Method", we obtained an energy (-4.0 au) which was lower than experiment (-2.9037 au).

Isn't this a violation of the Variational Theorem??

No, because we did not use the complete Hamiltonian in our calculation.

A Trial Wavefunction for Helium

Recall that when we assumed an Independent Particle model for Helium, we obtained a wavefunction which is the product of two 1s He+ functions.

$$\varphi = \psi_1^{100}(\vec{r}_1) \cdot \psi_2^{100}(\vec{r}_2) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr_1} e^{-Zr_2} = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Z(r_1+r_2)}$$

For a trial wavefunction on which to apply the Variational Method, we can use an "effective" atomic number, Z', rather than Z=2.

By using methods similar to those above (Independent Particle Model + First Order Perturbation Theory Integral), it can be shown that

for $\quad H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$ $\qquad$ Z = 2 for He

and $\quad \varphi = \left(\frac{Z'^3}{\pi}\right)^{1/2} e^{-Z'(r_1+r_2)}$

$$E_{trial} = \frac{\langle \varphi|H|\varphi \rangle}{\langle \varphi|\varphi \rangle} = \frac{Z'^2}{2} + \frac{Z'^2}{2} - ZZ' - ZZ' + \frac{5}{8}Z'$$

KE(1) KE(2)   PE(1)   PE(2) PE(12)

$$E_{trial} = Z'^2 - 2ZZ' + \frac{5}{8}Z' = Z'^2 - 4Z' + \frac{5}{8}Z' = Z'^2 - \frac{27}{8}Z'$$

He: Z = 2
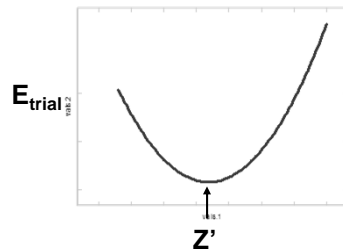
(Z E)

We want to find the value of Z' which minimizes the energy, E_{trial}.

Once again, we can either use trial-and-error (Yecch!!) or basic Calculus.

$$E_{trial} = Z'^2 - \frac{27}{8}Z'$$

At minimum: $\dfrac{dE_{trial}}{dZ'} = 0 = 2Z' - \dfrac{27}{8}$

For lowest E_{trial}: $Z' = \dfrac{27}{16} = 1.6875$

$$E_{trial} = \left(\frac{27}{16}\right)^2 - \frac{27}{8}\cdot\frac{27}{16}$$

(Z E)

$E_{trial} = -2.848\ au$ (1.9% higher than experiment)

vs. $E_{expt} = -2.9037\ au$
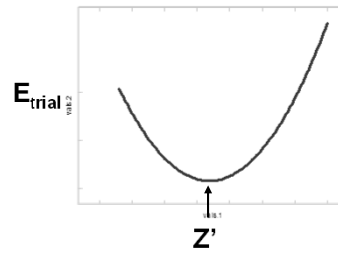
The lower value for the "effective" atomic number (Z'=1.69 vs. Z=2) reflects "screening" due to the mutual repulsion of the electrons.

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Better Variational Wavefunctions

One can improve (i.e. lower the energy) by employing improved wavefunctions with additional variational parameters.

A Two Parameter Wavefunction

Let the two electrons have different values of Z_{eff}:

$$\varphi = A\left[e^{-Z'r_1}e^{-Z''r_2} + e^{-Z''r_1}e^{-Z'r_2} \right]$$ (we must keep treatment of the two electrons symmetrical)

If one computes E_{trial} as a function of Z' and Z'' and then finds the values of the two parameters that minimize the energy, one finds:

Z' = 1.19 E_{trial} = -2.876 au (1.0% higher than experiment)
Z'' = 2.18

The very different values of Z' and Z'' reflects **correlation** between the positions of the two electrons; i.e. if one electron is close to the nucleus, the other prefers to be far away.

Another Wavefunction Incorporating Electron Correlation

$$\varphi = A\left[e^{-Z'(r_1+r_2)}\left(1+b \cdot r_{12}\right) \right]$$

When E_{trial} is evaluated as a function of Z' and b, and the values of the two parameters are varied to minimize the energy, the results are:

Z' = 1.19 E_{trial} = -2.892 au (0.4% higher than experiment)
b = 0.364

The second term, $1+br_{12}$, accounts for electron correlation.

It increases the probability (higher ϕ^2) of finding the two electrons further apart (higher r_{12}).

A Three Parameter Wavefunction

$$\varphi = A\left[\left(e^{-Z'r_1}e^{-Z''r_2} + e^{-Z''r_1}e^{-Z'r_2}\right)\bullet\left(1 + b\cdot r_{12}\right)\right]$$

We have incorporated both ways of including electron correlation.

When E_{trial} is evaluated as a function of Z', Z" and b, and the values of the 3 parameters are varied to minimize the energy, the results are:

Z' = 1.435 E_{trial} = -2.9014 au (0.08% higher than experiment)
Z" = 2.209
b = 0.292

Even More Parameters

When we used a wavefunction of the form: $\varphi = A\left[e^{-Z'(r_1+r_2)}\left(1 + b\cdot r_{12}\right)\right]$

The variational energy was within 0.4% of experiment.

We can improve upon this significantly by generalizing ϕ to:

$$\varphi = A\left[e^{-Z'(r_1+r_2)}\left(1 + g(r_1, r_2, r_{12})\right)\right]$$

$g(r_1, r_2, r_{12})$ is a polynomial function of the 3 interparticle distances.

Hylleras (1929) used a 9 term polynomial (10 total parameters) to get: E_{trial} = -2.9036 au (0.003% higher than experiment)

Kinoshita (1957) used a 38 term polynomial (39 total parameters) to get: E_{trial} = -2.9037 au (~0% Error)

To my knowledge, the record to date was a 1078 parameter wavefunction [Pekeris (1959)]

A Summary of Results

$E_{expt.}$ = -2.9037 au

Wavefunction	Energy	% Error
$Ae^{-Z(r_1+r_2)}$	-2.75 au	+5.3%
$Ae^{-Z'(r_1+r_2)}$	-2.848	+1.9%
$A\left[e^{-Z'r_1}e^{-Z''r_2} + e^{-Z''r_1}e^{-Z'r_2} \right]$	-2.876	+1.0%
$A\left[e^{-Z'(r_1+r_2)}\left(1+b\cdot r_{12}\right) \right]$	-2.892	+0.4%
$A\left[\left(e^{-Z'r_1}e^{-Z''r_2} + e^{-Z''r_1}e^{-Z'r_2} \right)\cdot\left(1+b\cdot r_{12}\right) \right]$	-2.9014	+0.08%
$\varphi = A\left[e^{-Z'(r_1+r_2)}\left(1+g(r_1,r_2,r_{12})\right) \right]$ (39 parameters)	-2.9037	~0%

Notes: 1. The computed energy is always higher than experiment.

2. One can compute an "approximate" energy to whatever degree of accuracy desired.

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Chapter 7

Multielectron Atoms

Part B: Electron Spin and the Pauli Principle

Part B: Electron Spin and the Pauli Principle

- **The Energy of Ground State Helium**

- Electron Spin and the Pauli Principle

- Inclusion of Spin in Helium Atom Wavefunctions

- Spin Angular Momentum of Ground State Helium

- The Wavefunctions of Excited State Helium

- Excited State Helium Energies: He($1s^12s^1$)

The Helium Hamiltonian and Wavefunctions

The Helium Hamiltonian (Chapter 7) is:

$$H = -\frac{1}{2}\nabla_1^2 \;-\; \frac{1}{2}\nabla_2^2 \;-\; \frac{2}{r_1} \;-\; \frac{2}{r_2} \;+\; \frac{1}{r_{12}}$$

KE(1)   **KE(2)**   **PE(1)**   **PE(2)**   **PE(12)**

$$H = \left[-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}\right] + \left[-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}\right] + \frac{1}{r_{12}}$$

$$H = H_1 + H_2 + \frac{1}{r_{12}}$$ H_1 and H_2 are the one electron Hamiltonians for He$^+$

In the ground state, both electrons are in 1s orbitals and the wavefunction can be written as:

$$\psi = \phi_{1s}(\vec{r_1})\phi_{1s}(\vec{r_2}) = 1s(1)1s(2)$$

We will assume that each 1s orbital is already normalized.

$$H = H_1(\vec{r_1}) + H_2(\vec{r_2}) + \frac{1}{r_{12}} \qquad\qquad \psi = \phi_{1s}(\vec{r_1})\phi_{1s}(\vec{r_2}) = 1s(1)1s(2)$$

The Helium Ground State Energy

$$\langle E\rangle_{GS} = \langle \psi(\vec{r_1},\vec{r_2})|H|\psi(\vec{r_1},\vec{r_2})\rangle = \langle 1s(1)1s(2)|H|1s(1)1s(2)\rangle$$

$$= \langle 1s(1)1s(2)|H_1 + H_2 + \frac{1}{r_{12}}|1s(1)1s(2)\rangle$$

$$= \langle 1s(1)1s(2)|H_1|1s(1)1s(2)\rangle + \langle 1s(1)1s(2)|H_2|1s(1)1s(2)\rangle$$

$$+ \langle 1s(1)1s(2)|\frac{1}{r_{12}}|1s(1)1s(2)\rangle$$

$$= \langle 1s(2)|1s(2)\rangle\langle 1s(1)|H_1|1s(1)\rangle + \langle 1s(1)|1s(1)\rangle\langle 1s(2)|H_2|1s(2)\rangle$$

$$+ \langle 1s(1)1s(2)|\frac{1}{r_{12}}|1s(1)1s(2)\rangle$$

$$\langle E\rangle_{GS} = \langle 1s(1)|H_1|1s(1)\rangle + \langle 1s(2)|H_2|1s(2)\rangle + \langle 1s(1)1s(2)|\frac{1}{r_{12}}|1s(1)1s(2)\rangle$$

$$\langle E \rangle_{GS} = \langle 1s(1)|H_1|1s(1)\rangle + \langle 1s(2)|H_2|1s(2)\rangle + \langle 1s(1)1s(2)|\frac{1}{r_{12}}|1s(1)1s(2)\rangle$$

$$\langle E \rangle_{GS} = \underset{\mathbf{1}}{\varepsilon_{1s}} + \underset{\mathbf{1}}{\varepsilon_{1s}} + \underset{\mathbf{2}}{J_{1s1s}}$$

1 $\quad \varepsilon_{1s} = \langle 1s(1)|H_1|1s(1)\rangle = \langle 1s(2)|H_2|1s(2)\rangle$

This is the energy of an electron in the 1s orbital of a He$^+$ ion.

2 $\quad J_{1s1s} = \langle 1s(1)1s(2)|\frac{1}{r_{12}}|1s(1)1s(2)\rangle$

J_{1s1s} is called the **Coulomb Integral.**
This is the total repulsion energy between the two 1s electrons.

We will compare this energy of ground state Helium with
the energy of excited state Helium in a later section.

Further comments on the Coulomb Integral

$$J_{1s1s} = \langle 1s(1)1s(2)|\frac{1}{r_{12}}|1s(1)1s(2)\rangle$$

Coulomb Integral: Electron-Electron Repulsion.

To better understand this integral, it is convenient to rewrite it
in SI units with the traditional integral format.

$$J_{1s1s} = \int\int [1s(1)1s(2)]^* \frac{e^2}{4\pi\varepsilon_0 r_{12}} [1s(1)1s(2)] \, d\vec{r}_1 d\vec{r}_2$$

$$= \int\int \frac{e^2 [1s(1)]^2 [1s(2)]^2}{4\pi\varepsilon_0 r_{12}} \, d\vec{r}_1 d\vec{r}_2 = \int\int \frac{\{e[1s(1)]^2 \, d\vec{r}_1\}\{e[1s(2)]^2 \, d\vec{r}_2\}}{4\pi\varepsilon_0 r_{12}}$$

$$= \int\int \frac{\{dq_1\}\{dq_2\}}{4\pi\varepsilon_0 r_{12}}$$

From this last equation, we see that the Coulomb Integral is really
just adding up the product of the two charges divided by the
distance between them over all possible volume elements.

Part B: Electron Spin and the Pauli Principle

- The Energy of Ground State Helium

- **Electron Spin and the Pauli Principle**

- Inclusion of Spin in Helium Atom Wavefunctions

- Spin Angular Momentum of Ground State Helium

- The Wavefunctions of Excited State Helium

- Excited State Helium Energies: He($1s^1 2s^1$)

Electron Spin

We've known since Freshman Chemistry or before that electrons have spins and there's a spin quantum number (there actually are two).

Yet, we never mentioned electron spin, or the Pauli Exclusion Principle (actually the Pauli Antisymmetry Principle), in our treatment of ground state Helium in Chapter 7.

This is because Helium is a closed shell system.
That is, its electrons fill the n=1 shell.

