Helium Atom, Many-Electron Atoms, Variational Principle, Approximate Methods, Spin

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I. The Helium Atom and Variational Principle: Approximation Methods for Complex Atomic Systems

The hydrogen atom wavefunctions and energies, we have seen, are determined as a combination of the various quantum "dynamical" analogues of classical motions (translation, vibration, rotation) and a central-force interaction (i.e, the Coulomb interaction between an electron and a nucleus).

Now, we consider the Helium atom and will see that due to the attendant 3-body problem for which we cannot determine a closed-form, first-principles analytic solution, we will have to find recourse in approximate methods.

The Helium atom has **2 electrons** with coordinates $\mathbf{r_1}$ and $\mathbf{r_2}$ as well as a single nucleus with coordinate $\mathbf{R}$. The nucleus carries a $Z = +2e$ charge.

The Schrodinger equation is:

$$\left(-\frac{\hbar^2}{2M}\nabla^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 \right)\psi(\mathbf{R}, \mathbf{r_1}, \mathbf{r_2}) +$$

$$\left(-\frac{2e^2}{4\pi\epsilon_o\left|R - r_1\right|} - \frac{2e^2}{4\pi\epsilon_o\left|R - r_2\right|} + \frac{e^2}{4\pi\epsilon_o\left|r_1 - r_2\right|} \right)\psi(\mathbf{R}, \mathbf{r_1}, \mathbf{r_2}) = E\psi(\mathbf{R}, \mathbf{r_1}, \mathbf{r_2})$$

where the symbol "nabla", when squared, is given by:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Keep in mind that the $\mathbf{R}$, $\mathbf{r_1}$, and $\mathbf{r_2}$ represent the Cartesian coordinates of each paticle. This is a 3-body problem and such problems are not solved exactly. Thus, the problem will be reformulated in terms of coordinates of two particles, the electrons. The first approximation: $M >> m_e$, fix the nucleus at the origin $(\mathbf{R}) = \mathbf{0}$. This is more rigorously shown by transforming

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the origin to the center of mass of the system. For the two electron-nucleus coordinates, this is much like what we have seen for the hydrogen atom electron-nucleus formulation from earlier discussion. Thus, the Schrodinger equation in *relative variables* is:

$$\frac{\hbar^2}{2m_e}\left(-\nabla_1^2 - \nabla_2^2\right)\psi(\mathbf{r_1},\mathbf{r_2}) - \frac{2e^2}{4\pi\epsilon_o}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_o\,|r_2 - r_1|}\psi(\mathbf{r_1},\mathbf{r_2}) = E\psi(\mathbf{r_1},\mathbf{r_2})$$

The ∇^2 terms represent the kinetic energy of the two electrons. The $\frac{1}{r_1}$ and $\frac{1}{r_2}$ terms represent the nucleus-electron Coulomb interaction. The last term on the left hand side of the equation represents the electron-electron repulsion taken as a Coulomb interaction based on the absolute value of the electron-electron separation.

NOTE: *The electron-nucleus Coulomb interaction is a radially symmetric potential. It depends on the* **radial** *positions of the electrons from the nucleus taken as the origin. The electron-electron repulsion does not possess inherent symmetry (radial or otherwise). It depends on the absolute value of the separation between electrons.*

Recall that the ∇^2, representing the kinetic energy operator, in spherical polar coordinates is:

$$\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r_1^2 sin\theta_1}\frac{\partial}{\partial\theta_1}\left(sin\theta_1\frac{\partial}{\partial\theta_1}\right) + \frac{1}{r_1^2 sin^2\theta_1}\frac{\partial^2}{\partial\phi_1^2}$$

The Independent Electron Approximation to Solving the Helium Atom Schrodinger Equation
If we neglect **electron-electron repulsion** in the Helium atom problem, we can simplify and solve the effective 2-body problem.

- Solve the relative motion problem (separate out the center of mass motion as we have seen earlier)

- Center of mass is assumed to be the nucleus; good approximation for heavier nuclei

The Hamiltonian is now:

$$\hat{H} = (KE)_{e_1} + (KE)_{e_2} + V_{Ne_1} + V_{Ne_2}$$

$$
\begin{aligned}
&= \frac{\hbar^2}{2m_e}\left(-\nabla_1^2 - \nabla_2^2\right) - \frac{2e^2}{4\pi\epsilon_o}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \\
&= \left(\frac{-\hbar^2}{2m_e}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_o}\left(\frac{1}{r_1}\right)\right) + \left(\frac{-\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_o}\left(\frac{1}{r_2}\right)\right) \\
&= \hat{H}^1 + \hat{H}^2
\end{aligned}
$$

Under the independent electron approximation, if we take the total He atom wavefunction as a product of the individual electron wavefunctions (here approxmiated as hydrogen-like wavefunctions):

$$
\begin{aligned}
\Psi(\mathbf{r}_1, \mathbf{r}_2) &= \psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \\
\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2) &= \hat{H}_1\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) + \hat{H}_2\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \\
&= E_1\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) + E_2\psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \\
&= (E_1 + E_2)\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)
\end{aligned}
$$

This yields $E = E_1 + E_2$. Recal the hydrogen-like energies and wavefunctions are:

- $\Psi_{nlm}(\mathbf{r}) = R_{nl}(Zr/a_o)Y_{lm}(\theta, \phi)$ (Z=1 for hydrogen, Z=2 for helium)

