Variational Methods for Electronic Structure

The hydrogen atom is a two-body system consisting of a proton and an electron. If spin and relativistic effects are ignored, then the Schrödinger equation for the hydrogen atom can be solved exactly. In this respect, it is similar to the Kepler problem in classical mechanics.

The classical three-body problem is nonintegrable and exact solutions exist only in very special cases. The analogous quantum mechanical system is the Helium atom, which consists of a nucleus and two electrons. This quantum mechanical problem cannot be solved exactly even if spin and relativistic effects are ignored. The following table from the review article Rev. Mod. Phys. 72, 497-544 (2000) by Tanner et al.

<table>
<thead>
<tr>
<th>Year</th>
<th>Semiclassical Method</th>
<th>−E</th>
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<td>1913</td>
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gives an overview of theoretical and numerical work on the Helium atom since the discovery of quantum mechanics almost 100 years ago. The ground state energy is expressed in atomic units $e = \hbar = m_e = 1$. In these units, the ground state energy of the hydrogen atom is $-0.5$. 

The variational method for the Schrödinger equation

The variational method is used very widely in condensed matter and quantum chemistry to find energies and wavefunctions. It forms the basis for more sophisticated methods such as Hartree-Fock and density functional methods.

The variational theorem

A quantum system is described by a vector $|\psi\rangle$ in an infinite dimensional Hilbert space. If $H$ is the energy (Hamiltonian) operator for the system, we can compute its expectation value

$$E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle},$$

in various possible states $|\psi\rangle$. The variational theorem states that the extrema of $E[\psi]$ are eigenstates of $H$:

$$\delta E \equiv E[\psi + \delta \psi] - E[\psi] = 0 \quad \Rightarrow \quad H\psi = E\psi.$$

In principle we could compute the energy functional in the Hilbert space and then look for its stationary points: these would give us the eigen energies and eigenvectors. This is not practical however because the space is infinite dimensional! It is hard enough to find a stationary point in a one-dimensional space!

The variational method looks for stationary points in a finite dimensional subspace of the Hilbert space. Suppose this subspace in $N$-dimensional. If $|\chi_p\rangle, p = 1, \ldots, N$ is a set of orthonormal basis vectors, i.e., unit vectors

$$\langle \chi_p | \chi_q \rangle = \delta_{pq},$$
then \( H \) can be represented by an \( N \times N \) matrix \( H \) with elements

\[
H_{pq} = \langle \chi_p | H | \chi_q \rangle, \quad p, q = 1, \ldots, N.
\]

We are looking for stationary states

\[
\psi = \sum_{p=1}^{N} C_p | \chi_p \rangle,
\]

where \( C_p \) are complex coefficients to be determined. The stationary condition becomes a matrix eigenvalue equation:

\[
HC = EC, \quad \sum_{q=1}^{N} H_{pq} C_q = EC_p, \quad p = 1, \ldots, N.
\]

Let’s recall some results from quantum mechanics:

- \( H \) is Hermitian \( H^\dagger = H \), i.e., \( H_{pq} = H_{qp}^* \). Actually in the problems we will consider, \( H \) is a real symmetric matrix.
- There are exactly \( N \) real eigenvalues.
- The \( N \) eigenvectors corresponding to these eigenvalues span the subspace and can be chosen to be orthonormal.

**The generalized eigenvalue problem**
It is actually not necessary to choose an orthonormal basis set $|\chi_p\rangle$. Any **linearly independent** set of basis vectors can be used as we will see in the examples. The eigenvalue equation for a generalized basis set is

$$ HC = ESC , \quad \sum_{q=1}^{N} H_{pq} C_q = E \sum_{q=1}^{N} S_{pq} C_q , \quad p = 1, \ldots, N . $$

where the **overlap matrix** $S$ has elements

$$ S_{pq} = \langle \chi_p | \chi_q \rangle . $$

It can be shown that

- $S$ is Hermitian, and
- The eigenvalues of $S$ are real and positive definite, i.e., $> 0$.

These properties can be used to convert the generalized eigenvalue problem to an eigenvalue problem with an orthonormal basis.

Thus the variational method is essentially a problem in **linear algebra**, i.e., the solution of linear equations involving matrices in a finite dimensional space.