As we shall see, in open shell systems, such as the Lithium atom ($1s^2 2s^1$) or excited state Helium (e.g. $1s^1 2s^1$), the electron's spin and the Pauli Principle play an important role in determining the electronic energy.

A Brief Review of Orbital Angular Momentum in Hydrogen

An electron moving about the nucleus in a hydrogen atom has **orbital angular momentum**.

The wavefunction for the electron in a hydrogen atom is: $\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r) \cdot Y_{lm}(\theta,\varphi)$

In addition to being eigenfunctions of the Hamiltonian (with eigenvalues E_n), the wavefunctions are eigenfunctions of the angular momentum operators, $\hat{L}^2$ and $\hat{L}_z$:

Shorthand

$$\hat{L}^2\psi_{nlm} = \ell(\ell+1)\hbar^2\psi_{nlm} \qquad \hat{L}^2\left|nlm\right\rangle = \ell(\ell+1)\hbar^2\left|nlm\right\rangle$$

$$\hat{L}_z\psi_{nlm} = m\hbar\psi_{nlm} \qquad \hat{L}_z\left|nlm\right\rangle = m\hbar\left|nlm\right\rangle$$

Do Electrons Spin??

I don't know. I've never seen an electron up close and personal.

What can be said is that their magnetic properties are consistent with the hypothesis that they behave "as though" they are spinning.

When a beam of electrons is directed through a magnetic field, they behave like little magnets, with half of their North poles parallel and half antiparallel to the magnetic field's North pole.
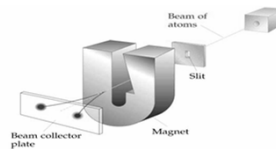
Because a rotating charge is known to behave like a magnet, the electrons are behaving as though they are spinning in one of two directions about their axes.
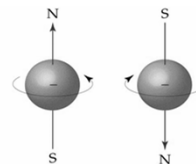
Spin Angular Momentum and Quantum Numbers

A rotating (or spinning) charge possesses angular momentum.

To characterize the **spin angular momentum** of an electron, two new quantum numbers are introduced, s and m_s (analogous to l and m_l), with s = ½ and $m_s = \pm$½.

The state of the electron is characterized by s and m_s and is written as:

$$\left| s\, m_s \right\rangle = \left| \frac{1}{2}\frac{1}{2} \right\rangle \quad or \quad \left| \frac{1}{2}\ -\frac{1}{2} \right\rangle$$

In direct analogy to orbital angular momentum, spin angular momentum operators are introduced with the properties that:

$$\hat{S}^2 \left| s\, m_s \right\rangle = s(s+1)\hbar^2 \left| s\, m_s \right\rangle \qquad \hat{S}^2 \left| \frac{1}{2}\frac{1}{2} \right\rangle = \frac{3}{4}\hbar^2 \left| \frac{1}{2}\frac{1}{2} \right\rangle \qquad \hat{S}^2 \left| \frac{1}{2}\ -\frac{1}{2} \right\rangle = \frac{3}{4}\hbar^2 \left| \frac{1}{2}\ -\frac{1}{2} \right\rangle$$

and

$$\hat{S}_z \left| s\, m_s \right\rangle = m_s \hbar \left| s\, m_s \right\rangle \qquad \hat{S}_z \left| \frac{1}{2}\frac{1}{2} \right\rangle = \frac{1}{2}\hbar \left| \frac{1}{2}\frac{1}{2} \right\rangle \qquad \hat{S}_z \left| \frac{1}{2}\ -\frac{1}{2} \right\rangle = -\frac{1}{2}\hbar \left| \frac{1}{2}\ -\frac{1}{2} \right\rangle$$

Because one always has s = ½, the standard shorthand is:

$$\left| \alpha \right\rangle \equiv \left| \frac{1}{2}\frac{1}{2} \right\rangle \quad and \quad \left| \beta \right\rangle \equiv \left| \frac{1}{2}\ -\frac{1}{2} \right\rangle$$

$$\hat{S}^2 \left| \alpha \right\rangle = \frac{3}{4}\hbar^2 \left| \alpha \right\rangle \qquad \hat{S}^2 \left| \beta \right\rangle = \frac{3}{4}\hbar^2 \left| \beta \right\rangle$$

$$\hat{S}_z \left| \alpha \right\rangle = \frac{1}{2}\hbar \left| \alpha \right\rangle \qquad \hat{S}_z \left| \beta \right\rangle = -\frac{1}{2}\hbar \left| \beta \right\rangle$$

Orthonormality of the Spin Wavefunctions

One can define integrals of the spin functions in analogy to integrals of spatial wavefunctions, keeping in mind that one is not really using calculus to evaluate integrals. Their values are defined below:

$$\langle \alpha | \alpha \rangle = \int \alpha * \alpha \, d\sigma \equiv 1 \quad \textbf{By definition}$$

$$\langle \beta | \beta \rangle = \int \beta * \beta \, d\sigma \equiv 1 \quad \textbf{By definition}$$

$$\langle \alpha | \beta \rangle = \int \alpha * \beta \, d\sigma \equiv 0 \quad \textbf{By definition}$$

$$\langle \beta | \alpha \rangle = \int \beta * \alpha \, d\sigma \equiv 0 \quad \textbf{By definition}$$

Therefore, by definition, the spin wavefunctions are orthonormal.

The Pauli Principle

The Permutation Operator

By definition, this operator permutes (i.e. exchanges) two particles (usually electrons) in a wavefunction.

$$\hat{P}_{ij} \psi(\vec{r}_i, \vec{r}_j) = \psi(\vec{r}_j, \vec{r}_i) = p_{ij} \psi(\vec{r}_i, \vec{r}_j)$$

For a 2 electron system: $\hat{P}_{12} \psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1) = p_{12} \psi(\vec{r}_1, \vec{r}_2)$

This is an eigenvalue equation, with eigenvalue p_{ij}.

Permuting two identical particles will not change the probability density:

$$\left[\hat{P}_{ij} \psi(\vec{r}_i, \vec{r}_j) \right]^2 = \left[p_{ij} \psi(\vec{r}_i, \vec{r}_j) \right]^2$$

Therefore: $p_{ij} = \pm 1$

The Pauli Principle

Postulate 6: All elementary particles have an intrinsic angular momentum called spin. There are two types of particles, with different permutation properties:

   Bosons: Integral spin (0, 1, 2,…) $P_{ij}(\psi) = +\psi$

   Fermions: Half integral spin (1/2, 3/2,…) $P_{ij}(\psi) = -\psi$

Fermions include electrons, protons, ^{3}He nuclei, etc.

Bosons include ^{4}He nuclei (s=0), ^{2}H nuclei (s=1), etc.

Electrons (s = ½) are fermions.

Therefore, electronic wavefunctions are antisymmetric with respect to electron exchange (permutation).

Note that the permutation operator exchanges both the spatial and spin coordinates of the electrons.

Part B: Electron Spin and the Pauli Principle

• The Energy of Ground State Helium

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• **Inclusion of Spin in Helium Atom Wavefunctions**

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• Excited State Helium Energies: He($1s^12s^1$)

Inclusion of Spin in Helium Atom Wavefunctions

The Hamiltonian for Helium does not contain any spin operators. Therefore, one can take the total wavefunction to be the product of spatial and spin parts.

If we use the approximation that the spatial part can be represented by 1s orbitals for each electron, then 4 possibilities for the total wavefunction are:

$$\Phi_1 = \varphi_{1s}(\vec{r}_1)\alpha_1 \cdot \varphi_{1s}(\vec{r}_2)\beta_2 = 1s(1)\alpha_1 \cdot 1s(2)\beta_2$$

Electron 1 has α spin.
Electron 2 has β spin.

$$\Phi_2 = \varphi_{1s}(\vec{r}_1)\beta_1 \cdot \varphi_{1s}(\vec{r}_2)\alpha_2 = 1s(1)\beta_1 \cdot 1s(2)\alpha_2$$

Electron 1 has β spin.
Electron 2 has α spin.

$$\Phi_3 = \varphi_{1s}(\vec{r}_1)\alpha_1 \cdot \varphi_{1s}(\vec{r}_2)\alpha_2 = 1s(1)\alpha_1 \cdot 1s(2)\alpha_2$$

Electron 1 has α spin.
Electron 2 has α spin.

$$\Phi_4 = \varphi_{1s}(\vec{r}_1)\beta_1 \cdot \varphi_{1s}(\vec{r}_2)\beta_2 = 1s(1)\beta_1 \cdot 1s(2)\beta_2$$

Electron 1 has β spin.
Electron 2 has β spin.

Shorthand Notation: $\varphi_{1s}(\vec{r}_1) = 1s(1)$ $\varphi_{1s}(\vec{r}_2) = 1s(2)$

None of these 4 functions satisfies the Pauli Antisymmetry Principle.

$$\Phi_1 = 1s(1)\alpha_1 \cdot 1s(2)\beta_2$$
$$\Phi_2 = 1s(1)\beta_1 \cdot 1s(2)\alpha_2$$
$$\Phi_3 = 1s(1)\alpha_1 \cdot 1s(2)\alpha_2$$
$$\Phi_4 = 1s(1)\beta_1 \cdot 1s(2)\beta_2$$

$$P_{12}\Phi_1 = P_{12}\left[1s(1)\alpha_1 \cdot 1s(2)\beta_2\right] = 1s(2)\alpha_2 \cdot 1s(1)\beta_1 = +\Phi_2$$

Similarly: $P_{12}\Phi_2 = +\Phi_1$

$$P_{12}\Phi_3 = P_{12}\left[1s(1)\alpha_1 \cdot 1s(2)\alpha_2\right] = 1s(2)\alpha_2 \cdot 1s(1)\alpha_1 = +\Phi_3$$

Similarly: $P_{12}\Phi_4 = +\Phi_4$

A wavefunction that satisfies the Pauli Principle

We can construct a linear combination of Φ_1 and Φ_2 that ***does*** satisfy the Pauli Principle.

$$\psi = N\left[\Phi_1 - \Phi_2\right] = N\left[1s(1)\alpha_1 \cdot 1s(2)\beta_2 - 1s(1)\beta_1 \cdot 1s(2)\alpha_2\right]$$

$$P_{12}\psi = P_{12}N\left[\Phi_1 - \Phi_2\right] = N\left[\Phi_2 - \Phi_1\right] = -\psi$$

Thus, ψ is antisymmetric with respect to electron exchange, as required by the Pauli Principle.

Note: The sum of Φ_1 and Φ_2 would **not** be a satisfactory wavefunction.

$$\Phi_1 = 1s(1)\alpha_1 \cdot 1s(2)\beta_2$$
$$\Phi_2 = 1s(1)\beta_1 \cdot 1s(2)\alpha_2$$
$$\Phi_3 = 1s(1)\alpha_1 \cdot 1s(2)\alpha_2$$
$$\Phi_4 = 1s(1)\beta_1 \cdot 1s(2)\beta_2$$

$$P_{12}\left(N\left[\Phi_1 + \Phi_2\right]\right) = N\left[P_{12}\Phi_1 + P_{12}\Phi_2\right] = +N\left[\Phi_2 + \Phi_1\right]$$

Because $P_{12}\Phi_3 = +\Phi_3$ and $P_{12}\Phi_4 = +\Phi_4$ neither of these functions can be used in the construction of an antisymmetric wavefunction

This is the basis for the more famous, but less general, form of the Pauli Principle, known as the Exclusion Principle:

Two electrons in an atom cannot have the same set of 4 quantum numbers, n, l, m_l and m_s. That is, if two electrons have the same spatial part of the wavefunction (100 for both electrons in the Helium ground state), then they cannot have the same spin.