- Energies are: $E_n = -\frac{Z^2 E_h}{2}\frac{1}{n^2}$

Thus, approximate wavefunctions and energies for helium:

$$
\begin{aligned}
\Psi n_1, l_1, m_1, n_2, l_2, m_2(\mathbf{r}_1, \mathbf{r}_2) &= \Psi n_1, l_1, m_1(\mathbf{r}_1)\Psi n_2, l_2, m_2(\mathbf{r}_2) \\
E_{n_1, l_1, m_1, n_2, l_2, m_2} &= -\frac{Z^2 E_h}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)
\end{aligned}
$$

How sound is the independent electron approximation (no electron-electron repulsion model)? We can compare the predicted **ionization potentials** with the exerimental values. The ionization potential is the energy required to extract an electron from an atom. For the Helium atom, this can be represented as an equation such as:

$$He \rightarrow He^+ + e^-$$

The energy change associated is:

$$
\begin{aligned}
\Delta E &= E_{He,1s} - E_{He,(1s)^2} \\
&= -54.4eV - (-108.8eV) = 54.4eV \\
&= 24.6 \ eV \qquad experiment
\end{aligned}
$$

The ground state energy for Helium can also be contrasted as:

$$
\begin{aligned}
E^0 &= E_{1s,1s} = -\frac{2^2 E_h}{2}\left(\frac{1}{1^2} + \frac{1}{1^2}\right) \\
&= -4E_h \\
&= -108.8eV \qquad significantly \ too \ negative \\
&= -79 \ eV \qquad experiment
\end{aligned}
$$

The experimental value for the ionization potential (from mass spectroscopic measurements) is 24.6 eV; so the independent electron approach entails significan error. Because the electrons are not allowed Coulombic repulsion, the energy required to remove a particular electron is higher than the experimental value. This is also validated by the much lower (and thus more attractive/favorable) ground state energy predicted by the independent electron model compared to experiment.

Moving Beyond the Independent Electron Model: Perturbative and Variational Methods
Perturbation Theory

The Helium atom Hamiltonian, we recall, is:

$$
\begin{aligned}
\hat{H} &= \frac{\hbar^2}{2m_e}\left(-\nabla_1^2 - \nabla_2^2\right) - \frac{2e^2}{4\pi\epsilon_o}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_o |\mathbf{r_2} - \mathbf{r_1}|} \\
&= \hat{H}^0 + \hat{H}^1 \qquad \left(\hat{H}^0 \psi^0 = E^0 \psi^0\right)
\end{aligned}
$$

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We see that the electron-electron repulsion term can be treated as a "perturbation" to the independent electron Hamiltonian. In this sense, we can choose to define, develop, and include various orders of perturbative corrections to the energies and wavefunctions determined via exact solution of the independent-electron model. Though we are currently applying this to the problem of electron-electron repulsion, we will see later that modern advanced methods for electronic strucuture calculations employ perturbation methods to account for important electron correlation. For now, we concern ourselves with the development of perturbation theory and application to correct for two-body Coulomb repulsion in the Helium atom.

First Order Perturbation Theory
First, expand the total wavefunction up to first order contributions. The subscript "n" refers to any energy level in general (perturbation theory is capable of giving us energy levels and wavefunctions in addition to those for the ground state; as we will see below, variational approaches give us ground state information only):

$$
\begin{aligned}
\psi_n &= \psi_n^0 + \psi_n^1 \quad \left(\int_{all\ space} \psi_n^{0*} \psi_n^1 d\tau = 0 \right) \\
E_n &= E_n^0 + E_n^1 \\
\left(\hat{H}^0 + \hat{H}^1 \right) \left(\psi_n^0 + \psi_n^1 \right) &= \left(E_n^0 + E_n^1 \right) \left(\psi_n^0 + \psi_n^1 \right)
\end{aligned}
$$

Expanding the expression:

$$
\hat{H}^0 \psi_n^0 + \hat{H}^1 \psi_n^0 + \hat{H}^0 \psi_n^1 + \hat{H}^1 \psi_n^1 = E_n^0 \psi_n^0 + E_n^1 \psi_n^0 + E_n^0 \psi_n^1 + E_n^1 \psi_n^1
$$

The first terms on each side are equivalent. Last terms are **approximated/assumed to be neglibly small–this is a perturbation energy and wavefunction**. This leaves:

$$
\hat{H}^1 \psi_n^0 + \hat{H}^0 \psi_n^1 = E_n^1 \psi^0 + E_n^0 \psi_n^1
$$

Solve for ψ_n^1 and E_n^1. Left multiply by ψ_n^{0*} and integrate:

$$
\int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^0 + \int d\tau \psi_n^{0*} \hat{H}^0 \psi_n^1 = \int d\tau \psi_n^{0*} E_n^1 \psi_n^0 + \int d\tau \psi_n^{0*} E_n^0 \psi_n^1
$$

Since $\hat{H}^0$ is Hermitian, $\int d\tau \psi_n^{0*} \hat{H}^0 \psi_n^1 = \int d\tau \left(\hat{H}^0 \psi_n^0 \right)^* \psi_n^1$.

$$\int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^0 + \int d\tau \psi_n^1 E_n^0 \psi_n^{0*} = E_n^0 \int d\tau \psi_n^{0*} \psi_n^1 + E_n^1$$

Solving for E_n^1 , **the fist order perturbative correction to the independent electron energy level for helium** gives:

$$E_n^1 \;\; = \;\; \int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^0$$

Expilcitly, this means, $E_n = E_n^0 + E_n^1$; we have added a "small" perturbative correction to the reference independent electron energy for a given energy level, n!

