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 close-for, first-principles analytic solution, we will have to find recourse in approximate methods.

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

The Schrödinger equation is:

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

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 $R$, $r$, and $r$ represent the Cartesian coordinates of each particle. This is a 3-body problem and such problems are not solved exactly. Thus, the problem will be reformulated in terms of 2 variables. The first approximations: $Mm_e$, fix the nucleus at the origin $(R) = 0$. Thus, the Schrödinger equation in relative variables is:
Recall that the $\nabla^2$, 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 Schrödinger 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:

$$
\hat{H} = KE_{e_1} + KE_{e_2} + V_{ne_1} + V_{ne_2}
$$

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

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

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

$$
\Psi(r_1, r_2) = \psi(r_1)\psi(r_2)
$$

$$
\hat{H}\Psi(r_1, r_2) = \hat{H}_1\psi(r_1) + \hat{H}_2\psi(r_2)
$$
This yields $E = E_1 + E_2$. Recal the hydrogen-like energies and wavefunctions are:

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

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

Thus, approximate wavefunctions and energies for helium:

$$\Psi_{n_1,l_1,m_1,n_2,l_2,m_2}(r_1,r_2)\psi_{spin} = \Psi_{n_1,l_1,m_1}(r_1)\Psi_{n_2,l_2,m_2}(r_2)$$

$$E_{n_1,l_1,m_1,n_2,l_2,m_2} = -\frac{Z^2E_h}{2} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

How sound is the independent electron approximation (no electron-electron repulsion model)? We can compare the predicted ionization potentials with the experimental 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:

$$\Delta E = E_{He,1s} - E_{He,(1s)^2}$$

$$= -54.4eV - (-108.8eV) = 54.4eV$$

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

$$E^0 = E_{1s,1s} = -\frac{2^2E_h}{2} \left( \frac{1}{1^2} + \frac{1}{1^2} \right)$$

$$= -4E_h$$

$$= -108.8eV$$ significantlytoonegative
The experimental value for the ionization potential (from mass spectroscopic measurements) is 24.6 eV; so the independent electron approach entails significant 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:

\[
\hat{H} = \frac{\hbar^2}{2m_e} \left( -\nabla_1^2 - \nabla_2^2 \right) \psi(r_1, r_2) - \frac{2e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0 |r_2 - r_1|} \]

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. WThough we are currently applying this to the problem of electron-electron repulsion, we will see later that modern advanced methods for electronic structure 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:

\[
\psi_n = \psi_n^0 + \psi_n^1 \\
E_n = E_n^0 + E_n^1 \\
(\hat{H}^0 + \hat{H}^1) (\psi_n^0 + \psi_n^1) = (E_n^0 + E_n^1) (\psi_n^0 + \psi_n^1)
\]

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 negligibly small—this is a perturbation energy and wavefunction. This leaves:

Expanding the expression:

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

Solve for \( \psi_n^1 \) and \( E_n^1 \). Left multiply by \( \psi_n^{0\ast} \) and integrate:

Expanding the expression:

\[ \int d\tau \psi_n^{0\ast} \hat{H}^1 \psi_n^0 + \int d\tau \psi_n^{0\ast} \hat{H}^0 \psi_n^1 = \int d\tau \psi_n^{0\ast} E_n^1 \psi_n^0 + \int d\tau \psi_n^{0\ast} E_n^0 \psi_n^1 \]

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

\[ \int d\tau \psi_n^{0\ast} \hat{H}^1 \psi_n^0 + \int d\tau \psi_n^{0\ast} E_n^1 \psi_n^0 = E_n^0 \int d\tau \psi_n^{0\ast} \psi_n^1 + E_n^1 \]

Solving for \( E_n^1 \), the first order perturbative correction to the independent electron energy level for helium gives:

\[ E_n^1 = \int d\tau \psi_n^{0\ast} \hat{H}^1 \psi_n^0 \]

Explicitly, 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:

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

We will solve for \( \psi_n^1 \) by expanding \( \psi_n \) 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 \( \psi_k^{0*} \) and integrate:

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

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

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

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

Now, we consider two cases:

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

\[
k \neq n \quad \rightarrow \quad a_{nk} = \frac{\int d\tau \psi_k^{0*} \hat{H}_n \psi_n^0}{E_n^0 - E_k^0} = \frac{\hat{H}_n^{jk}}{E_n^0 - E_k^0}
\]

Thus, the first order correction to the wavefunction is:

\[
\psi_n = \psi_n^0 + \psi_n^1 = \psi_n^0 + \sum_{j \neq n} a_{nj} \psi_j^0
\]

\[
= \psi_n^0 + \sum_{j \neq n} \left( \frac{\hat{H}_n^{jk}}{E_n^0 - E_j^0} \right) \psi_j^0 = \psi_n^0 + \sum_{j \neq n} \left( \frac{\int d\tau \psi_k^{0*} \hat{H}_n \psi_n^0}{E_n^0 - E_k^0} \right) \psi_j^0
\]