The wavefunction, ψ, can be written as the product of a spatial and spin part:

$$\psi = N\left[1s(1)\alpha_1 \cdot 1s(2)\beta_2 - 1s(1)\beta_1 \cdot 1s(2)\alpha_2\right] = N\,1s(1)1s(2)\left[\alpha_1\beta_2 - \beta_1\alpha_2\right]$$

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Normalization of the Antisymmetric Wavefunction

$$\psi = N\varphi_{1s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\left[\alpha_1\beta_2 - \beta_1\alpha_2\right] = N\,1s(1)1s(2)\left[\alpha_1\beta_2 - \beta_1\alpha_2\right]$$

We assume that the individual spatial wavefunctions have already been normalized.

$$1 = \int \psi^* \psi\, d\tau = \langle\psi|\psi\rangle$$ We must integrate over both the spin and spatial parts of the wavefunction.

$$1 = N^2 \underbrace{\int 1s(1)*1s(1)\,d\vec{r}_1}_{1} \underbrace{\int 1s(2)*1s(2)\,d\vec{r}_2}_{1} \iint\left[\alpha_1\beta_2 - \beta_1\alpha\right]^*\left[\alpha_1\beta_2 - \beta_1\alpha\right]d\sigma_1 d\sigma_2$$

or

$$1 = N^2 \underbrace{\langle 1s(1)|1s(1)\rangle}_{1} \underbrace{\langle 1s(2)|1s(2)\rangle}_{1} \langle\alpha_1\beta_2 - \beta_1\alpha_2|\alpha_1\beta_2 - \beta_1\alpha_2\rangle$$

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$$1 = N^2 \langle 1s(1)|1s(1)\rangle \langle 1s(2)|1s(2)\rangle \langle \alpha_1\beta_2 - \beta_1\alpha_2 | \alpha_1\beta_2 - \beta_1\alpha_2 \rangle$$

$$= N^2 \langle \alpha_1\beta_2 - \beta_1\alpha_2 | \alpha_1\beta_2 - \beta_1\alpha_2 \rangle$$

$$1 = N^2 \left[\langle \alpha_1\beta_2 | \alpha_1\beta_2 \rangle - \langle \alpha_1\beta_2 | \beta_1\alpha_2 \rangle - \langle \beta_1\alpha_2 | \alpha_1\beta_2 \rangle + \langle \beta_1\alpha_2 | \beta_1\alpha_2 \rangle \right]$$

$$1 = N^2 \left[\langle \alpha_1 | \alpha_1 \rangle \langle \beta_2 | \beta_2 \rangle - \langle \alpha_1 | \beta_1 \rangle \langle \beta_2 | \alpha_2 \rangle - \langle \beta_1 | \alpha_1 \rangle \langle \alpha_2 | \beta_2 \rangle + \langle \beta_1 | \beta_1 \rangle \langle \alpha_2 | \alpha_2 \rangle \right]$$

$$\begin{array}{cccccccc} \| & \| & \| & \| & \| & \| & \| & \| \\ 1 & 1 & 0 & 0 & 0 & 0 & 1 & 1 \end{array}$$

$$1 = 2N^2 \quad \longrightarrow \quad \boxed{N = \frac{1}{\sqrt{2}}}$$

$$\psi = \frac{1}{\sqrt{2}} \varphi_{1s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\left[\alpha_1\beta_2 - \beta_1\alpha_2\right] = \frac{1}{\sqrt{2}} 1s(1)1s(2)\left[\alpha_1\beta_2 - \beta_1\alpha_2\right]$$

Spin and the Energy of Ground State Helium

Earlier in this chapter, prior to reducing electron spin, we showed that the energy of ground state helium is given by:

$$\langle E \rangle_{GS} = \varepsilon_{1s} + \varepsilon_{1s} + J_{1s1s}$$

Would its inclusion have affected the results?

$$\psi = \frac{1}{\sqrt{2}} \varphi_{1s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\left[\alpha_1\beta_2 - \beta_1\alpha_2\right] = \frac{1}{\sqrt{2}} 1s(1)1s(2)\left[\alpha_1\beta_2 - \beta_1\alpha_2\right]$$

We will examine this question below.

The expression for the expectation value of the energy is given by:

$$\langle E \rangle = \langle \psi | H | \psi \rangle = \left\langle \frac{1}{\sqrt{2}} 1s(1)1s(2)(\alpha_1\beta_2 - \beta_1\alpha_2) \left| H \right| \frac{1}{\sqrt{2}} 1s(1)1s(2)(\alpha_1\beta_2 - \beta_1\alpha_2) \right\rangle$$

$$\langle E \rangle = \langle \psi | H | \psi \rangle \;\; = \left\langle \frac{1}{\sqrt{2}} 1s(1)1s(2)(\alpha_1\beta_2 - \beta_1\alpha_2) \middle| H \middle| \frac{1}{\sqrt{2}} 1s(1)1s(2)(\alpha_1\beta_2 - \beta_1\alpha_2) \right\rangle$$

$$\langle E \rangle = \frac{1}{2} \langle 1s(1)1s(2) | H | 1s(1)1s(2) \rangle \langle \alpha_1\beta_2 - \beta_1\alpha_2 | \alpha_1\beta_2 - \beta_1\alpha_2 \rangle$$

We can factor out the spin part of the wave function
because H is independent of spin

$$\langle E \rangle = \frac{1}{2} \langle 1s(1)1s(2) | H | 1s(1)1s(2) \rangle \cdot (2) = \boxed{\langle 1s(1)1s(2) | H | 1s(1)1s(2) \rangle}$$

Thus, inclusion of the spin portion of the wavefunction has no
effect on the computed energy in a closed shell system such
as ground state Helium.

Note: It can be shown that one arrives at the same conclusion if
a more sophisticated spatial function is used to characterize the
two electrons.

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Spin Angular Momentum of Ground State Helium

z-Component of Spin Angular Momentum

For a two electron system, the operator for S_z is

$$\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$$

Therefore $\hat{S}_z \psi = \left(\hat{S}_{1z} + \hat{S}_{2z} \right)\left(\frac{1}{\sqrt{2}}\left[\alpha_1\beta_2 - \beta_1\alpha_2 \right] \right)$

$$\hat{S}_z \psi = \frac{1}{\sqrt{2}}\left(\hat{S}_{1z}\alpha_1\beta_2 + \hat{S}_{2z}\alpha_1\beta_2 - \hat{S}_{1z}\beta_1\alpha_2 - \hat{S}_{2z}\beta_1\alpha_2 \right)$$

$$\hat{S}_z \psi = \frac{1}{\sqrt{2}}\left(\frac{1}{2}\hbar\alpha_1\beta_2 - \frac{1}{2}\hbar\alpha_1\beta_2 + \frac{1}{2}\hbar\beta_1\alpha_2 - \frac{1}{2}\hbar\beta_1\alpha_2 \right) = 0$$

Therefore, the eigenvalue of $\hat{S}_z$ is 0. The z-component of angular momentum is $M_S = 0$.

Total Spin Angular Momentum

The $\hat{S}^2$ operator for a two electron system and the calculation of the eigenvalue of this operator is significantly more complicated than the calculation of the z-component.

This calculation requires application of spin raising and lowering operators (introduced in various texts**), and is a digression from our prime focus.

Therefore, we will just present the results.

The result is $\hat{S}^2\psi = 0$

Thus, for ground state Helium: S=0 and M_S=0

We say that GS helium is a "singlet" because there is only one possible combination of S and M_S (0 and 0).

**See for example, "Quantum Chemistry", by I. N. Levine (5th. Ed.) Sect. 10.10

Generalization

In general, the spin wavefunctions of multielectron atoms are eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$, with eigenvalues $S(S+1)\hbar^2$ and $M_S\hbar$.

$$\hat{S}^2 \left| SM_S \right\rangle = S(S+1)\hbar^2 \left| SM_S \right\rangle$$

$$S_z \left| SM_S \right\rangle = M_S\hbar \left| SM_S \right\rangle$$

Some possible combinations of S and M_S that can be encountered are given in the table below

S	M_S	Designation
0	0	Singlet
1/2	1/2, -1/2	Doublet
1	1, 0, -1	Triplet
3/2	3/2, 1/2, -1/2, -3/2	Quartet

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The Wavefunctions of Excited State Helium

In ground state Helium, we were able to write the wavefunction as the product of spatial and spin parts.

$$\psi = \varphi_{1s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\left[\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\right] = 1s(1)1s(2)\left[\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\right]$$

I have included the normalization constant with the spin function, which is what it is normalizing (it is assumed that the spatial part includes its own normalization constant)

In ground state Helium, the spatial wavefunction is symmetric with respect to electron exchange. Therefore, it is necessary for the spin function to be antisymmetric with respect to exchange in order to satisfy the Pauli Principle.

If one of the electrons is excited to the 2s orbital to give He($1s^1 2s^1$), the spatial wavefunction can be either symmetric or antisymmetric with respect to electron exchange, broadening the possibilities for valid spin functions.

Symmetric and Antisymmetric Spatial Wavefunctions

Neither $\varphi(\vec{r}_1,\vec{r}_2) = 1s(1)2s(2)$ nor $\varphi(\vec{r}_1,\vec{r}_2) = 2s(1)1s(2)$ are valid spatial wavefunctions because they are neither symmnetric nor antisymmetric with respect to the exchange of the two electrons.

However, one can "build" combinations of these wavefunctions that are either symmetric or antisymmetric with respect to electron exchange.

$$\psi_{sym}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) + 2s(1)1s(2)\right)$$
Symmetric

We have denoted this as a symmetric function, because it is easy to show that: $P_{12}\psi_{sym}(\vec{r}_1,\vec{r}_2) = +\psi_{sym}(\vec{r}_1,\vec{r}_2)$

$$\psi_{antisym}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)$$
Antisymmetric

For this function $P_{12}\psi_{antisym}(\vec{r}_1,\vec{r}_2) = -\psi_{antisym}(\vec{r}_1,\vec{r}_2)$

Symmetric and Antisymmetric Spin Wavefunctions

Two symmetric spin wavefunctions are: $\alpha_1\alpha_2$ and $\beta_1\beta_2$ because

$$P_{12}\alpha_1\alpha_2 = +\alpha_1\alpha_2 \quad \text{and} \quad P_{12}\beta_1\beta_2 = +\beta_1\beta_2$$

We could not use either of these symmetric spin functions for ground state Helium because the symmetric spatial function required that we must have an antisymmetric spin function to satisfy the Pauli Principle.

A third symmetric spin wavefunction is: $\dfrac{1}{\sqrt{2}}\left(\alpha_1\beta_2 + \beta_1\alpha_2\right)$

It is straightforward to apply the permutation operator, P_{12}, to this function to prove that it is symmetric with respect to exchange.

As shown when discussing ground state Helium, a spin wavefunction that is antisymmetric with respect to electron exchange is:

$$\frac{1}{\sqrt{2}}\left(\alpha_1\beta_2 - \beta_1\alpha_2\right)$$

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S and M_S of the Spin Wavefunctions

$$\hat{S}_z\alpha_1\alpha_2 = \left(\hat{S}_{1z} + \hat{S}_{2z}\right)\alpha_1\alpha_2 = \hat{S}_{1z}\alpha_1\alpha_2 + \hat{S}_{2z}\alpha_1\alpha_2 = \frac{1}{2}\hbar\alpha_1\alpha_2 + \frac{1}{2}\hbar\alpha_1\alpha_2 = 1\hbar\alpha_1\alpha_2$$

Therefore, M_S=+1 for $\alpha_1\alpha_2$

Similarly, M_S=0 for $\dfrac{1}{\sqrt{2}}\left(\alpha_1\beta_2 + \beta_1\alpha_2\right)$

M_S=-1 for $\beta_1\beta_2$

Using advanced methods,** (you are **not** responsible for it), one can show that when the S^2 operator is applied to any of the 3 symmetric spin functions, the eigenvalue is $2\hbar^2$ [= S(S+1) $\hbar^2$].

Therefore, S=1 for the 3 symmetric spin wavefunctions.

Together, these functions are a triplet with S=1 and M_S=+1,0,-1.

**e.g. *Introduction to Quantum Mechanics in Chemistry*, by M. A. Ratner and G. C. Schatz, Sect. 8.3

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When S_z operates on the antisymmetric spin function $\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$ one finds that $M_S=0$.

It can be shown that when S^2 operates on this function, the eigenvalue is 0. Therefore, S=0 for the antisymmetric spin function.

Therefore the antisymmetric spin wavefunction is a singlet, with S=0 and $M_S=0$.