Now, what about the correction to the wavefunction? Let's recall:

$$\hat{H}^1 \psi_n^0 + \hat{H}^0 \psi_n^1 = E_n^1 \psi^0 + E_n^0 \psi_n^1$$

We will solve for ψ_n^1 by expanding ψ_n as a linear combination of **unperturbed** wavefunctions as follows:

$$\psi_n \;\; = \;\; \psi_n^0 + \sum_{j \neq n} a_{nj} \psi_j^0$$

Left multiply by ψ_k^{0*} and integrate:

$$\int d\tau \psi_k^{0*} \hat{H}^1 \psi_n^0 + \int d\tau \psi_k^{0*} \hat{H}^0 \psi_n^1 \;\; = \;\; \int d\tau \psi_k^{0*} E_n^1 \psi_n^0 + \int d\tau \psi_k^{0*} E_n^0 \psi_n^1$$

$$\int d\tau \psi_k^{0*} \hat{H}^1 \psi_n^0 + \int d\tau \psi_k^{0*} \hat{H}^0 \sum_{j \neq n} a_{nj} \psi_j^0 \;\; = \;\; \int d\tau \psi_k^{0*} E_n^1 \psi_n^0 + \int d\tau \psi_k^{0*} E_n^0 \sum_{j \neq n} a_{nj} \psi_j^0$$

$$\int d\tau \psi_k^{0*} \hat{H}^1 \psi_n^0 + \sum_{j \neq n} a_{nj} E_j^0 \int d\tau \psi_k^{0*} \psi_j^0 \;\; = \;\; E_n^1 \int d\tau \psi_k^{0*} \psi_n^0 + E_n^0 \sum_{j \neq n} a_{nj} \int d\tau \psi_k^{0*} \psi_j^0$$

$$a_{nk} \left(E_k^0 - E_n^0 \right) \;\; = \;\; E_n^1 \int d\tau \psi_k^{0*} \psi_n^0 - \int d\tau \psi_k^{0*} \hat{H}^1 \psi_n^0$$

Now, we consider two cases:

$$k = n \quad \rightarrow \quad E_n^1 = \int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^0$$

$$k \neq n \quad \rightarrow \quad a_{nk} = \frac{\int d\tau \psi_k^{0*} \hat{H}^1 \psi_n^0}{E_n^0 - E_k^0} \equiv \frac{\hat{H}_{kn}^1}{E_n^0 - E_k^0}$$

Thus, the **first order correction to the wavefuntion is**:

$$
\begin{aligned}
\psi_n &= \psi_n^0 + \psi_n^1 = \psi_n^0 + \sum_{j \neq n} a_{nj} \psi_j^0 \\
&= \psi_n^0 + \sum_{j \neq n} \left(\frac{\hat{H}_{jn}^1}{E_n^0 - E_j^0} \right) \psi_j^0 = \psi_n^0 + \sum_{j \neq n} \left(\frac{\int d\tau \psi_j^{0*} \hat{H}^1 \psi_n^0}{E_n^0 - E_j^0} \right) \psi_j^0
\end{aligned}
$$

Higher Order Corrections
For higher order corrections, energies and wavefunctions are expanded in like manner:

$$\psi_n = \psi_n^0 + \psi_n^1 + \psi_n^2 \quad E_n = E_n^0 + E_n^1 + E_n^2$$

The second-order correction to the energy is thus determined to be (see other sources for derivation):

$$
\begin{aligned}
E_n^2 &= \int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^1 = \int d\tau \psi_n^{0*} \hat{H}^1 \sum_{j \neq n} \frac{\hat{H}_{jn}^1}{E_n^0 - E_j^0} \psi_j^0 \\
&= \sum_{j \neq n} \frac{\hat{H}_{nj}^1 \hat{H}_{jn}^1}{E_n^0 - E_j^0}
\end{aligned}
$$

Helium Atom: First Order Perturbation Correction to Account for Electron-Electron Repulsion
From the above discussion, the first order correction to the ground state

energy of Helium is:

$$E_n^1 = \int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^0$$

If we assume an unperturbed wavefunction as the product of the 2 Helium electrons in 1s orbitals:

$$\psi^0(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1)phi_{1s}(\mathbf{r}_2) = \left(\left(\frac{Z^3}{\pi}\right)^{1/2}\right)^2 e^{-Zr_1} e^{-Zr_2}$$

$$\hat{H}^1 = \frac{1}{r_{12}}$$

$$E_n^1 = \int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^0 = \frac{Z^6}{\pi^2} \int d\tau e^{-Zr_1} e^{-Zr_2} \left(\frac{1}{r_{12}}\right) e^{-Zr_1} e^{-Zr_2}$$

$$= \frac{Z^6}{\pi^2} \int d\tau \frac{e^{-2Zr_1} e^{-2Zr_2}}{r_{12}} = \frac{5}{8} Z E_h$$

Thus, the ground state energy with first order correction is :

$$E_0 = E_0^0 + E_0^1 = -4E_h + \frac{5}{8} Z E_h = \frac{-11}{4} E_h = -74.8 eV$$

- Neglect of electron-electron repulsion: E_0 = -108.8 eV

- First order correction: E_0 = -74.8 eV

- 13th order correction: E_0 = -79.01 eV

- Experiment: E = -79.0 eV

- Perturbation theory results may be greater or less than the true energy, unlike variational results

- Perturbation, unlike variational theory, can be used to calculate any energy level, not just the ground state.