**The Hydrogen Atom**

The Hydrogen atom is a system with two particles, electron and proton. The configuration space in which the system moves is therefore six dimensional. By moving to the center-of-mass system, the problem becomes effectively 3 dimensional, with Hamiltonian

$$ H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} , $$
where \( r = r_e - r_p \) is the relative coordinate of the electron with respect to the proton, \( e \) is the magnitude of the electron’s charge, and \( m = m_e m_p / (m_e + m_p) \) is the reduced mass.

**Reduction to a one-dimensional problem**

By using conservation of angular motion and the fact that the ground state is spherically symmetric, i.e., it has zero orbital angular momentum, the problem can be reduced to one dimension with Hamiltonian operator

\[
H = -\frac{\hbar^2}{2m} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] - \frac{e^2}{4\pi\epsilon_0 r},
\]

which depends on the radial coordinate \( r \).

**Exact solution for the ground state**

The exact ground state energy and wavefunction are given by

\[
E_0 = -\frac{e^2}{2a_0}, \quad \psi_0(r) \sim e^{-r/a_0}.
\]

where the *Bohr radius*

\[
a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2}.
\]

It is convenient to use *atomic units* in which \( \hbar = m = e^2 / (4\pi\epsilon_0) = 1 \) so

\[
H = -\frac{1}{2} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] - \frac{1}{r}, \quad E_0 = -\frac{1}{2}, \quad \psi_0(r) \sim e^{-r}.
\]
Simple variational trial wave function

A simple trial wave function for the Hydrogen atom ground state is
\[
\psi_{T,\alpha}(r) = e^{-\alpha r}.
\]

The Hamiltonian acting on this function gives:
\[
H \psi_{T,\alpha}(r) = \left[ -\frac{\hbar^2 \alpha^2}{2m} + \left( \frac{\hbar^2 \alpha}{m} - \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{r} \right] \psi_{T,\alpha}(r) \equiv E(r) \psi_{T,\alpha}(r).
\]

The quantity \( E(r) \) is called the local energy of the trial wavefunction. Note that choosing the variational parameter
\[
\alpha = \frac{me^2}{4\pi\epsilon_0\hbar^2} = \frac{1}{a_0}
\]
equal to the inverse Bohr radius makes the local energy independent of \( r \) and the trial wavefunction is proportional to the exact ground state wave function.
Linear Combination of Atomic Orbitals

Trial wavefunctions that consist of linear combinations of simple functions

$$\psi(r) = \sum_n d_n \chi_n(r)$$

form the basis of the Linear Combination of Atomic Orbitals or LCAO method introduced by Lennard-Jones and others around 1929 to compute the energies and wavefunctions of atoms and molecules. The functions $\chi$ are chosen so that matrix elements can be evaluated analytically.

Slater orbitals using Hydrogen-like wavefunctions

$$\chi(r) = Y_{\ell m}(\theta, \phi)e^{-\alpha r}$$

and Gaussian orbitals of the form

$$\chi(r) = Y_{\ell m}(\theta, \phi)e^{-\alpha r^2}$$

are the most widely used forms. Gaussian orbitals form the basis of many quantum chemistry computer codes.


$$\psi(r) = \sum_{i=0}^{N-1} d_i g_s(\alpha_i, r)$$
where

\[ g_s(\alpha, \mathbf{r}) = \left( \frac{2\alpha}{\pi} \right)^{\frac{3}{4}} e^{-\alpha r^2} \]

for the \( \ell = 0 \) s-wave states.

Because products of Gaussians are also Gaussian, the required matrix elements are easily computed:

\[
S_{ij} = \int d^3r \ e^{-\alpha_i r^2} e^{-\alpha_j r^2} = \left( \frac{\pi}{\alpha_i + \alpha_j} \right)^{3/2} ,
\]

\[
T_{ij} = -\frac{\hbar^2}{2m} \int d^3r \ e^{-\alpha_i r^2} \nabla^2 e^{-\alpha_j r^2} = \frac{3\hbar^2}{m} \frac{\alpha_i \alpha_j \pi^{3/2}}{(\alpha_i + \alpha_j)^{5/2}} ,
\]

\[
V_{ij} = -e^2 \int d^3r \ e^{-\alpha_i r^2} \frac{1}{r} e^{-\alpha_j r^2} = -\frac{2\pi e^2}{\alpha_i + \alpha_j} .
\]

The 1998 Nobel Prize in Chemistry was divided equally between Walter Kohn ”for his development of the density-functional theory” and John A. Pople ”for his development of computational methods in quantum chemistry”.