The Total Wavefunction for Excited State Helium

Spatial Wavefunctions   **Spin Wavefunctions**

$$\psi_{sym}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) + 2s(1)1s(2)\right)$$ Singlet $\psi_{spin}^{00} = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$

$$\psi_{antisym}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)$$ Triplet $\psi_{spin}^{11} = \alpha_1\alpha_2$

$$\psi_{spin}^{10} = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2)$$

$$\psi_{spin}^{1-1} = \beta_1\beta_2$$

One can write the total wavefunction as the product of spin and spatial parts.

$$\psi = \psi_{spat}(\vec{r}_1,\vec{r}_2) \cdot \psi_{spin}^{SM_S}(\sigma_1,\sigma_2)$$

Singlet Wavefunction

$$\psi = \psi_{sym}(\vec{r}_1, \vec{r}_2) \cdot \psi_{spin}^{00}$$

$$\psi_{Sing} = \left[\frac{1}{\sqrt{2}} \left(1s(1)2s(2) + 2s(1)1s(2)\right) \right] \cdot \left[\frac{1}{\sqrt{2}} \left(\alpha_1 \beta_2 - \beta_1 \alpha_2\right) \right]$$

Triplet Wavefunctions

$$\psi = \psi_{antisym}(\vec{r}_1, \vec{r}_2) \cdot \psi_{spin}^{1M_S}$$

$$\psi_{T1} = \left[\frac{1}{\sqrt{2}} \left(1s(1)2s(2) - 2s(1)1s(2)\right) \right] \cdot \left[\alpha_1 \alpha_2 \right]$$

$$\psi_{T2} = \left[\frac{1}{\sqrt{2}} \left(1s(1)2s(2) - 2s(1)1s(2)\right) \right] \cdot \left[\frac{1}{\sqrt{2}} \left(\alpha_1 \beta_2 + \beta_1 \alpha_2\right) \right]$$

$$\psi_{T3} = \left[\frac{1}{\sqrt{2}} \left(1s(1)2s(2) - 2s(1)1s(2)\right) \right] \cdot \left[\beta_1 \beta_2 \right]$$

Part B: Electron Spin and the Pauli Principle

• The Energy of Ground State Helium

• Electron Spin and the Pauli Principle

• Inclusion of Spin in Helium Atom Wavefunctions

• Spin Angular Momentum of Ground State Helium

• The Wavefunctions of Excited State Helium

• **Excited State Helium Energies: He($1s^1 2s^1$)**

Excited State Helium Energies: He(1s^{1}2s^1)

The expectation value for energy is given by:

$$\langle E \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int \psi * H \psi \, d\vec{r}_1 d\vec{r}_2 d\sigma_1 d\sigma_2}{\int \psi * \psi \, d\vec{r}_1 d\vec{r}_2 d\sigma_1 d\sigma_2}$$

The Helium Hamiltonian is:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

KE(1)   KE(2)   PE(1)   PE(2)   PE(12)

$$H = \left[-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} \right] + \left[-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} \right] + \frac{1}{r_{12}}$$

$$H = H_1 + H_2 + \frac{1}{r_{12}}$$

H_1 and H_2 are the one electron Hamiltonians for He$^+$

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Triplet State Energy

$$\langle E \rangle_{Trip} = \frac{\left\langle \psi_{antisym}(\vec{r}_1, \vec{r}_2) \cdot \psi_{spin}^{1M_S}(\sigma_1, \sigma_2) \middle| H \middle| \psi_{antisym}(\vec{r}_1, \vec{r}_2) \cdot \psi_{spin}^{1M_S}(\sigma_1, \sigma_2) \right\rangle}{\left\langle \psi_{antisym}(\vec{r}_1, \vec{r}_2) \cdot \psi_{spin}^{1M_S}(\sigma_1, \sigma_2) \middle| \psi_{antisym}(\vec{r}_1, \vec{r}_2) \cdot \psi_{spin}^{1M_S}(\sigma_1, \sigma_2) \right\rangle}$$

Because the Hamiltonian does not contain any spin operators, the above expression can be simplified.

$$\langle E \rangle_{Trip} = \frac{\left\langle \psi_{spin}^{1M_S}(\sigma_1, \sigma_2) \middle| \psi_{spin}^{1M_S}(\sigma_1, \sigma_2) \right\rangle \left\langle \psi_{antisym}(\vec{r}_1, \vec{r}_2) \middle| H \middle| \psi_{antisym}(\vec{r}_1, \vec{r}_2) \right\rangle}{\left\langle \psi_{spin}^{1M_S}(\sigma_1, \sigma_2) \middle| \psi_{spin}^{1M_S}(\sigma_1, \sigma_2) \right\rangle \left\langle \psi_{antisym}(\vec{r}_1, \vec{r}_2) \middle| \psi_{antisym}(\vec{r}_1, \vec{r}_2) \right\rangle}$$

$$\langle E \rangle_{Trip} = \frac{\left\langle \psi_{antisym}(\vec{r}_1, \vec{r}_2) \middle| H \middle| \psi_{antisym}(\vec{r}_1, \vec{r}_2) \right\rangle}{\left\langle \psi_{antisym}(\vec{r}_1, \vec{r}_2) \middle| \psi_{antisym}(\vec{r}_1, \vec{r}_2) \right\rangle}$$

Note that the energy does not depend directly on the spin wavefunction.

It is the fact that the triplet state symmetric spin wavefunction requires us to use the antisymmetric spatial wavefunction that affects the calculated energy.

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$$\langle E \rangle_{Trip} = \frac{\langle \psi_{antisym}(\vec{r}_1,\vec{r}_2) | H | \psi_{antisym}(\vec{r}_1,\vec{r}_2) \rangle}{\langle \psi_{antisym}(\vec{r}_1,\vec{r}_2) | \psi_{antisym}(\vec{r}_1,\vec{r}_2) \rangle} = \langle \psi_{antisym}(\vec{r}_1,\vec{r}_2) | H | \psi_{antisym}(\vec{r}_1,\vec{r}_2) \rangle$$

We have assumed that the spatial wavefunction is normalized, in which case the denominator is 1.

$$\psi_{antisym}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\big(1s(1)2s(2) - 2s(1)1s(2)\big)$$

The energy can then be calculated from:

$$\langle E \rangle_{trip} = \left\langle \frac{1}{\sqrt{2}}\big(1s(1)2s(2) - 2s(1)1s(2)\big) \middle| H \middle| \frac{1}{\sqrt{2}}\big(1s(1)2s(2) - 2s(1)1s(2)\big) \right\rangle$$

$$\langle E \rangle_{trip} = \frac{1}{2}\langle 1s(1)2s(2) | H | 1s(1)2s(2) \rangle + \frac{1}{2}\langle 2s(1)1s(2) | H | 2s(1)1s(2) \rangle$$

$$\qquad - \frac{1}{2}\langle 1s(1)2s(2) | H | 2s(1)1s(2) \rangle - \frac{1}{2}\langle 2s(1)1s(2) | H | 1s(1)2s(2) \rangle$$

$$\langle E \rangle_{trip} = I_1 + I_2 - I_3 - I_4$$

$$\langle E \rangle_{trip} = I_1 + I_2 - I_3 - I_4$$

$$I_1 = \frac{1}{2}\langle 1s(1)2s(2) | H | 1s(1)2s(2) \rangle = \frac{1}{2}\langle 1s(1)2s(2) | H_1 + H_2 + \frac{1}{r_{12}} | 1s(1)2s(2) \rangle$$

$$I_1 = \frac{1}{2}\langle 1s(1)2s(2) | H_1 | 1s(1)2s(2) \rangle + \frac{1}{2}\langle 1s(1)2s(2) | H_2 | 1s(1)2s(2) \rangle$$

$$\qquad + \frac{1}{2}\langle 1s(1)2s(2) | \frac{1}{r_{12}} | 1s(1)2s(2) \rangle$$

$$I_1 = \frac{1}{2}\langle 2s(2) | 2s(2) \rangle\langle 1s(1) | H_1 | 1s(1) \rangle + \frac{1}{2}\langle 1s(1) | 1s(1) \rangle\langle 2s(2) | H_2 | 2s(2) \rangle$$

$$\qquad + \frac{1}{2}\langle 1s(1)2s(2) | \frac{1}{r_{12}} | 1s(1)2s(2) \rangle$$

$$I_1 = \frac{1}{2}\langle 1s(1) | H_1 | 1s(1) \rangle + \frac{1}{2}\langle 2s(2) | H_2 | 2s(2) \rangle + \frac{1}{2}\langle 1s(1)2s(2) | \frac{1}{r_{12}} | 1s(1)2s(2) \rangle$$

$$I_1 = \frac{1}{2}\langle 1s(1)2s(2)|H_1 + H_2 + \frac{1}{r_{12}}|1s(1)2s(2)\rangle$$

$$I_1 = \frac{1}{2}\langle 1s(1)|H_1|1s(1)\rangle + \frac{1}{2}\langle 2s(2)|H_2|2s(2)\rangle + \frac{1}{2}\langle 1s(1)2s(2)|\frac{1}{r_{12}}|1s(1)2s(2)\rangle$$

$$I_1 = \frac{1}{2}\varepsilon_{1s} + \frac{1}{2}\varepsilon_{2s} + \frac{1}{2}J_{1s2s} \quad \text{where} \quad J_{1s2s} = \langle 1s(1)2s(2)|\frac{1}{r_{12}}|1s(1)2s(2)\rangle$$

Similarly,

$$I_2 = \frac{1}{2}\langle 2s(1)1s(2)|H_1 + H_2 + \frac{1}{r_{12}}|2s(1)1s(2)\rangle$$

$$I_2 = \frac{1}{2}\varepsilon_{2s} + \frac{1}{2}\varepsilon_{1s} + \frac{1}{2}J_{1s2s}$$

$$\langle E\rangle_{trip} = I_1 + I_2 - I_3 - I_4$$

$$I_3 = \frac{1}{2}\langle 1s(1)2s(2)|H|2s(1)1s(2)\rangle$$

$$I_3 = \frac{1}{2}\langle 1s(1)2s(2)|H_1 + H_2 + \frac{1}{r_{12}}|2s(1)1s(2)\rangle$$

$$I_3 = \frac{1}{2}\langle 1s(1)2s(2)|H_1|2s(1)1s(2)\rangle + \frac{1}{2}\langle 1s(1)2s(2)|H_2|2s(1)1s(2)\rangle$$
$$+ \frac{1}{2}\langle 1s(1)2s(2)|\frac{1}{r_{12}}|2s(1)1s(2)\rangle$$

$$
\begin{array}{cc}
0 & 0 \\
\| & \|
\end{array}
$$
$$I_3 = \frac{1}{2}\langle 2s(2)|1s(2)\rangle\langle 1s(1)|H_1|2s(1)\rangle + \frac{1}{2}\langle 1s(1)|2s(1)\rangle\langle 2s(2)|H_2|1s(2)\rangle$$
$$+ \frac{1}{2}\langle 1s(1)2s(2)|\frac{1}{r_{12}}|2s(1)1s(2)\rangle$$

$$I_3 = \frac{1}{2}\langle 1s(1)2s(2)|\frac{1}{r_{12}}|2s(1)1s(2)\rangle$$

$$\langle E \rangle_{trip} = I_1 + I_2 - I_3 - I_4$$

$$I_3 = \frac{1}{2}\langle 1s(1)2s(2)|H_1 + H_2 + \frac{1}{r_{12}}|2s(1)1s(2)\rangle$$

$$I_3 = \frac{1}{2}\langle 1s(1)2s(2)|\frac{1}{r_{12}}|2s(1)1s(2)\rangle$$

$$I_3 = \frac{1}{2}K_{1s2s} \quad \text{where} \quad K_{1s2s} = \langle 1s(1)2s(2)|\frac{1}{r_{12}}|2s(1)1s(2)\rangle$$

Similarly,

$$I_4 = \frac{1}{2}\langle 2s(1)1s(2)|H_1 + H_2 + \frac{1}{r_{12}}|1s(1)2s(2)\rangle$$

$$I_4 = \frac{1}{2}K_{1s2s}$$

$$\langle E \rangle_{trip} = I_1 + I_2 - I_3 - I_4$$

$$\langle E \rangle_{trip} = \left(\frac{1}{2}\varepsilon_{1s} + \frac{1}{2}\varepsilon_{2s} + \frac{1}{2}J_{1s2s}\right) + \left(\frac{1}{2}\varepsilon_{2s} + \frac{1}{2}\varepsilon_{1s} + \frac{1}{2}J_{1s2s}\right) - \left(\frac{1}{2}K_{1s2s}\right) - \left(\frac{1}{2}K_{1s2s}\right)$$

$$\langle E \rangle_{trip} = \underset{1}{\varepsilon_{1s}} + \underset{2}{\varepsilon_{2s}} + \underset{3}{J_{1s2s}} - \underset{4}{K_{1s2s}}$$

where $\quad J_{1s2s} = \langle 1s(1)2s(2)|\frac{1}{r_{12}}|1s(1)2s(2)\rangle \quad K_{1s2s} = \langle 1s(1)2s(2)|\frac{1}{r_{12}}|2s(1)1s(2)\rangle$

$$J_{1s2s} = \iint \frac{1s(1)^2 2s(2)^2}{r_{12}} d\vec{r}_1 d\vec{r}_2 \qquad K_{1s2s} = \iint \frac{[1s(1)2s(1)]\cdot[1s(2)2s(2)]}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

1. Energy of electron in 1s He$^+$ orbital   3. Coulomb (repulsion) Integral

2. Energy of electron in 2s He$^+$ orbital   4. Exchange Integral

$$\langle E \rangle_{trip} = \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} - K_{1s2s}$$

1   2   3   4

$$J_{1s2s} = \int\int \frac{1s(1)^2 2s(2)^2}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad \textbf{Always positive}$$

3. Coulomb (repulsion) Integral

The integrand of the Coulomb integral represents the repulsion of two infinitesimal electron densities, $\rho(1)=1s(1)^2$ and $\rho(2)=2s(2)^2$, separated by a distance, r_{12}. The repulsion is summed over all infinitesimal electron densities.

$$K_{1s2s} = \int\int \frac{[1s(1)2s(1)]\cdot[1s(2)2s(2)]}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad \textbf{Usually positive}$$

4. Exchange Integral

Arises purely from the antisymmetry of the spatial function with respect to electron exchange. It has no classical analog.