Some comments on the Many-Electron Problem: Coordinate dependence and correlation

Solving the Schrodinger equation for an N-electron atom means solving for a function of 3N coordinates. Such problems are treated numerically as we will see further below. Moreover, if we acknowledge that the individual electrons present differing environemnts (core versus valence eletrons), we can approxmiate the N-electron wavefunction (eigenfunction of Schrodinger equation) in terms of **individual electron orbitals, each dependent on the coordinates of a single electron**. This is the **orbital approximation**. The wavefunctions are written:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\phi_3(\mathbf{r}_3)...\phi_n(\mathbf{r}_n)$$

Each of the functions, ϕ_n, is associated with an **orbital energy**, ϵ_n. It is important to note that this form does not imply fully indepdent electrons, since, as will be evident, each electron's dynamics (and hance wavefunction) is governed by the effective field/potential of all the other electrons in the atom. The one-electron orbitals turn out to be well-approximated by the hydrogen-atom wavefunctions.

NOTE:

- Due to the electron-electron repulsion term in the He atom Hamiltonian not being spherically symmetric, the Schrodinger equation cannot be solved analytically. Numerical methods are applied along with **approximations**.

- One such approxmiation is the neglect of full electron-electron correlation (motion of electrons is correlated; electrons stay out of each other's way; correlation opposes repulsion, and thus contributes an energy-lowering influence).

- Advanced electron correlation methods are well-developed and routinely applied.

The Hartree Model

If we neglect, for the moment, any electron-electron correlation, then we can say that electron 1 can interact with the nucleus and a **spatially averaged charge distribution due to elecron 2**. The "physical" picture here is of electron 2 "smeared" out sphercially around the nucleus; thus, its charge density is also diffuse around the nucleus. The charge in a given volume element $d\tau$ at a point around the nucleus is given by:

$$-e\phi^*(\mathbf{r}_2)\phi(\mathbf{r}_2)d\tau$$

The effective potential that electron 1 interacts with now is determined by the electron-nucleus interaction and the interaction of electron 1 with the **spherically symmetric** (smeared out) charge distribution arising from a diffuse electron 2:

$$V_1^{eff}(\mathbf{r}_1) = \frac{-2e^2}{4\pi\epsilon_o\,|\mathbf{r}_1|} + \int \phi_2^*(\mathbf{r}_2)\frac{e^2}{r\pi\epsilon_o\,|\mathbf{r}_1 - \mathbf{r}_2|}\phi_2(\mathbf{r}_2)d\mathbf{r}_2$$

This model is the Hartree model and serves as a starting point for treating many-electron atoms.

Thus, for many-electron atoms, the approach to solving the Schrodinger Equation is:
Note:

- Approxmiate the total wavefunction as a product of individual orbitals, each orbital depending on the coordinates of a single electron (reduce N-body problem to N one-body problems)

- The set of N equations is solved self-consistenly to obtain the one-electron energies, ϵ_i and orbitals ϕ_i.

- The approach is approximate due to neglect of electron correlation.

Electron Spin: Extension to Intrinsic Angular Momentum
Discussion of angular momentum: spin does not arise naturally (using a non-relativistic formalism). Experimentally, spin is required to explain deflection of Ag atoms in a magnetic field (recall Stern-Gerlach experiment from chapter 17). Silver atoms are deflected in either **one of two directions** in a magnetic field oriented along the z-diretion of the lab frame of reference; the direction is either up or down. Consider:

- For an Ag atom to be deflected, it requires **non-zero total magnetic moment** and **an associated non-zero total angular momentum**

- Current in a loop of wire generates a magnetic field; the loop has a magnetic moment

- Ag atoms have a closed inner shell (no net angular momentum for closed shells; symmetry); outer valence electron, 5s must contain all magnetic moment.

- s-orbital has no angular momentum

- Thus, the 5s electron in Ag contains an **intrinsic spin angular momentum**; we associate this with **spin**. Spin is intrinsic since it is independent of environment; **spin does not depend on** $r, \theta, and \phi$.

- Note that this idea and picture of intrinsic particle spin is a convenient classical way of accounting for experiment.

Introduce spin angular momentum. (spin angular momentum operators)

- Spin operators: $\hat{s}^2$ and $\hat{s}_z$
- Spin wave functions: α and β
- Spin quantum number: $s = 1/2$, m_s (takes on two values, $m_s = 1/2$ and $m_s = -1/2$.

Spin angular momentum follows general angular momentum behavior as we discussed for orbital angular momentum.

$$
\begin{aligned}
\hat{s}^2 \alpha &= \hbar^2 s(s+1)\alpha(\sigma) = \frac{\hbar^2}{2}\left(\frac{1}{2}+1\right)\alpha(\sigma) \\
\hat{s}^2 \beta &= \hbar^2 s(s+1)\beta(\sigma) = \frac{\hbar^2}{2}\left(\frac{1}{2}+1\right)\beta(\sigma) \\
\hat{s}_z \alpha &= m_s \hbar \alpha(\sigma) = \frac{\hbar}{2}\alpha(\sigma) \\
\hat{s}_z \beta &= m_s \hbar \beta(\sigma) = -\frac{\hbar}{2}\beta(\sigma)
\end{aligned}
$$

The orthonormality conditions are:

$$
\int \alpha(\sigma)^* \beta(\sigma) d\sigma = \int \beta(\sigma)^* \alpha(\sigma) d\sigma = 0
$$
$$
\int \alpha(\sigma)^* \alpha(\sigma) d\sigma = \int \beta(\sigma)^* \beta(\sigma) d\sigma = 1
$$

Bear in mind that for electrons, $s = \frac{1}{2}$ always, and that $m_s = \pm\frac{1}{2}$. The "up" spin is $m_s = \frac{1}{2}$ and the "down" spin is $m_s = -\frac{1}{2}$.

With the introduction of spin, and the spin functions α and β, we can write wavefunctions as:

$$\psi(\mathbf{r}_1, \alpha) = \phi(\mathbf{r}_1)\alpha(\sigma_1) \tag{1}$$

For the following discussions, the spin variable σ will be assumed implicitly, and we will only consider particle number subscripts for compactness.