**C++ Code for Hydrogen**

The BFGS method from the GNU Scientific Library 36 Multidimensional Minimization can be used to minimize the variational energy.
The Helium Atom

The Helium atom is a 3-particle problem: two electrons orbit around a nucleus, which consists of two protons with charge $e$ each and two neutral neutrons. The nucleus, which is $\sim 8,000$ times more massive than an electron, can be assumed to be at rest at the origin of the coordinate system. The electrons have positions $r_1$ and $r_2$. This is simpler than making a transformation to the center-of-mass system of the three particles, and it is sufficiently accurate.

If we use atomic units with $\hbar = m_e = e = 1$, the Hamiltonian for the motion of the two electrons can be written

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

where

$$r_{12} = |r_{12}| = |r_1 - r_2|.$$

The terms $-2/r_i$ represent the negative (attractive) potential energy between each electron with charge $-1$ and the Helium nucleus with charge $+2$, and the term $+1/r_{12}$ represents the positive (repulsive) potential energy between the two electrons.
A simple choice of variational trial wave function

If the repulsive term $1/r_{12}$ were not present, then the Hamiltonian would be that of two independent Hydrogen-like atoms. It can be shown that the energy and ground state wave function of a Hydrogen-like atom whose nucleus has charge $Z$ are given by

$$E_0 = -\frac{Z^2}{2}, \quad \psi_0 \sim e^{-Z}\cdot$$

The wave function of the combined atom with two non-interacting electrons would be the product of two such wave functions:

$$\psi(r_1, r_2) \sim e^{-2r_1}e^{-2r_2}.$$ 

This suggests a trial wave function of the form

$$\Psi_{T,\alpha} = e^{-\alpha r_1}e^{-\alpha r_2},$$

similar to what was done for the Hydrogen atom. If the electron-electron interaction is neglected, then the average energy with this wave function can be calculated

$$\left\langle -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} \right\rangle = 2 \times \frac{\alpha^2}{2} - 2 \times 2 \times \alpha,$$

which has a minimum at $\alpha = 2$, which gives $\langle E \rangle = -4$. The experimentally measured ground state energy is $E_0 = -2.904$. 
In fact, the average energy can be evaluated exactly for this trial wave function even if the electron-electron interaction is included:

\[ \left\langle -\frac{1}{2} \nabla^2_1 - \frac{1}{2} \nabla^2_2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right\rangle = \alpha^2 - \frac{27}{8} \alpha , \]

which has a minimum at \( \alpha = 27/16 \), which gives \( \langle E \rangle = -2.8477 \). This shows that the electron-electron interaction is important, and including it gives remarkably good agreement with the experimental value.
Variational Calculations of Hylleraas and others

The variational method for the Helium atom using Slater orbitals with multiple variational parameters was pioneered by E.A. Hylleraas in *Z. Phys.* 48, 469 (1929). He used a variational wave function

\[ \psi = e^{-ks/2} \left( 1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2 \right), \]

where the variables

\[ s = r_1 + r_2, \quad t = r_2 - r_1, \quad u = r_{12} \]

were chosen to deal with singularities in the potential energy. Minimizing the energy by varying \(k, \beta, \gamma, \delta, \epsilon, \zeta\), he found the value

\[ E_0 = -2.90324 \text{ a.u.} \]

for the ground state energy of the Helium atom.

Chandrasekhar, Elbert and Herzberg *Phys. Rev.* 91, 1172 (1953) improved on Hylleraas’ calculation by using 9 parameters

\[ e^{-ks/2} \left( 1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2 + \chi_6 s u + \chi_7 t^2 u + \chi_8 u^3 + \chi_9 t^2 u^2 \right) \]

and found

\[ E_0 = -2.903603 \text{ a.u.} \]

Numerous other variational calculations have since been performed, one of the most recent being by V.I. Korobov *Phys. Rev. A* 66, 024501 (2002) who used 5200 variational parameters and obtained

\[ E_0 = -2.903724377034119598311159 \text{ a.u.} \]

**Evaluation of Matrix Elements**

The expectation value of the energy in the variational state can be evaluated analytically using formulas in [Wikipedia: Slater type orbital](https://en.wikipedia.org/wiki/Slater_type_orbital).
C++ Code for Helium

```cpp
int main()
{
    return 0;
}
```