If the above calculation had been performed with a simple product wavefunction, ψ_{spat} = 1s(1)2s(2), there would be no exchange integral

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Singlet State Energy

Triplet: **One of 3 components of the Triplet**

$$\psi_{T2} = \left[\frac{1}{\sqrt{2}}(1s(1)2s(2) - 2s(1)1s(2))\right]\cdot\left[\frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2)\right]$$

$$\langle E \rangle_{trip} = \left\langle \psi_{antisym}(\vec{r}_1,\vec{r}_2) \middle| H \middle| \psi_{antisym}(\vec{r}_1,\vec{r}_2) \right\rangle = \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} - K_{1s2s}$$

Singlet: $\psi_{Sing} = \left[\frac{1}{\sqrt{2}}(1s(1)2s(2) + 2s(1)1s(2))\right]\cdot\left[\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\right]$

$$\langle E \rangle_{Sing} = \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} + K_{1s2s}$$

$$\psi_{T2} = \left[\frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)\right] \cdot \left[\frac{1}{\sqrt{2}}\left(\alpha_1\beta_2 + \beta_1\alpha_2\right)\right]$$

$$\psi_{Sing} = \left[\frac{1}{\sqrt{2}}\left(1s(1)2s(2) + 2s(1)1s(2)\right)\right] \cdot \left[\frac{1}{\sqrt{2}}\left(\alpha_1\beta_2 - \beta_1\alpha_2\right)\right]$$

$$\left\langle E \right\rangle_{Trip} = \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} - K_{1s2s} \qquad J_{1s2s} = \left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|1s(1)2s(2)\right\rangle$$

$$\left\langle E \right\rangle_{Sing} = \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} + K_{1s2s} \qquad K_{1s2s} = \left\langle 1s(1)2s(2)\left|\frac{1}{r_{12}}\right|2s(1)1s(2)\right\rangle$$

Because the exchange integral is almost always positive, the
energy of excited triplet state Helium is lower than that of the
excited state singlet.

The physical basis for the lower energy of the triplet is that
the wavefunction (and therefore the probability) is small when
the coordinates of the two electrons are close to each other.

Therefore, the electron-electron repulsion energy is minimized

Chapter 7

Multielectron Atoms

Part C: Many Electron Atoms

Part C: Many Electron Atoms

- **The Hamiltonian for Multielectron Atoms**

- The Hartree Method: Helium

- Koopman's Theorem

- Extension to Multielectron Atoms

- Antisymmetrized Wavefunctions: Slater Determinants

- The Hartree-Fock Method

- Hartree-Fock Orbital Energies for Argon

- Electron Correlation

The Hamiltonian for Multielectron Atoms

Helium

SI Units: $\quad H = -\dfrac{\hbar^2}{2m}\nabla_1^2(\vec{r}_1) - \dfrac{\hbar^2}{2m}\nabla_2^2(\vec{r}_2) - \dfrac{2e^2}{4\pi\varepsilon_0 r_1} - \dfrac{2e^2}{4\pi\varepsilon_0 r_2} + \dfrac{e^2}{4\pi\varepsilon_0 r_{12}}$ $\quad$ Z = 2

Atomic Units: $\quad H = -\dfrac{1}{2}\nabla_1^2(\vec{r}_1) - \dfrac{1}{2}\nabla_2^2(\vec{r}_2) - \dfrac{2}{r_1} - \dfrac{2}{r_2} + \dfrac{1}{r_{12}}$

Multielectron Atoms

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 \;-\; \sum_{i=1}^{N}\frac{Z}{r_i} \;+\; \sum_{i=1}^{N-1}\sum_{j>i}\frac{1}{r_{ij}}$$

Elect   **Elect-**   **Elect-**
KE   **Nuc**   **Elect**
               PE   **PE**

$$\sum_{i=1}^{N-1}\sum_{j>i}\frac{1}{r_{ij}} = \frac{1}{r_{12}} + \frac{1}{r_{13}} + \cdots + \frac{1}{r_{23}} + \frac{1}{r_{24}} + \cdots + \frac{1}{r_{34}} + \frac{1}{r_{35}} + \cdots$$

Atomic Orbitals

In performing quantum mechanical calculations on multielectron atoms, it is usually assumed that each electron is in an atomic orbital, ϕ, which can be described as a Linear Combination of Hydrogen-like orbitals, which are called Slater Type Orbitals (STOs).

These STOs are usually denoted as χ_i (although some texts and articles will use a different symbol).

Thus: $\quad \varphi = \sum c_i \chi_i$

The goal of quantum mechanical calculations is to find the values of the c_i which minimize the energy (via the Variational Principle).

These STOs are also used to characterize the Molecular Orbitals occupied by electrons in molecules.

We will discuss these STOs in significantly greater detail in Chapter 11, when we describe quantum mechanical calculations on polyatomic molecules.

Part C: Many Electron Atoms

- The Hamiltonian for Multielectron Atoms

- **The Hartree Method: Helium**

- Koopman's Theorem

- Extension to Multielectron Atoms

- Antisymmetrized Wavefunctions: Slater Determinants

- The Hartree-Fock Method

- Hartree-Fock Orbital Energies for Argon

- Electron Correlation

The Hartree Method: Helium

Hartree first developed the theory, but did not consider that electron wavefunctions must be antisymmetric with respect to exchange.

Fock then extended the theory to include antisymmetric wavefunctions.

We will proceed as follows:

1. Outline Hartree method as applied to Helium

2. Show the results for atoms with >2 electrons

3. Discuss antisymmetric wavefunctions for multielectron atoms (Slater determinants)

4. Show how the Hartree equations are modified to get the the "Hartree-Fock" equations.

Basic Assumption

Each electron is in an orbital, ϕ_i (e.g. a sum of STOs).

The total "variational" wavefunction is the product of one electron wavefunctions: $\psi(\vec{r}_1, \vec{r}_2) = \varphi_1(\vec{r}_1) \cdot \varphi_2(\vec{r}_2)$

Procedure

"Guess" initial values the individual atomic orbitals: $\varphi_1^{init}(\vec{r}_1)$ and $\varphi_2^{init}(\vec{r}_2)$
(This would be an initial set of coefficients in the
linear combination of STOs). i.e. $\phi_1 = \sum c_i \chi_i = c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + ...$

Let's first look at electron #1. Assume that its interaction with the second electron (or with electrons #2, #3, #4, ... in multielectron atoms) is with the average "smeared" out electron density of the second electron.

SI Units   **Atomic Units**

$$V_1^{eff}(\vec{r}_1) = e \cdot \int \frac{e\left|\varphi_2^{init}(\vec{r}_2)\right|^2}{4\pi\varepsilon_0 r_{12}} d\vec{r}_2 \quad \text{or} \quad V_1^{eff}(\vec{r}_1) = \int \frac{\left|\varphi_2^{init}(\vec{r}_2)\right|^2}{r_{12}} d\vec{r}_2$$

$$= \left\langle \varphi_2^{init}(2) \left| \frac{1}{r_{12}} \right| \varphi_2^{init}(2) \right\rangle$$

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It can be shown (using the Variational Principle and a significant amount of algebra) that the "effective" Schrödinger equation for electron #1 is:

$$H_1^{eff}\varphi_1 = \varepsilon_1 \varphi_1 \quad \text{where} \quad H_1^{eff} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{eff} \qquad V_1^{eff} = \left\langle \varphi_2^{init}(2) \left| \frac{1}{r_{12}} \right| \varphi_2^{init}(2) \right\rangle$$

elect   **elect-**   **"Effective"**
   KE   **Nuc**   **elect-elect**
        PE   **PE**

This equation can be solved exactly to get a new estimate for the function, ϕ_1^{new} (e.g. a new set of coefficients of the STOs).

There is an analogous equation for ϕ_2:

$$H_2^{eff}\varphi_2 = \varepsilon_2 \varphi_2 \quad \text{where} \quad H_2^{eff} = -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + V_2^{eff} \qquad V_2^{eff} = \left\langle \varphi_1^{init}(1) \left| \frac{1}{r_{12}} \right| \varphi_1^{init}(1) \right\rangle$$

This equation can be solved exactly to get a new estimate for the function, ϕ_2^{new} (e.g. a new set of coefficients of the STOs).

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4

A Problem of Consistency

We used initial guesses for the atomic orbitals, $\varphi_1^{init}(\vec{r}_2)$ and $\varphi_2^{init}(\vec{r}_2)$, to compute V_1^{eff} and V_2^{eff} in the Hartree Equations: .

$$H_1^{eff}\varphi_1 = \varepsilon_1\varphi_1 \quad \text{where} \quad H_1^{eff} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{eff} \quad V_1^{eff} = \left\langle \varphi_2^{init}(2)\left|\frac{1}{r_{12}}\right|\varphi_2^{init}(2)\right\rangle \quad \longleftarrow$$

$$H_2^{eff}\varphi_2 = \varepsilon_2\varphi_2 \quad \text{where} \quad H_2^{eff} = -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + V_2^{eff} \quad V_2^{eff} = \left\langle \varphi_1^{init}(1)\left|\frac{1}{r_{12}}\right|\varphi_1^{init}(1)\right\rangle \quad \longleftarrow$$

We then solved the equations to get new orbitals, $\varphi_1^{new}(\vec{r}_2)$ and $\varphi_2^{new}(\vec{r}_2)$

If these new orbitals had been used to calculate V_1^{eff} and V_2^{eff} , we would have gotten different effective potentials.

Oy Vey!!! What a mess!!!

What can we do to fix the problem that the orbitals resulting from solving the effective Schrödinger equations are not the same as the orbitals that we used to construct the equations??

The Solution: Iterate to Self-Consistency

Repeat the procedure. This time, use $\varphi_1^{new}(\vec{r}_1)$ and $\varphi_2^{new}(\vec{r}_2)$ to construct V_1^{eff} and V_2^{eff} and solve the equations again.

Now, you'll get an even newer pair of orbitals, $\varphi_1^{newer}(\vec{r}_1)$ and $\varphi_2^{newer}(\vec{r}_2)$

BUT: You have the same problem again. The effective Hamiltonians that were used to compute this newest pair of orbitals were constructed from the older set of orbitals.

Well, I suppose you could repeat the procedure again, and again, and again, and again, until you either: (1) go insane

(2) quit Chemistry and establish a multibillion dollar international trucking conglomerate (please remember me in your will).

Fortunately, the problem is not so dire. Usually, you will find that the new orbitals predicted by solving the equations get closer and closer to the orbitals used to construct the effective Hamiltonians.

When they are sufficiently close, you stop, declare victory, and go out and celebrate with a dozen Krispy Kreme donuts (or pastrami sandwiches on rye, if that's your preference).

When the output orbitals are consistent with the input orbitals, you have achieved a "Self-Consistent Field" (SCF).

Often, you will reach the SCF criterion within 10-20 iterations, although it may take 50-60 iterations or more in difficult cases.

While the procedure appears very tedious and time consuming, it's actually quite fast on modern computers. A single SCF calculation on a moderate sized molecule (with 50-100 electrons) can take well under 1 second.

The Energy

A. The total energy

$$H = -\frac{1}{2}\nabla_1^2(\vec{r_1}) - \frac{1}{2}\nabla_2^2(\vec{r_2}) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} = \left[-\frac{1}{2}\nabla_1^2(\vec{r_1}) - \frac{2}{r_1} \right] + \left[-\frac{1}{2}\nabla_2^2(\vec{r_2}) - \frac{2}{r_2} \right] + \frac{1}{r_{12}}$$

$$H = H_1^{He^+}(1) + H_2^{He^+}(2) + \frac{1}{r_{12}} \quad \text{where} \quad H_1^{He^+} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} \quad \text{and} \quad H_2^{He^+} = -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}$$

H_1 and H_2 are just each the Hamiltonian for the electron in a He$^+$ ion.

$$E = \int \psi * H\psi \, d\tau = \left\langle \varphi_1(1)\varphi_2(2) \middle| H \middle| \varphi_1(1)\varphi_2(2) \right\rangle$$

$$E = \left\langle \varphi_1(1)\varphi_2(2) \middle| H_1^{He^+}(1) + H_2^{He^+}(2) + \frac{1}{r_{12}} \middle| \varphi_1(1)\varphi_2(2) \right\rangle$$

We're assuming that ϕ_1 and ϕ_2 have both been normalized.

$$E = \left\langle \varphi_1(1)\varphi_2(2) \middle| H_1^{He^+}(1) + H_2^{He^+}(2) + \frac{1}{r_{12}} \middle| \varphi_1(1)\varphi_2(2) \right\rangle$$

$E = I_1 + I_2 + J_{12}$ Remember, this is the total energy of the two electrons.

$$I_1 = \left\langle \varphi_1(1)\varphi_2(2) \middle| H_1^{He^+}(1) \middle| \varphi_1(1)\varphi_2(2) \right\rangle = \left\langle \varphi_2(2) \middle| \varphi_2(2) \right\rangle \left\langle \varphi_1(1) \middle| H_1^{He^+}(1) \middle| \varphi_1(1) \right\rangle = \left\langle \varphi_1(1) \middle| H_1^{He^+} \middle| \varphi_1(1) \right\rangle$$