Indistinguishability of Electrons and Pauli Exclusion

Electrons in an atom are indistinguishable for all practical purposes; on a macro scale, observables of an atomic system cannot change if we change the manner in which we "identify" (if possible) the individual electrons. Since we can consider that properties can be associated as averaged over electronic probability densities, i.e, $\psi^*\psi = |\psi|^2$, the following condition arises:

If:

$$\psi^2(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = \psi^2(\mathbf{r}_2, \sigma_2, \mathbf{r}_1, \sigma_1)$$
$$\psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = \pm\psi(\mathbf{r}_2, \sigma_2, \mathbf{r}_1, \sigma_1)$$

For fermions, the negative sign applies, and the wavefunction is said to be **antisymmetric**. For bosons, the positive sign applies and the wavefunctions are said to be **symmetric**. The nature of these particles is described by different statistics, from which the names arise (Fermi-Dirac for the former, and Bose-Einstein for the latter).

The implication of the previous relations is that for a Helium, the antisymmetric wavefunction becomes (recall 2 electrons must be accounted for):

$$\psi = \phi_{1s}(\mathbf{r}_1)\alpha(1)\phi_{1s}(\mathbf{r}_2)\beta(2) - \phi_{1s}(\mathbf{r}_1)\beta(1)\phi_{1s}(\mathbf{r}_2)\alpha(2)$$

Thus:

$$\psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = -\psi(\mathbf{r}_2, , \sigma_2, \mathbf{r}_1, \sigma_1)$$

Pauli exclusion tells us that for **two electrons in the same spatial orbital**, the spins must be opposite (no two electrons share all four quantum numbers). This avoids distinguishing between the 2 electrons, and is antisymmetric with respect to interchange of identical particles.

A more compact (and standard) way to write such antisymmetric wavefunctions is in Slater Determinantal form:

$$\begin{aligned}
\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) &= \frac{1}{\sqrt{2}} |\phi_{1s}(\mathbf{r}_1)\alpha(1)\phi_{1s}(\mathbf{r}_2)\beta(2) - \phi_{1s}(\mathbf{r}_2)\alpha(2)\phi_{1s}(\mathbf{r}_1)\beta(1)| \\
&= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}(\mathbf{r}_1)\alpha(1) & \phi_{1s}(\mathbf{r}_1)\beta(1) \\ \phi_{1s}(\mathbf{r}_2)\alpha(2) & \phi_{1s}(\mathbf{r}_2)\beta(2) \end{vmatrix}
\end{aligned}$$

The Slater determinantal form is automatically antisymmetric with respect to interchange of any two rows or columns (corresponding to interchange of any two particles), hold for systems with greater than 2 electrons. The rows correspond to all the products of spatial and spin orbitals for a particular electron (i.e., the electron index does not change going across the rows of the determinant).

For $N - electron$ systems, the Slater determinant is of the form (N electrons, thus N orbitals):

$$\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, ..., \mathbf{r}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1)\alpha(1) & \phi_1(\mathbf{r}_1)\beta(1) & \dots & \phi_N(\mathbf{r}_1)\beta(1) \\ \phi_1(\mathbf{r}_2)\alpha(2) & \phi_1(\mathbf{r}_2)\beta(2) & \dots & \phi_N(\mathbf{r}_2)\beta(2) \\ \phi_1(\mathbf{r}_3)\alpha(3) & \phi_1(\mathbf{r}_3)\beta(3) & \dots & \phi_N(\mathbf{r}_3)\beta(3) \\ \vdots & \vdots & & \vdots \\ \phi_1(\mathbf{r}_N)\alpha(N) & \phi_2(\mathbf{r}_N)\beta(N) & \dots & \phi_N(\mathbf{r}_N)\beta(N) \end{vmatrix}$$

where the ϕ are the spatial orbitals and the α and β are the spin orbitals.

For the Lithium atom, the Slater determinant for the ground state is:

$$\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \mathbf{r}_3, \sigma_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(\mathbf{r}_1)\alpha(1) & 1s(\mathbf{r}_1)\beta(1) & 2s(\mathbf{r}_1)\alpha(1) \\ 1s(\mathbf{r}_2)\alpha(2) & 1s(\mathbf{r}_2)\beta(2) & 2s(\mathbf{r}_2)\alpha(2) \\ 1s(\mathbf{r}_3)\alpha(3) & 1s(\mathbf{r}_3)\beta(3) & 2s(\mathbf{r}_3)\alpha(3) \end{vmatrix}$$

or

$$\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \mathbf{r}_3, \sigma_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(\mathbf{r}_1)\alpha(1) & 1s(\mathbf{r}_1)\beta(1) & 2s(\mathbf{r}_1)\beta(1) \\ 1s(\mathbf{r}_2)\alpha(2) & 1s(\mathbf{r}_2)\beta(2) & 2s(\mathbf{r}_2)\beta(2) \\ 1s(\mathbf{r}_3)\alpha(3) & 1s(\mathbf{r}_3)\beta(3) & 2s(\mathbf{r}_3)\beta(3) \end{vmatrix}$$

Finally, consider the caes of ground state Helium. Here the two electrons are in the same orbital and have different spin. Thus, the Slater Determinant for this case can be separated into its spatial and spin parts. The spin part is then the antisymmetric component of the wavefunction:

$$\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = \frac{1}{\sqrt{2}} 1s(\mathbf{r}_1)1s(\mathbf{r}_2)\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

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

Bear in mind that this **does not** hold in general.