**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):

\[ E_n^2 = \int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^1 = \int d\tau \psi_n^{0*} \hat{H}^1 \sum_{j \neq n} \frac{\hat{H}_{jn}^1}{E_{jn}^0 - E_{jn}^0} \psi_j^0 \]
\[ = \sum_{j \neq n} \frac{\hat{H}_{nj}^1 \hat{H}_{jn}^1}{E_{jn}^0 - E_{jn}^0} \]

**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:

\[ \psi^0(r_1, r_2) = \phi_{1s}(r_1) \phi_{1s}(r_2) = \left( \frac{Z^3}{\pi} \right)^{1/2} e^{-Zr_1} e^{-Zr_2} \]

\[ \hat{H}^1 = \frac{1}{r_{12}} \]

\[ E_n^1 = \int d\tau \psi_n^{0*} \hat{H}^1 \psi_n^0 = \frac{Z^6}{\pi^2} \int d\tau e^{-Zr_1} e^{-Zr_2} \left( \frac{1}{r_{12}} \right) e^{-Zr_1} e^{-Zr_2} \]
\[ = \frac{Z^6}{\pi^2} \int d\tau \frac{e^{-2Zr_1} e^{-2Zr_2}}{r_{12}} = \frac{5}{8} Z E_h \]
Thus, the ground state energy with first order correction is:

\[ E_0 = E_0^0 + E_0^1 = -4E_h + \frac{5}{8}ZE_h = \frac{-11}{4}E_h = -74.8 \text{eV} \]

- Neglect of electron-electron repulsion: \( E_0 = -108.8 \text{ eV} \)
- First order correction: \( E_0 = -78.8 \text{ eV} \)
- 13th order correction: \( E_0 = -79.01 \text{ eV} \)
- Experiment: \( E = -70.0 \text{ eV} \)
- 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 Schrödinger 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 environments (core versus valence electrons), we can approximate the N-electron wavefunction (eigenfunction of Schrödinger 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:

\[
\psi(r_1, r_2, ..., r_n) = \phi_1(r_1)\phi_2(r_2)\phi_3(r_3)\cdots\phi_n(r_n)
\]

Each of the functions, \( \phi_n \), is associated with an **orbital energy**, \( \epsilon_n \). It is important to note that this form does not imply fully independent electrons, since, as will be evident, each electron’s dynamics (and hence 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 Schrödinger equation cannot be solved analytically. Numerical methods are applied along with approximations.
• One such approximation 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 electron 2. The “physical” picture here is of electron 2 “smeared” out spherically 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:

$$-e\phi^*(r_2)\phi(r_2)d\tau$$

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:

$$V_1^{\text{eff}}(r_1) = \frac{-2e^2}{4\pi\epsilon_0 |r_1|} + \int \phi^*_2(r_2) \frac{e^2}{r_1 - r_2} \phi_2(r_2) d\tau$$

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 Schrödinger Equation is:

Note:

• Approximate 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-consistently to obtain the one-electron energies, $\epsilon_i$ and orbitals $\phi_i$.

• 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-direction 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 — NO ORBITAL 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.
- Note that this idea and picture of intrinsic particle spin is a convenient classical way of accounting for experiment.

Introduce spin angular momentum.

- Spin operators: \( \hat{s}^2 \) and \( \hat{s}^z \) \(\text{Spinwavefunctions:} \alpha \) and \( \beta \)
- 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.

\[
\begin{align*}
\hat{s}^2 \alpha &= \hbar^2 s(s+1) \alpha = \hbar^2 \left( \frac{1}{2} + 1 \right) \alpha \\
\hat{s}^2 \beta &= \hbar^2 s(s+1) \beta = \hbar^2 \left( \frac{1}{2} + 1 \right) \beta
\end{align*}
\]
\[ \hat{s}_z \alpha = m_s \hbar \alpha = \frac{\hbar}{2} \alpha \]
\[ \hat{s}_z \beta = m_s \hbar \beta = -\frac{\hbar}{2} \beta \]

The orthonormality conditions are:

\[ \int \alpha^* \beta d\sigma = \int \beta^* \alpha d\sigma = 0 \]
\[ \int \alpha^* \alpha d\sigma = \int \beta^* \beta d\sigma = 1 \]

**Indistinguishability of Electrons and Pauli Exclusion**

**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:

\[ \hat{H} \psi_o = E_o \psi_o \]

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

\( \psi_o \) not known, so assume a trial function, \( \chi \). 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 normalization of the guess wavefunction, \( \chi \).