I_1 is the energy of an electron in a He$^+$ ion.

$$I_2 = \left\langle \varphi_1(1)\varphi_2(2) \middle| H_2^{He^+}(2) \middle| \varphi_1(1)\varphi_2(2) \right\rangle = \left\langle \varphi_1(1) \middle| \varphi_1(1) \right\rangle \left\langle \varphi_2(2) \middle| H_2^{He^+}(2) \middle| \varphi_2(2) \right\rangle = \left\langle \varphi_2(2) \middle| H_2^{He^+} \middle| \varphi_1(2) \right\rangle$$

I_2 is the energy of an electron in a He$^+$ ion.

$$J_{12} = \left\langle \varphi_1(1)\varphi_2(2) \middle| \frac{1}{r_{12}} \middle| \varphi_1(1)\varphi_2(2) \right\rangle = \int_{\vec{r}_1} \int_{\vec{r}_2} \frac{\left[\varphi_1^*(\vec{r}_1)\varphi_1(\vec{r}_1) \right]\left[\varphi_2^*(\vec{r}_2)\varphi_2(\vec{r}_2) \right]}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

J_{12} is the Coulomb Integral and represents the coulombic repulsion energy of the two electrons

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The Energy

B. The Individual Orbital Energies, ε_1 and ε_2

Note: You are not responsible for the details of the calculation below - just the final comparison (slide after next)

$$H_1^{eff}\varphi_1 = \varepsilon_1\varphi_1 \quad \text{where} \quad H_1^{eff} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{eff} = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + \left\langle \varphi_2(2) \middle| \frac{1}{r_{12}} \middle| \varphi_2(2) \right\rangle$$

$$\varepsilon_1 = \left\langle \varphi_1(1) \middle| H_1^{eff} \middle| \varphi_1(1) \right\rangle = \left\langle \varphi_1(1) \middle| \left\{ -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + \left\langle \varphi_2(2) \middle| \frac{1}{r_{12}} \middle| \varphi_2(2) \right\rangle \right\} \middle| \varphi_1(1) \right\rangle$$

$$\varepsilon_1 = \left\langle \varphi_1(1) \middle| -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} \middle| \varphi_1(1) \right\rangle + \left\langle \varphi_1(1) \middle| \left\{ \left\langle \varphi_2(2) \middle| \frac{1}{r_{12}} \middle| \varphi_2(2) \right\rangle \right\} \middle| \varphi_1(1) \right\rangle$$

$$\varepsilon_1 = \left\langle \varphi_1(1) \middle| H_1^{He^+} \middle| \varphi_2(1) \right\rangle + \left\langle \varphi_1(1)\varphi_2(2) \middle| \frac{1}{r_{12}} \middle| \varphi_1(1)\varphi_2(2) \right\rangle$$

$$\boxed{\varepsilon_1 = I_1 + J_{12}}$$

$$\text{where} \quad J_{12} = \left\langle \varphi_1(1)\varphi_2(2) \middle| \frac{1}{r_{12}} \middle| \varphi_1(1)\varphi_2(2) \right\rangle = \int\int \frac{\left[\varphi_1^*\varphi_1 \right]\left[\varphi_2^*\varphi_2 \right]}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

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The Energy

B. The Individual Orbital Energies, ε_1 and ε_2 (Cont'd.)

Analogously, one finds for ε_2:

$$H_2^{eff}\varphi_2 = \varepsilon_2\varphi_2 \quad \text{where} \quad H_2^{eff} = -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + V_2^{eff} = -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + \left\langle\varphi_1(1)\Big|\frac{1}{r_{12}}\Big|\varphi_1(1)\right\rangle$$

$$\varepsilon_2 = \left\langle\varphi_2(2)\big|H_2^{eff}\big|\varphi_2(2)\right\rangle = \left\langle\varphi_2(2)\Big|\left\{-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + \left\langle\varphi_1(1)\Big|\frac{1}{r_{12}}\Big|\varphi_1(1)\right\rangle\right\}\Big|\varphi_2(2)\right\rangle$$

$$\varepsilon_2 = \left\langle\varphi_2(2)\Big|-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}\Big|\varphi_2(2)\right\rangle + \left\langle\varphi_2(2)\Big|\left\{\left\langle\varphi_1(1)\Big|\frac{1}{r_{12}}\Big|\varphi_1(1)\right\rangle\right\}\Big|\varphi_2(2)\right\rangle$$

$$\varepsilon_2 = \left\langle\varphi_2(2)\big|H_2^{He^+}\big|\varphi_2(2)\right\rangle + \left\langle\varphi_1(1)\varphi_2(2)\Big|\frac{1}{r_{12}}\Big|\varphi_1(1)\varphi_2(2)\right\rangle$$

$$\boxed{\varepsilon_2 = I_2 + J_{12}}$$

$$\text{where} \quad J_{12} = \left\langle\varphi_1(1)\varphi_2(2)\Big|\frac{1}{r_{12}}\Big|\varphi_1(1)\varphi_2(2)\right\rangle = \iint\frac{\left[\varphi_1^*\varphi_1\right]\left[\varphi_2^*\varphi_2\right]}{r_{12}}d\vec{r}_1 d\vec{r}_2$$

$$\varepsilon_1 = I_1 + J_{12} \qquad\qquad \varepsilon_2 = I_2 + J_{12}$$

The sum of orbital energies: $\varepsilon_1 + \varepsilon_2 = \left(I_1 + J_{12}\right) + \left(I_2 + J_{12}\right) = I_1 + I_2 + 2J_{12}$

C. Total Energy versus sum of orbital energies

The sum of orbital energies: $\varepsilon_1 + \varepsilon_2 = I_1 + I_2 + 2J_{12}$

The total energy: $E = I_1 + I_2 + J_{12}$

The sum of the orbital energies has one too many Coulomb integrals, J_{12}.

The reason is that **each** orbital energy has the full electron-electron repulsion – You're counting it one time too many!!!

$$\varepsilon_1 + \varepsilon_2 = I_1 + I_2 + 2J_{12}$$

$$E = I_1 + I_2 + J_{12}$$

Therefore: $E = (I_1 + J_{12}) + (I_2 + J_{12}) - J_{12}$

$$\boxed{E = \varepsilon_1 + \varepsilon_2 - J_{12}}$$

We conclude that one must subtract the Coulomb repulsive energy, J_{12}, from the sum of orbital energies, $\varepsilon_1 + \varepsilon_2$, to correct for the double counting of the repulsion between the two electrons.

Part C: Many Electron Atoms

- The Hamiltonian for Multielectron Atoms

- The Hartree Method: Helium

- **Koopman's Theorem**

- Extension to Multielectron Atoms

- Antisymmetrized Wavefunctions: Slater Determinants

- The Hartree-Fock Method

- Hartree-Fock Orbital Energies for Argon

- Electron Correlation

Koopman's Theorem

Estimation of Atomic (or Molecular) Ionization Energies

Ionization Energy (IE): $M \rightarrow M^+ + e^-$ M is a neutral atom or molecule

$$\Delta E = IE = E(M^+) - E(M)$$

$$\varepsilon_1 = I_1 + J_{12} = \left(I_1 + I_2 + J_{12}\right) - I_2 = E - I_2$$

$$-\varepsilon_1 = I_2 - E = E(He^+) - E(He) = IE(He)$$

I_2 is the energy of the He^+ ion
E is the energy of the He atom

Koopman's Theorem: The ionization energy of an atom or molecule can be estimated as $-\varepsilon_H$, which is the orbital energy of the highest occupied orbital.

$M \rightarrow M^+ + e^-$ M is a neutral atom or molecule

$$\Delta E = IE = E(M^+) - E(M)$$

Koopman's Theorem: The ionization energy of an atom or molecule can be estimated as $-\varepsilon_H$, which is the orbital energy of the highest occupied orbital.

There are two approximations in using Koopman's theorem to estimate ionization energies which limit the accuracy:

1. Electron "relaxation" of the remaining N-1 electrons is neglected.

2. Differences in the "correlation energy" [to be discussed later] of the electrons in the ion and neutral atom are ignored.

To obtain an accurate estimate of the ionization energy, one should perform quantum mechanical energy calculations on the neutral atom and ion to get E(M) and E(M+), from which the IE can be computed by the definition.

Electron Affinity

Electron Affinity (EA): $M + e^- \rightarrow M^-$ M is a neutral atom or molecule

$$\Delta E = EA = E(M^-) - E(M)$$

With this "new" definition of Electron Affinity, a negative
value of EA means that adding an electron to the atom
is an exothermic process.

Note: The "old" definition of Electron Affinity is the energy "released"
when an electron is added to a neutral atom.

EA(old) = - EA(new)

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The Hartree Method for Multielectron Atoms

The Hartree method for the more general N electron atom is a straightforward extension of the method outlined for the two electrons in Helium

Each of the N electrons has an effective Hamiltonian. For electron #1, for example:

$$H_1^{eff} \varphi_1 = \varepsilon_1 \varphi_1 \quad \text{where} \quad H_1^{eff} = -\frac{1}{2}\nabla_1^2 \; -\frac{Z}{r_1} \; + \; V_1^{eff}$$

<div align="center">
elect elect- "Effective"
KE   Nuc elect-elect
PE   PE
</div>

$$V_1^{eff} = \sum_{j=2}^{N} \left\langle \varphi_j^{init}(j) \left| \frac{1}{r_{1j}} \right| \varphi_j^{init}(j) \right\rangle = \left\langle \varphi_2^{init} \left| \frac{1}{r_{12}} \right| \varphi_2^{init} \right\rangle + \left\langle \varphi_3^{init} \left| \frac{1}{r_{13}} \right| \varphi_3^{init} \right\rangle + \cdots + \left\langle \varphi_N^{init} \left| \frac{1}{r_{1N}} \right| \varphi_N^{init} \right\rangle$$

As before, we are assuming that electron #1 is interacting with the "smeared out" electron density of electrons #2 to N.

There are equivalent equations for each electron, i, of the N electrons:

$$H_i^{eff} \varphi_i = \varepsilon_i \varphi_i \quad \text{where} \quad H_i^{eff} = -\frac{1}{2}\nabla_i^2 \; -\frac{Z}{r_i} \; + \; V_i^{eff}$$

$$V_i^{eff} = \sum_{j \neq i} \left\langle \varphi_j^{init}(j) \left| \frac{1}{r_{ij}} \right| \varphi_j^{init} \right\rangle = \sum_{j \neq i} \int \frac{\left| \varphi_j^{init}(\vec{r}_j) \right|^2}{r_{ij}} d\vec{r}_j$$

As in the two electron case, one assumes that the total wavefunction is the product of one electron wavefunctions:

$$\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \prod_{i=1}^{N} \varphi_i(\vec{r}_i) = \varphi_1(\vec{r}_1) \cdot \varphi_2(\vec{r}_2) \cdot \ldots \cdot \varphi_N(\vec{r}_N)$$

Initial guesses are made for each of the atomic functions, ϕ_i^{init}, which are used to compute the effective potentials, V_i^{eff}, and the N equations are solved to get a new set of ϕ's.

The procedure is repeated (iterated) until the guess wavefunctions are the same as the ones which are computed; i.e. until you reach a Self-Consistent Field (SCF)

The Energy

$$E = \sum_{i=1}^{N} \varepsilon_i - \sum_{i=1}^{N-1} \sum_{j>i} J_{ij}$$

$$E = \varepsilon_1 + \varepsilon_2 + \cdots - J_{12} - J_{13} - J_{14} - \cdots - J_{23} - J_{24} - \cdots$$

ε_i is the orbital energy of the i'th. electron. This is the eigenvalue of the effective Hamiltonian for the i'th. electron

J_{ij} is the Coulomb Integral describing the repulsion between an electron in orbital ϕ_i and an electron in orbital ϕ_j.

$$J_{ij} = \left\langle \varphi_i \varphi_j \left| \frac{1}{r_{12}} \right| \varphi_i \varphi_j \right\rangle = \int_{\vec{r}_1} \int_{\vec{r}_2} \frac{\left|\varphi_i(\vec{r}_1)\right|^2 \left|\varphi_j(\vec{r}_2)\right|^2}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

Note: If N=2 (i.e. He), the above expression for E reduces to

$$E = \varepsilon_1 + \varepsilon_2 - J_{12}$$

Math. Preliminary: Determinants

A determinant of order N is an NxN array of numbers (elements). The total number of elements is N^2.