To summarize:

- Wavefunctions describing a many-electron system must change sign upon exchange of any two electrons (antisymmetry)
- Wavefunction is zero if all quantum numbers (n, l, m_l, m_s) of any two electrons are the same.
- Pauli Exclusion requires that a maximum of two electrons occupy any given orbital

Variational Method for Ground State
We can make use of the quantum mechanical postulate relating the expectation value of an observable, in this case the ground state energy, E_0, to arrive at a bounding value for the ground state energy

and associated wavefunction.

Recall the relations:

$$\hat{H}\psi_o = E_o\psi_o$$

$$\int \psi_o^* \hat{H}\psi_o d\mathbf{r} = \int \psi_o^* E_o \psi_o d\mathbf{r} = E_o$$

ψ_o not known, so assume a trial funtion, χ. Determine the expectation of the Hamiltonian, $\hat{H}$ and define it to be the **Variational energy**, E_{var}.

$$E_{var} = \frac{\int \chi^* \hat{H}\chi d\mathbf{r}}{\int \chi^* \chi d\mathbf{r}} = \int \chi^* \hat{H}\chi d\mathbf{r}$$

The last equality assumes normaalization of the guess wavefunction, χ.

The Variational Theorem states:

$$E_{var} \geq E_o \; for \; any \; choice \; of \; wavefunction \; \chi$$

short "proof" of variational theorem. Begin by expanding the test wavefunction as a linear combination of orthonormal wavefunctions (recall idea of expansions of functions using orthonormal, complete basis functions):

$$\chi = \sum_n a_n \psi_n$$

$$\int \chi^* \chi d\mathbf{r} = \sum_n |a_n|^2 = 1 \quad normalization$$

The variational energy is:

$$E_{var} = \int \chi^* \hat{H}\chi d\mathbf{r} = \sum_n |a_n|^2 E_n$$

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Now, subtract the ground state energy, whatever that may be, from the approximate variational energy:

$$E_{var} - E_o = \sum_n |a_n|^2 E_n - \sum_n |a_n|^2 E_o = \sum_n |a_n|^2 (E_n - E_o) \geq 0$$

since all the individual energies must be equal to or greater than the ground state energy! Thus, as an approximation, one can posit several trial wavefunctions, determine the variational energy, and then optimize in the space of wavefunctions. No doubt, this is not the most efficient approach to determine a valid functional form, but such information is generally obtained from chemical intuition.

The variational method also requires that variational parameters appear in the formulation so as to allow optimization, as the following example shows.

The one-dimensional harmonic oscillator:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d}{dx^2} + \frac{kx^2}{2}$$

Let's consider a trial wavefunction:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d}{dx^2} + \frac{kx^2}{2}$$

Trial wavefunction:

$$\chi = \left(\frac{\gamma}{\pi}\right)^{1/4} e^{-\gamma x^2/2}; \qquad \gamma \text{ variable (variational parameter)}$$

$$E_{var} = \int \chi^* \hat{H} \chi d\mathbf{r} = \left(\frac{\gamma}{\pi}\right)^{1/2} \int e^{-\gamma x^2/2} \left(-\frac{\hbar^2}{2\mu} \frac{d}{dx^2} + \frac{kx^2}{2}\right) e^{-\gamma x^2/2} dx$$

$$= -\frac{\hbar^2}{2\mu} \left(\frac{\gamma}{\pi}\right)^{1/2} \left[\int_{-\infty}^{\infty} \gamma e^{-\gamma x^2} dx + \int_{-\infty}^{\infty} (\gamma x)^2 e^{-\gamma x^2} dx\right] + \frac{k}{2} \left(\frac{\gamma}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\gamma x^2} dx = \frac{\hbar^2 \gamma}{4\mu} + \frac{k}{4\gamma} \geq E_o$$

Now, allow γ to **vary** and optimize E_{var}:

$$\frac{dE_{var}}{d\gamma} = \frac{\hbar^2}{4\mu} - \frac{k}{4\gamma^2} = 0$$

$$\gamma = \frac{(k\mu)^{1/2}}{\hbar} \equiv \alpha$$

This leads, with no surprise, to the exact solutions to the 1-D H.O.

$$\chi = \psi_o(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \quad \rightarrow \quad E_{var} = \frac{\hbar\omega}{2} = E_o$$

Now, returning to the Helium atom, we can attempt to use the variational principle to determine appropriate wavefunctions and energies. Recall from earlier the Helium atom Hamiltonian operator:

$$\frac{\hbar^2}{2m_e}(-\nabla_1^2 - \nabla_2^2)\,\psi(r_1, r_2) - \frac{2e^2}{4\pi\epsilon_o}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_o |r_2 - r_1|}\psi(r_1, r_2) = E\psi(r_1, r_2)$$

This can be rewritten in *atomic units* to arrive at:

$$\hat{H}_{He} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - 2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{|r_2 - r_1|}$$

$$E_{var} = \int \chi^* \hat{H}\chi d\mathbf{r}$$

We can try a wavefunction that is a *product* of two hydrogenic 1s orbitals, each one included to represent the relative motion of the electron-nucleus system:

$$\chi = \phi_{1s}^{\tilde{Z}}(\mathbf{r_1})\phi_{1s}^{\tilde{Z}}(\mathbf{r_2})$$

Here, we roll a variational parameter, $\tilde{Z}$ into our definition of the trial wavefunction:

$$\phi_{1s}^{\tilde{Z}} = \frac{1}{\sqrt{\pi}}\left(\frac{\tilde{Z}}{a_o}\right)^{3/2} e^{-\tilde{Z}r/a_o} \quad (1 - electron\ H\ atom\ orbitals)$$