The Variational Theorem states:
$E_{\text{var}} \geq E_o$ 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):

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

$$\int \chi^* \chi \, dr = \sum_n |a_n|^2 = 1 \quad \text{normalization}$$

The variational energy is:

$$E_{\text{var}} = \int \chi^* \hat{H} \chi \, dr = \sum_n |a_n|^2 E_n$$

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

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

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:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{kx^2}{2}$$
Let’s consider a trial wavefunction:

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

Trial wavefunction:

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

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

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

Now, allow \( \gamma \) to vary and optimize \( E_{\text{var}} \):

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

\[ \gamma = \left( \frac{k\mu}{\hbar} \right)^{1/2} = \alpha \]

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

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

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:

\[ \frac{\hbar^2}{2m_e} (-\nabla_1^2 - \nabla_2^2) \psi(r_1, r_2) - \frac{2e^2}{4\pi \epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi \epsilon_0 |r_2 - r_1|} \psi(r_1, r_2) = E \psi(r_1, r_2) \]

This can be rewritten in atomic units to arrive at:
\[ \hat{H}_{He} = -\frac{1}{2} \left( \nabla_1^2 + \nabla_2^2 \right) - 2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{|r_2 - r_1|} \]

\[ E_{var} = \int \chi^* \hat{H} \chi \, dr \]

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:

\[ \chi = \phi_{1s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2) \]

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

\[ \phi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{\tilde{Z}}{\alpha_o} \right)^{3/2} e^{-\tilde{Z}/\alpha_o} \quad (1 - \text{electron } H \text{ atom orbitals}) \]

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

\[ \chi(r_1, r_2) = \left( \frac{\tilde{Z}^3}{\pi} \right)^{1/2} e^{-\tilde{Z}_1/\alpha_o} \left( \frac{\tilde{Z}^3}{\pi} \right)^{1/2} e^{-\tilde{Z}_2/\alpha_o} \]

The variational energy is:

\[ E_{var} = \tilde{Z}^6 \int \frac{1}{\pi} e^{-\tilde{Z}_1/\alpha_o} e^{-\tilde{Z}_2/\alpha_o} \left[ -\frac{1}{2} \left( \nabla_1^2 + \nabla_2^2 \right) - 2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{|r_2 - r_1|} \right] e^{-\tilde{Z}_1/\alpha_o} e^{-\tilde{Z}_2/\alpha_o} \, d\tau \]

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

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

\[ = -77.5 eV \]
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 individual electrons feel an effective potential from the other electrons as discussed above.

\[ \chi(r_1, r_2) = \phi(r_1)\phi(r_2) \]

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 \( \phi^{HF}(r_1) \), \( \phi^{HF}(r_2) \). 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 parameter.

If we interpret the charge density of electron 2 as:

\[ e\phi^*(r_2)\phi(r_2) = e |\phi(r_2)|^2 \]
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:

\[
U_{1}^{\text{eff}}(r_1) = e^2 \int \phi^*(r_2) \frac{1}{r_{12}} \phi(r_2) dr_2
\]

Now we can write an effective Hamiltonian and single-electron Schrodinger equation for electron 1 as:

\[
\hat{H}_1^{\text{eff}}(r_1) = -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} + U_{1}^{\text{eff}}(r_1)
\]

\[
\hat{H}_1^{\text{eff}}(r_1) \phi^{HF}(r_1) = \epsilon_1 \phi^{HF}(r_1)
\]

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 distribution 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, \( \phi(r_2) \)
- Use \( \phi(r_2) \) to calculate \( U_{1}^{\text{eff}}(r_1) \)
  * \( U_{1}^{\text{eff}}(r_1) = e^2 \int \phi^*(r_2) \frac{1}{r_{12}} \phi(r_2) dr_2 \)
- Solve Schrodinger Eqn. for electron 1
  * \( \hat{H}_1^{\text{eff}}(r_1) = -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} + U_{1}^{\text{eff}}(r_1) \)
  * \( \hat{H}_1^{\text{eff}}(r_1) \phi^{HF}(r_1) = \epsilon_1 \phi^{HF}(r_1) \)
- Use \( \phi(r_1) \) to calculate \( U_{1}^{\text{eff}}(r_2) \)
  * \( U_{2}^{\text{eff}}(r_2) = e^2 \int \phi^*(r_1) \frac{1}{r_{12}} \phi(r_1) dr_1 \)
- Solve Schrodinger Eqn. for electron 2
We now have the solution to the full Schrodinger equation as:

\[ \chi(r_1, r_2) = \phi(r_1)\phi(r_2) \]

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

- Koopman’s theorem (ionization energies related to orbital energies)
- Filling of many-electron atom orbitals (corrections to orbital energy perspective)

**Pauli Exclusion and Anti-Symmetry of Wavefunctions**

**Good Quantum Numbers, Terms, Levels, and States**