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1N} \\ a_{21} & & & & a_{2N} \\ a_{31} & & & & a_{3N} \\ \vdots & & & & \vdots \\ a_{N1} & a_{N2} & a_{N3} & \cdots & a_{NN} \end{vmatrix}$$

Second Order Determinant

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{21}a_{12}$$

Note: The expansion has 2 terms

Third (and higher) Order Determinant: Expansion by Cofactors

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

$$= a_{11}(a_{22}a_{33} - a_{32}a_{23}) - a_{12}(a_{21}a_{33} - a_{31}a_{23}) + a_{13}(a_{21}a_{32} - a_{31}a_{22})$$

Note: The expansion has 6 terms

Example: Determinant Expansion/Evaluation

Determine the numerical value of the determinant: $\begin{vmatrix} 1 & 2 & 3 \\ 4 & 1 & 5 \\ 6 & 0 & 2 \end{vmatrix}$

$$\begin{vmatrix} 1 & 2 & 3 \\ 4 & 1 & 5 \\ 6 & 0 & 2 \end{vmatrix} = 1 \cdot \begin{vmatrix} 1 & 5 \\ 0 & 2 \end{vmatrix} - 2 \cdot \begin{vmatrix} 4 & 5 \\ 6 & 2 \end{vmatrix} + 3 \cdot \begin{vmatrix} 4 & 1 \\ 6 & 0 \end{vmatrix}$$

$$= 1 \cdot \left[(1)(2) - (0)(5) \right] - 2 \cdot \left[(4)(2) - (6)(5) \right] + 3 \cdot \left[(4)(0) - (6)(1) \right]$$

$$= 1 \cdot \left[2 - 0 \right] - 2 \cdot \left[8 - 30 \right] + 3 \cdot \left[0 - 6 \right]$$

$$= 1 \cdot (2) - 2 \cdot (-22) + 3 \cdot (-6) = 2 + 44 - 18 = 28$$

Fourth Order Determinant

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix} = a_{11} \left| 3x3 \right| - a_{12} \left| 3x3 \right| + a_{13} \left| 3x3 \right| - a_{14} \left| 3x3 \right|$$

Note: Each 3x3 determinant has 6 terms.
Therefore, the 4x4 determinant has 4x6 = 24 terms.

General Properties of Determinants

Property #1: An NxN determinant has N! terms.

Property #2: If two columns or rows of a determinant are exchanged, then the value of the determinant changes sign.

Property #3: If two columns or rows of a determinant are the same, then the value of the determinant is 0.

Part C: Many Electron Atoms

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Slater Determinants

Review: The Pauli Antisymmetry Principle

The permutation operator, $\hat{P}_{ij}$, exchanges the coordinates of two electrons in a wavefunction.

Permuting two identical particles will not change the probability

density:
$$\left[\hat{P}_{ij}\psi(\vec{r}_i,\vec{r}_j)\right]^2 = \left[p_{ij}\psi(\vec{r}_i,\vec{r}_j)\right]^2$$

Therefore: $p_{ij} = \pm 1$

Pauli Principle: All elementary particles have an intrinsic angular momentum called spin. There are two types of particles, with different permutation properties:

Bosons: Integral spin (0, 1, 2,…) $P_{ij}(\psi) = +\psi$

Fermions: Half integral spin (1/2, 3/2,…) $P_{ij}(\psi) = -\psi$

Electrons (s = ½) are fermions.

Therefore, wavefunctions are antisymmetric with respect to electron exchange (permutation).

$$\hat{P}_{ij}\psi(\vec{r}_i,\vec{r}_j) = \psi(\vec{r}_j,\vec{r}_i) = -\psi(\vec{r}_i,\vec{r}_j)$$

Note that the permutation operator exchanges both the spatial and spin coordinates of the electrons.

Review: Ground State Helium

$$\psi = \frac{1}{\sqrt{2}}\left[\varphi_{1s}(\vec{r}_1)\alpha_1\varphi_{1s}(\vec{r}_2)\beta_2 - \varphi_{1s}(\vec{r}_1)\beta_1\varphi_{1s}(\vec{r}_2)\alpha_2\right]$$

or $\psi = \frac{1}{\sqrt{2}}\left[1s(1)\alpha_1 1s(2)\beta_2 - 1s(1)\beta_1 1s(2)\alpha_2\right]$ This wavefunction is antisymmetric with respect to exchange of electrons 1 and 2.

Shorthand

or $\psi = \frac{1}{\sqrt{2}}1s(1)1s(2)\left[\alpha_1\beta_2 - \beta_1\alpha_2\right]$

Factored Form

The electron configuration of ground state Lithium is $1s^2 2s^1$.

The wavefunction, $\psi(1,2,3) = 1s(1)\alpha_1 1s(2)\beta_2 2s(3)\alpha_3$, just won't do.

It's not either symmetric or antisymmetric with respect to electron exchange.

An appropriate antisymmetric wavefunction is:

$$\psi(1,2,3) = \frac{1}{\sqrt{6}}\begin{bmatrix} 1s(1)\alpha_1 1s(2)\beta_2 2s(3)\alpha_3 - 1s(1)\alpha_1 2s(2)\alpha_2 1s(3)\beta_3 \\ -1s(1)\beta_1 1s(2)\alpha_2 2s(3)\alpha_3 + 1s(1)\beta_1 2s(2)\alpha_2 1s(3)\alpha_3 \\ +2s(1)\alpha_1 1s(2)\alpha_2 1s(3)\beta_3 - 2s(1)\alpha_1 1s(2)\beta_2 1s(3)\alpha_3 \end{bmatrix}$$

Question: How do I know that this wavefunction is antisymmetric?

Answer: Try it out. Exchange electrons 1 and 2.

Terms 1 and 3 switch with each other, but each with opposite sign.

Terms 2 and 5 switch with each other, but each with opposite sign.

Terms 4 and 6 switch with each other, but each with opposite sign.

Voila!! The wavefunction has changed sign.

Question: How did I figure out how to pick out the appropriate six terms?

Answer: It was easy!!   Mookie showed me how.

Problem: The Mookster won't be around to write out the antisymmetric wavefunctions for you on a test.

Solution: I guess I should impart the magic of King Mookie, and show you how it's done.

Slater Determinants

The ground state Helium wavefunction is:

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[1s(1)\alpha_1 1s(2)\beta_2 - 1s(1)\beta_1 1s(2)\alpha_2\right]$$

It can be written as a 2x2 determinant, called a Slater determinant (named after J. C. Slater, who first came up with the idea).

$$\psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\beta_1 \\ 1s(2)\alpha_2 & 1s(2)\beta_2 \end{vmatrix} = \frac{1}{\sqrt{2}}\left[1s(1)\alpha_1 1s(2)\beta_2 - 1s(1)\beta_1 1s(2)\alpha_2\right]$$

Note that different "spinorbitals"** are put in different columns.

Different electrons are put in different rows.

The coefficient is to normalize the antisymmetrized wavefunction.

**A spinorbital is just the combination of the spatial and spin part of an orbital taken together.

$$\psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\beta_1 \\ 1s(2)\alpha_2 & 1s(2)\beta_2 \end{vmatrix} = \frac{1}{\sqrt{2}} \left[1s(1)\alpha_1 1s(2)\beta_2 - 1s(1)\beta_1 1s(2)\alpha_2 \right]$$

Two properties of determinants come in very handy.

Property #2: If two columns or rows of a determinant are exchanged, then the value of the determinant changes sign.

$$P_{12}\psi(1,2) = \psi(2,1) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(2)\alpha_2 & 1s(2)\beta_2 \\ 1s(1)\alpha_1 & 1s(1)\beta_1 \end{vmatrix} = \frac{1}{\sqrt{2}} \left[1s(1)\beta_1 1s(2)\alpha_2 - 1s(1)\alpha_1 1s(2)\beta_2 \right]$$

$$= -\frac{1}{\sqrt{2}} \left[1s(1)\alpha_1 1s(2)\beta_2 - 1s(1)\beta_1 1s(2)\alpha_2 \right] = -\psi(1,2)$$

Hey!! That's nice!!

A Slater Determinant is automatically antisymmetric with respect to the exchange of two electrons.

Property #3: If two columns or rows of a determinant are the same, then the value of the determinant is 0.

Let's put both electrons in the same spinorbital, say 1sα, and see what happens.

$$\psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\alpha_1 \\ 1s(2)\alpha_2 & 1s(2)\alpha_2 \end{vmatrix} = \frac{1}{\sqrt{2}} \left[1s(1)\alpha_1 1s(2)\alpha_2 - 1s(1)\alpha_1 1s(2)\alpha_2 \right] = 0$$

This explains the more commonly stated form of the Pauli Principle:

No two electrons can occupy the same orbital with the same spin.

The Lithium Ground State Wavefunction

The electron configuration of ground state Lithium is $1s^2 2s^1$.

The antisymmetrized wavefunction is:

$$\psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\beta_1 & 2s(1)\alpha_1 \\ 1s(2)\alpha_2 & 1s(2)\beta_2 & 2s(2)\alpha_2 \\ 1s(3)\alpha_3 & 1s(3)\beta_3 & 2s(3)\alpha_3 \end{vmatrix}$$

The factor, $\frac{1}{\sqrt{3!}}$, is to normalize the wavefunction (which has 3! terms)

Expanding the wavefunction

$$\psi(1,2,3) = \frac{1}{\sqrt{6}} \left[\begin{array}{l} 1s(1)\alpha_1 \begin{vmatrix} 1s(2)\beta_2 & 2s(2)\alpha_2 \\ 1s(3)\beta_3 & 2s(3)\alpha_3 \end{vmatrix} - 1s(1)\beta_1 \begin{vmatrix} 1s(2)\alpha_2 & 2s(2)\alpha_2 \\ 1s(3)\alpha_3 & 2s(3)\alpha_3 \end{vmatrix} \\ +2s(1)\alpha_1 \begin{vmatrix} 1s(2)\alpha_2 & 1s(2)\beta_2 \\ 1s(3)\alpha_3 & 1s(3)\beta_3 \end{vmatrix} \end{array} \right]$$

$$\psi(1,2,3) = \frac{1}{\sqrt{6}} \left[\begin{array}{l} 1s(1)\alpha_1 \left[1s(2)\beta_2 2s(3)\alpha_3 - 2s(2)\alpha_2 1s(3)\beta_3 \right] \\ -1s(1)\beta_1 \left[1s(2)\alpha_2 2s(3)\alpha_3 - 2s(2)\alpha_2 1s(3)\alpha_3 \right] \\ +2s(1)\alpha_1 \left[1s(2)\alpha_2 1s(3)\beta_3 - 1s(2)\beta_2 1s(3)\alpha_3 \right] \end{array} \right]$$

$$\psi(1,2,3) = \frac{1}{\sqrt{6}} \left[\begin{array}{l} 1s(1)\alpha_1 1s(2)\beta_2 2s(3)\alpha_3 - 1s(1)\alpha_1 2s(2)\alpha_2 1s(3)\beta_3 \\ -1s(1)\beta_1 1s(2)\alpha_2 2s(3)\alpha_3 + 1s(1)\beta_1 2s(2)\alpha_2 1s(3)\alpha_3 \\ +2s(1)\alpha_1 1s(2)\alpha_2 1s(3)\beta_3 - 2s(1)\alpha_1 1s(2)\beta_2 1s(3)\alpha_3 \end{array} \right]$$

We discussed earlier that this expanded (6 term) wavefunction is antisymmetric with respect to electron exchange.

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$$\psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\beta_1 & 2s(1)\alpha_1 \\ 1s(2)\alpha_2 & 1s(2)\beta_2 & 2s(2)\alpha_2 \\ 1s(3)\alpha_3 & 1s(3)\beta_3 & 2s(3)\alpha_3 \end{vmatrix}$$

The antisymmetry can also be shown by using the property of determinants.

Exchanging two electrons:

$$\psi(1,3,2) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\beta_1 & 2s(1)\alpha_1 \\ 1s(3)\alpha_3 & 1s(3)\beta_3 & 2s(3)\alpha_3 \\ 1s(2)\alpha_2 & 1s(2)\beta_2 & 2s(2)\alpha_2 \end{vmatrix} = -\psi(1,2,3)$$

Let's put all 3 electrons in the 1s orbital:

$$\psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\beta_1 & 1s(1)\alpha_1 \\ 1s(2)\alpha_2 & 1s(2)\beta_2 & 1s(2)\alpha_2 \\ 1s(3)\alpha_3 & 1s(3)\beta_3 & 1s(3)\alpha_3 \end{vmatrix} = 0$$

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General

$$\psi(1,2,3,\ldots) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi(1)\alpha_1 & \varphi(1)\beta_1 & \cdots & \varphi_n(1)\beta_1 \\ \varphi(2)\alpha_2 & \varphi(2)\beta_2 & & \\ \vdots & \vdots & & \\ \varphi(N)\alpha_N & \varphi(N)\beta_N & \cdots & \varphi_n(N)\beta_N \end{vmatrix}$$

Shorthand Notations (Various types)

$$\psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1) & \overline{1s}(1) & 2s(1) \\ 1s(2) & \overline{1s}(2) & 2s(2) \\ 1s(3) & \overline{1s}(3) & 2s(3) \end{vmatrix}$$

Use bars to indicate β spin. Lack of a bar means the spin is α

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Show diagonal terms only.   Lithium

$$\psi = \frac{1}{\sqrt{3!}} \left| 1s(1)\alpha_1 \quad 1s(2)\beta_2 \quad 2s(3)\alpha_3 \right|$$

Beryllium

$$\psi = \frac{1}{\sqrt{4!}} \left| 1s(1)\alpha_1 \quad 1s(2)\beta_2 \quad 2s(3)\alpha_3 \quad 2s(4)\beta_4 \right|$$

Other shorthand notations include:

Leaving out the normalization constant.