$\tilde{Z}$ is an effective charge representing a *variational parameter*. Our trial wavefunction now becomes:

$$\chi(r_1, r_2) = \left(\frac{\tilde{Z}^3}{\pi}\right)^{1/2} e^{\frac{-\tilde{Z}r_1}{a_o}} \left(\frac{\tilde{Z}^3}{\pi}\right)^{1/2} e^{\frac{-\tilde{Z}r_2}{a_o}}$$

The variational energy is:

$$E_{var} = \frac{\tilde{Z}^6}{\pi} \int e^{\frac{-\tilde{Z}r_1}{a_o}} e^{\frac{-\tilde{Z}r_2}{a_o}} \left[\frac{-1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - 2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}\right] e^{\frac{-\tilde{Z}r_1}{a_o}} e^{\frac{-\tilde{Z}r_2}{a_o}} d\tau$$

$$= E_{var}(\tilde{Z}) = \tilde{Z}^2 - \frac{27}{8}\tilde{Z}$$

$$\frac{dE_{var}(\tilde{Z})}{d\tilde{Z}} = 2\tilde{Z} - \frac{27}{8} = 0 \quad \tilde{Z} = \frac{27}{16} < 2$$

$$= -77.5eV$$

The variational approximation gives reasonable results, but keep in mind that the effective nuclear charge is no longer 2, but less.

The Hartree-Fock Self-Consistent Field Method
Let's now consider the Hartree-Fock approach to solving the many-electron atom Schrodinger wave equation. We discuss this approach as it is the starting point for modern computational electronic structure methods. The method, along with many of the approximations and mathematical/physical insights and observations required to employ them, made possible what are today considered "off-the-shelf" canned computational chemistry software packages. Work continues to refine, innovate, and bring advanced theoretical approaches to these methods.

A general approach to Hartree-Fock Methods Based on the Helium Atom

To solve the Schrodinger equation, we must first assume some functional form of the wavefunction. As discussed above, the **orbital approximation** within which the total wavefunction is written as a product of individual **atomic** orbitals (**each orbital depends on**

the coordinates of a single electron and each orbital is associated with a unique orbital energy). This effectively transforms the problem into an independent electron problem, with the caveat that the "independence" is not strict; the individal electrons feel an effective potential from the other electrons as discussed above.

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$$

Since we don't know yet what these orbitals may look like (though we can guess that they will be much like the hydrogenic orbital wavefunctions) we can label these individual orbitals as $\phi^{HF}(\mathbf{r}_1), \phi^{HF}(\mathbf{r}_2)$. These are the Hartree-Fock orbitals. We can also solve for the orbital energies in a variational manner; this suggests that the orbitals we use will incorporate a **variational parameters**. In practice, it is the radial portion of the Hartree-Fock orbitals that differ from the standard hydrogenic orbitals. The radial components incorporate an "effective nuclear charge" as opposed to the actual nuclear charge of a many-electron atom. This effective charge attempts to capture the shielding effect of other electrons on the particular electron in a given orbital. The effective charge is usually referred to as ζ.

If we interpret the charge density of electron 2 as:

$$e\phi^*(\mathbf{r}_2)\phi(\mathbf{r}_2) = e\left|\phi(\mathbf{r}_2)\right|^2$$

we can write an effective potential for electron 1 by integrating the Coulomb interaction over the charge density of electron 2. This is the Coulomb potential felt by electron 1 averaged over all positions of electron 2, weighted by the charge density:

$$U_1^{eff}(\mathbf{r}_1) = e^2 \int \phi^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi(\mathbf{r}_2)d\mathbf{r}_2$$

This is known as the **central field approximation** or the **central force problem**. Now we can write an effective Hamiltonian and

single-electron Schrodinger equation for electron 1 as:

$$\hat{H}_1^{eff}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(\mathbf{r}_1)$$

$$\hat{H}_1^{eff}(\mathbf{r}_1)\phi^{HF}(\mathbf{r}_1) = \epsilon_1\phi^{HF}(\mathbf{r}_1)$$

Note that these are written in terms of coordinates of a **single electron!**. It is evident, however, that we are still not completely absolved from knowing anything about electron 2, since we need the distrubition function (probability density) of electron 2 to construct the effective potential for electron 1. Likewise, for a many-electron problem, we would need information on all other electrons to solve this one-electron problem. The approach thus requires a **self-consistent** approach as outlined below.

- Start with trial wavefunction, $\phi(\mathbf{r}_2)$
- Use $\phi(\mathbf{r}_2)$ to calculate $U_1^{eff}(\mathbf{r}_1)$
    * $U_1^{eff}(\mathbf{r}_1) = e^2 \int \phi^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi(\mathbf{r}_2)d\mathbf{r}_2$
- Solve Schrodinger Eqn. for electron 1
    * $\hat{H}_1^{eff}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + U_1^{eff}(\mathbf{r}_1)$
    * $\hat{H}_1^{eff}(\mathbf{r}_1)\phi^{HF}(\mathbf{r}_1) = \epsilon_1\phi^{HF}(\mathbf{r}_1)$
- Use $\phi(\mathbf{r}_1)$ to calculate $U_1^{eff}(\mathbf{r}_2)$
    * $U_2^{eff}(\mathbf{r}_2) = e^2 \int \phi^*(\mathbf{r}_1)\frac{1}{r_{12}}\phi(\mathbf{r}_1)d\mathbf{r}_1$
- Solve Schrodinger Eqn. for electron 2
    * $\hat{H}_2^{eff}(\mathbf{r}_2) = -\frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + U_2^{eff}(\mathbf{r}_2)$
    * $\hat{H}_2^{eff}(\mathbf{r}_2)\phi^{HF}(\mathbf{r}_2) = \epsilon_2\phi^{HF}(\mathbf{r}_2)$
- Continue iteration until **SELF-CONSISTENT** results for $\phi^{HF}(\mathbf{r}_1)$ and $\phi^{HF}(\mathbf{r}_2)$ are obtained, i.e., wavefunctions don't change from one iteration to the next.