Leaving out the normalization constant and electron numbering.

Beryllium

$$\psi = \left| 1s\alpha \quad 1s\beta \quad 2s\alpha \quad 2s\beta \right|$$

To avoid confusion, the **only** shorthand I might use is the diagonal form at the top of this page.

Part C: Many Electron Atoms

- The Hamiltonian for Multielectron Atoms

- The Hartree Method: Helium

- Koopman's Theorem

- Extension to Multielectron Atoms

- Antisymmetrized Wavefunctions: Slater Determinants

- **The Hartree-Fock Method**

- Hartree-Fock Orbital Energies for Argon

- Electron Correlation

The Hartree-Fock Method

Hartree's original method neglected to consider that the wavefunction in a multielectron atom (or molecule) must be antisymmetric with respect to electron exchange.

The Hartree-Fock is an extension, using antisymmetrized wavefunctions.

It results in additional **"Exchange"** terms in the Effective Hamiltonians

and **"Exchange Integrals"** in the expression for the energy.

We actually encountered Exchange Integrals when we calculated the energy of excited state Helium in the $1s^12s^1$ electron configuration.

Review: The Energy of Triplet State Helium ($1s^12s^1$)

$$\psi = \psi_{antisym}(\vec{r}_1, \vec{r}_2) \cdot \psi_{spin}^{1M_S}$$

$$\psi_{T1} = \left[\frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)\right] \cdot [\alpha_1\alpha_2]$$

$$\psi_{antisym}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)$$

Remember that ψ_{spin} does not contribute directly to the energy.

$$H = \left[-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}\right] + \left[-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}\right] + \frac{1}{r_{12}}$$

$$\langle E\rangle_{trip} = \left\langle \frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)\middle| H \middle| \frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)\right\rangle$$

$$\langle E \rangle_{trip} = \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} - K_{1s2s}$$
$$\quad\quad\quad\quad \mathbf{1} \quad\quad \mathbf{2} \quad\quad \mathbf{3} \quad\quad \mathbf{4}$$

where $\quad J_{1s2s} = \langle 1s(1)2s(2) | \frac{1}{r_{12}} | 1s(1)2s(2) \rangle \quad K_{1s2s} = \langle 1s(1)2s(2) | \frac{1}{r_{12}} | 2s(1)1s(2) \rangle$

$$J_{1s2s} = \iint \frac{1s(1)^2 2s(2)^2}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad\quad\quad K_{1s2s} = \iint \frac{[1s(1)2s(1)] \cdot [1s(2)2s(2)]}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

1. Energy of electron in 1s He$^+$ orbital
2. Energy of electron in 2s He$^+$ orbital
3. Coulomb (repulsion) Integral
4. Exchange Integral

$$\langle E \rangle_{trip} = \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} - K_{1s2s}$$
$$\quad\quad\quad\quad \mathbf{1} \quad\quad \mathbf{2} \quad\quad \mathbf{3} \quad\quad \mathbf{4}$$

$$J_{1s2s} = \iint \frac{1s(1)^2 2s(2)^2}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad \textbf{Always positive}$$

3. Coulomb (repulsion) Integral

The integrand of the Coulomb integral represents the repulsion of two infinitesimal electron densities, $\rho(1)=1s(1)^2$ and $\rho(2)=2s(2)^2$, separated by a distance, r_{12}. The repulsion is summed over all infinitesimal electron densities.

$$K_{1s2s} = \iint \frac{[1s(1)2s(1)] \cdot [1s(2)2s(2)]}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad \textbf{Usually positive}$$

4. Exchange Integral

Arises purely from the antisymmetry of the spatial function with respect to electron exchange. It has no classical analog.

If the above calculation had been performed with a simple product wavefunction, $\psi_{spat} = 1s(1)2s(2)$, there would be no exchange integral

The Hartree-Fock Energy

Hartree Energy: $E = \sum_{i=1}^{N} \varepsilon_i - \sum_{i=1}^{N} \sum_{j>i} J_{ij}$ Using simple product wavefunction: not antisymmetric w.r.t. exchange

$$J_{ij} = \left\langle \varphi_i \varphi_j \left| \frac{1}{r_{12}} \right| \varphi_i \varphi_j \right\rangle = \int_{\vec{r}_1} \int_{\vec{r}_2} \frac{|\varphi_i(\vec{r}_1)|^2 |\varphi_j(\vec{r}_2)|^2}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

J_{ij} is the Coulomb Integral describing the repulsion between an electron in orbital ϕ_i and an electron in orbital ϕ_j.

Hartree-Fock Energy: $E = \sum_{i=1}^{N} \varepsilon_i - \sum_{i=1}^{N} \sum_{j>i} \left(2J_{ij} - K_{ij} \right)$

Using antisymmetrized wavefunction: Slater Determinant

$$J_{ij} = \left\langle \varphi_i \varphi_j \left| \frac{1}{r_{12}} \right| \varphi_i \varphi_j \right\rangle = \int_{\vec{r}_1} \int_{\vec{r}_2} \frac{\left[\varphi_i^*(\vec{r}_1)\varphi_i(\vec{r}_1) \right]\left[\varphi_j^*(\vec{r}_2)\varphi_j(\vec{r}_2) \right]}{r_{12}} d\vec{r}_1 d\vec{r}_2$$ **Coulomb Integral**

$$K_{ij} = \left\langle \varphi_i \varphi_j \left| \frac{1}{r_{12}} \right| \varphi_j \varphi_i \right\rangle = \int_{\vec{r}_1} \int_{\vec{r}_2} \frac{\left[\varphi_i^*(\vec{r}_1)\varphi_j(\vec{r}_1) \right]\left[\varphi_j^*(\vec{r}_2)\varphi_i(\vec{r}_2) \right]}{r_{12}} d\vec{r}_1 d\vec{r}_2$$ **Exchange Integral**

The Exchange Integral arises from the antisymmetry of the wavefunction, and has no classical analog.

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Hartree-Fock Orbital Energies for Ar

0 eV —— Separated particles

-16.1 eV
—— ε_{3p} Note that the ns and np orbitals have different
-34.8 eV
—— ε_{3s} energies. This is due to screening of the p electrons.

Koopman's Theorem

$$IE \approx -\varepsilon$$

-260 eV —— ε_{2p}

-335 eV —— ε_{2s}

Electron Removed	IE(exp)	IE(Koop)
1s	3206 eV	3227 eV
2s	--	335
2p	249	260
3s	29.2	34.8
3p	15.8	16.1

-3227 eV —— ε_{1s}

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Electron Correlation

The principal approximation of the Hartree-Fock method is that a given electron interacts with the "smeared-out" electron density of the remaining N-1 electrons.
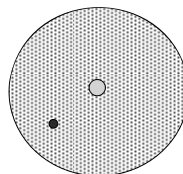
Actually, the other N-1 electrons are point particles, just like the one we're considering.

Thus, the motion of the electrons are correlated. That is, they try to avoid each other.

**High
Energy
Not favored**

**Low
Energy
Favored**

Because the Hartree-Fock (HF) method does not consider the **specific** electron-electron repulsions, which tend to keep two electrons apart, the HF energy is invariably too high.

The difference between the "exact" electronic energy and the HF energy is called the "Correlation Energy", E_{corr}.
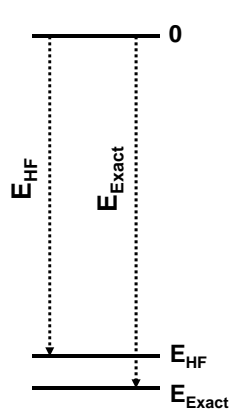
$$E_{corr} = E_{exact} - E_{HF}$$

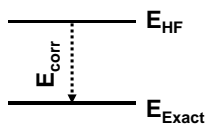Generally, the correlation energy is very small compared to the total energy (usually <1%)

However, in absolute terms, this can still represent a rather large energy.

The "exact" electronic energy can be measured as the negative of the sum of the Ionization Energies.

$$E_{exact} = E_{\exp} = -\sum_{i=1}^{N} IE_i$$

$$E_{corr} = E_{exact} - E_{HF} = E_{\exp} - E_{HF}$$

E_{HF} **E_{Exact}** **0**

E_{HF}

E_{Exact}

E_{HF} **E_{corr}** **E_{Exact}**

Helium

E_{HF} = -2.862 au

E_{Exact} = -2.904 au

$$\%Error = \left| \frac{E_{exact} - E_{HF}}{E_{exact}} \right| x100 = 1.4\%$$

However, the correlation energy can still be very large in absolute terms.

$$E_{corr} = E_{exact} - E_{HF} = -0.042 \ au \ x \frac{2625 \ kJ/mol}{1 \ au} = -110 \ kJ/mol$$

E$_{HF}$
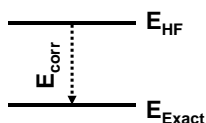
E$_{corr}$

E$_{Exact}$

Argon

E_{HF} = -526.807 au

E_{Exact} = -527.030 au

$$\%Error = \left| \frac{E_{exact} - E_{HF}}{E_{exact}} \right| x100 = 0.04\%$$

However, the correlation energy can still be very large in absolute terms.

$$E_{corr} = E_{exact} - E_{HF} = -0.223 \ au \ x \frac{2625 \ kJ/mol}{1 \ au} = -585 \ kJ/mol$$

For many applications (e.g. geometries and frequencies), inclusion of the correlation energy is not that important.

However, for applications involving bond breaking and bond making (e.g. reactions), inclusion of the correlation energy is critical in order to get good results.

We will qualitatively discuss methods used to determine the correlation energy in a later chapter.

An Example: Calculated Ionization Energy and Electron Affinity of Fluorine

Ionization Energy (IE): M $\rightarrow$ M$^+$ + e$^-$ M is a neutral atom or molecule

$$\Delta E = IE = E(M^+) - E(M)$$

Electron Affinity (EA): M + e$^-$ $\rightarrow$ M$^-$ M is a neutral atom or molecule

$$\Delta E = EA = E(M^-) - E(M)$$

Methods: E(HF) = HF/6-311++G(3df,2pd)   Hartree-Fock Energy

E(QCI) = QCISD(T)/6-311++G(3df,2pd)   Correlated Energy

This is the HF energy with a correction for electron correlation calculated at the QCISD(T) level (later Gator).

Species   E(HF)   E(QCI)

F   -99.402 au   -99.618 au

F⁺   -98.825   -98.984

F⁻   -99.446   -99.737

$$IE(HF) = E(F^+) - E(F)$$
$$= -98.825 - (-99.402) = 0.577\ au \cdot 2625\ \frac{kJ/mol}{au} = 1515\ kJ/mol$$

Similarly: $IE(QCI) = 1664\ kJ/mol$

$$EA(HF) = E(F^-) - E(F)$$
$$= -99.446 - (-99.402) = -0.044\ au \cdot 2625\ \frac{kJ/mol}{au} = -116\ kJ/mol$$

Similarly: $EA(QCI) = -312\ kJ/mol$

Quantity	Expt.	HF	QCI
IE	1681 kJ/mol	1514 kJ/mol	1664 kJ/mol
EA	-328	-115	-312

Koopman's Theorem IE

Energy of highest occupied orbital at HF/6-311++G(3df,2pd) level

$$\varepsilon_H = -0.733\ au$$

$$IE \approx -\varepsilon_H = +0.733\ au \bullet 2625\ kJ/mol\ /\ au = 1924\ kJ/mol$$

Notes: (1) Koopman's Theorem gives only rough approximation for Ionization Energy

(2) Accurate calculations of the IE or EA require the use of energies corrected for electron correlation.

$$E_{HF}$$

$$E_{corr} = E_{exact} - E_{HF} < 0$$

$$E_{exact} \approx E_{QCI}$$

$$\left| E_{corr}\left(F^+\right) \right| < \left| E_{corr}\left(F\right) \right| < \left| E_{corr}\left(F^-\right) \right|$$

$$IE = E(F^+) - E(F) > 0$$

$$EA = E(F^-) - E(F) < 0$$

$$E_{HF}(F^+)$$

$$E_{exact}(F^+) \approx E_{QCI}(F^+)$$

IE(HF)=1514 kJ/mol   **IE(QCI)=1664 kJ/mol**

$$E_{HF}(F)$$

$$E_{exact}(F) \approx E_{QCI}(F)$$

EA(HF)= -115 kJ/mol

$$E_{HF}(F^-)$$

EA(QCI)= -312 kJ/mol

$$E_{exact}(F^-) \approx E_{QCI}(F^-)$$