We now have the solution to the full Schrodinger equation as:

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = \phi^{HF}(\mathbf{r}_1)\phi^{HF}(\mathbf{r}_2)$$

We can calculate the Hartree-Fock energy using the full Hamiltonian as:

$$E^{HF} = \int \phi^{HF*}(\mathbf{r}_1)\phi^{HF*}(\mathbf{r}_2)\left[\frac{-1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}\right]\phi^{HF}(\mathbf{r}_1)\phi^{HF}(\mathbf{r}_2)d\mathbf{r}_1\mathbf{r}_2$$
$$= I_1 + I_2 + J_{12}$$

Several terms are evident:

$$I_1 = \int \phi^{HF*}(\mathbf{r}_1)\left[-\frac{\nabla_1^2}{2} - \frac{Z}{r_1}\right]\phi^{HF}(\mathbf{r}_1)d\mathbf{r}_1$$

$$I_2 = \int \phi^{HF*}(\mathbf{r}_2)\left[-\frac{\nabla_2^2}{2} - \frac{Z}{r_2}\right]\phi^{HF}(\mathbf{r}_2)d\mathbf{r}_2 = I_1$$

$$J_{12} = \int \phi^{HF*}(\mathbf{r}_1)\phi^{HF*}(\mathbf{r}_2)\frac{1}{r_{12}}\phi^{HF}(\mathbf{r}_1)\phi^{HF}(\mathbf{r}_2)d\mathbf{r}_1\ d\mathbf{r}_2 \quad Coulomb\ Integral$$

The I_1 and I_2 terms can be thought of as Helium ion energies.

For the Helium Atom, the ground state energies based on HF approach compare well to experiment:

$$E_{HF} = -77.87eV$$
$$E_{expt} = -79.0eV$$

What can we say about the *orbital energies*? Recall:

$$\hat{H}_1^{eff}(\mathbf{r}_1)\phi^{HF}(\mathbf{r}_1) = \epsilon_1\phi^{HF}(\mathbf{r}_1)$$

$$\epsilon_1 = \int \phi^{HF}(\mathbf{r}_1)\hat{H}_1^{eff}(\mathbf{r}_1)\phi^{HF}(\mathbf{r}_1)d\mathbf{r}_1$$

$$= I_1 + J_{12} = E^{HF} - I_2$$

If we consider that I_2 (or I_1) represents the energy of the Helium *ion*, the the orbital energy, let's say for electron 1 is:

$$\begin{aligned} \epsilon_1 &= E - I_2 = \quad (Total\ He\ energy\ -energy\ of\ He\ ion\ ) \\ \epsilon_1 &\approx -(\ Ionization\ \ Energy\ ) = -E_{ionization} \end{aligned}$$

This is known as Koopman's theorem, and it approximates ionization energies as orbital energies. Furthermore, it is the orbital energy of the highest occupied orbital that is associated with the ionization energy.

To a good approximation, the association of orbital energies to ionization energies provides a reasonable estimate for most systems. In certain cases, there are systematic errors which can be dealt with via correlation to experimental data. One must also bear in mind that the orbital energies will vary based on the form of the wavefunctions employed for the calculations. Correcting for electron correlation will also lead to differences.

Regarding the relationship between the orbital energies and the **total** energy of a particular electronic configuration of an atom, we can consider the sum of the two orbital energies, ϵ_1 and ϵ_2 for the He atom.

$$\epsilon_1 + \epsilon_2 = I_1 + I_2 + 2J_{12} = E^{HF} + J_{12}$$

Thus, a **a simple sum of orbital energies overcounts the electron-electron repulsion** since the orbital energies implicitly account for this via the effective Coulomb interaction with other "smeared-out" electrons. Thus, in terms of orbital energies, the total energy, in the Hartree-Fock approximation, is:

$$E^{HF} = \epsilon_1 + \epsilon_2 - J_{12}$$

The form of this expression corresponds to Equation 21.18 in Engel and Reid. Of course, in the present discussion we have not included electron correlation, which is included in Equation 21.18 of Engel and Reid (without proof).

Thus, for a many-electron atom, we see that the total energy for a particular electronic configuration is determined by the interplay of orbital energies and electron-electron repulsion. Furthermore, in deciding the stability of one particular electronic configuration relative to another, one must consider the total energy rather than relative differences in orbital energies only.

Filling of many-elecron atom orbitals (corrections to orbital energy perspective)

Shell 1	1s			
Shell 2	2s	2p		
Shell 3	3s	3p	3d	
Shell 4	4s	4p	4d	4f
Shell 5	5s	5p	5d	5f
Shell 6	6s	6p	6d	6f

Thus, we see that based on Hartree-Fock orbital energies, the Aufbau Principle provides a framework for ordering the available many-electron atom orbitals based on energy. We see that in the many-electron atom, the s,p,d,f,g,... orbitals are not degenerate as they were for the Hydrogen atom. This arises due to differing shielding of electrons in different orbitals based on the probabilities of finding electrons closer or further away from the nucleus. At the simplest level, including electron-electron repulsion in our description of many-electron atoms leads to a configuration dependence on the energy levels.

Note that not all atoms follow the Aufbau order of filling orbitals.