16 The Variation Method

Here we will discuss a method which allows us to approximate the ground state energy of a system without solving the Schrödinger equations. This method is known as the variation method and is based on the following theorem.

**The variation Theorem** For any normalized acceptable function $\phi$

\[
\int \phi^* \hat{H} \phi \, d\tau \geq E_0 \quad (578)
\]

where $E_0$ is the lowest eigenvalue of $\hat{H}$. The variation theorem allows us to calculate an upper bound for the system’s ground state energy. The prove the theorem first expand the function $\phi$ in terms of the complete, orthonormal set of eigenfunctions of $\hat{H}$

\[
\phi = \sum_k a_k \psi_k \quad (579)
\]

Substitution of this give

\[
\hat{H} \psi_k = E_k \psi_k \quad (580)
\]

using the eigenvalue equation and interchange the integration and summations gives

\[
\int \phi^* \hat{H} \phi \, d\tau = \sum_k |a_k|^2 E_k \geq \sum_k |a_k|^2 E_0 \quad (586)
\]

Since $E_k \geq E_0$ and $|a_k|^2$ is always positive we have $|a_k|^2 E_k \geq |a_k|^2 E_0$ for every $k$ which give $\sum_k |a_k|^2 E_k \geq \sum_k |a_k|^2 E_0$, we therefore have

\[
\int \phi^* \hat{H} \phi \, d\tau = \sum_k |a_k|^2 E_k \geq \sum_k |a_k|^2 E_0 = E_0 \sum_k |a_k|^2 \quad (586)
\]
Since $\phi$ is normalized we have

$$1 = \int \phi^* \phi d\tau$$

(587)

$$= \int \sum_k a_k^* \psi_k^* a_j \psi_j d\tau$$

(588)

$$= \sum_k \sum_j a_k^* a_j \int \psi_k^* \psi_j d\tau$$

(589)

$$= \sum_k \sum_j a_k^* a_j \delta_{kj}$$

(590)

$$= \sum_k |a_k|^2$$

(591)

Therefore

$$\int \phi^* \hat{H} \phi d\tau \geq E_0$$

(592)

What if the wavefunction is not normalized. In this case we have

$$|N|^2 \int \phi^* \hat{H} \phi d\tau \geq E_0$$

(593)

where we know that

$$1 = |N|^2 \int \phi^* \phi d\tau, |N|^2 = 1/ \int \phi^* \phi d\tau$$

(594)

this gives us

$$\frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0$$

(595)

Therefore, if we can express our trial wavefunction in terms of a set of parameters $\{\alpha_i\}$ we can find the optimum wavefunction by minimizing the expectation valued with respect to the parameters

$$\frac{\partial \langle E(\alpha_1, \alpha_2, \cdots, \alpha_n) \rangle}{\partial \alpha_i} = 0, i = 1, 2, \cdots, n$$

(596)
16.1 Variational treatment of the Hydrogen-like atom

Find the optimum form of a trial function \( \psi = \exp(-kr) \) and the upper bound to the ground state energy of the Hydrogen-like atom. The Hamiltonian of the system is

\[
\hat{H} = -\frac{1}{2} \nabla^2 - \frac{Z}{r}
\]  

(597)

First we need to evaluate the normalization integral

\[
\int \psi^* \psi \, d\tau = 4\pi \int_0^\infty \exp(-2kr) r^2 \, dr = 4\pi \frac{2!}{(2k)^3} = \frac{\pi}{k^3}
\]

(598)

Next we need to evaluate the repulsion integral

\[
\int \psi^* \frac{1}{r} \psi \, d\tau = 4\pi \int_0^\infty \exp(-2kr) r \, dr = 4\pi \frac{1!}{(2k)^2} = \frac{\pi}{k^2}
\]

(599)

and finally the kinetic energy integral

\[
\int \psi^* \nabla^2 \psi \, d\tau = \int \psi^* \left( \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \right) \exp(-kr) \, d\tau
\]

(600)

\[
= \int \psi^* \left( \frac{1}{r^2} \frac{d}{dr} r^2 \right) (-k) \exp(-kr) \, d\tau
\]

(601)

\[
= \int \psi^* \left( \frac{1}{r^2} (-2kr + k^2 r^2) \right) \exp(-kr) \, d\tau
\]

(602)

\[
= \int (k^2 - \frac{2k}{r}) \exp(-2kr) \, d\tau
\]

(603)

\[
= 4\pi \int (k^2 - \frac{2k}{r}) r^2 \exp(-2kr) \, d\tau
\]

(604)

\[
= 4\pi(k^2 \frac{2!}{(2k)^3} - 2k \frac{1}{(2k)^2}) = -\frac{\pi}{k}
\]

(605)

Therefore the variational ration is

\[
\langle E \rangle = \frac{\pi/2k - Z \pi/k^3}{\pi/k^3} = k^2/2 - Zk
\]

(606)

To find the minimum we differentiate with respect to \( k \)

\[
\frac{d \langle E \rangle}{dk} = k - Z = 0
\]

(607)
which gives \( k = Z \). Therefore, the minimum ground state energy is

\[
\langle E \rangle = Z^2/2 - Z^2 = -\frac{Z^2}{2}
\]  

(608)

and the wavefunction is

\[
\phi = \sqrt{Z^3\pi} \exp(-Zr)
\]

(609)

which is the exact solution for the Hydrogen-like atom.

### 16.2 Variational treatment of the Helium atom

Let’s find using the variational method the optimum form of the wavefunction for the Helium atom in the 1s\(^2\) configuration. In order to represent the correct screening of the nuclei due the second electron we will replace \( Z \) with a variable parameter \( \zeta \) as

\[
1s'(1) = \sqrt{\frac{\zeta^3}{\pi}} \exp(-\zeta r_1)
\]

(610)

Our normalized trial function of the Helium atom is then given by

\[
\phi(1, 2) = 1s'(1)1s'(2)
\]

(611)

The average energy is

\[
\langle E \rangle = \int \int \phi^*(1, 2)\hat{H}\phi(1, 2)d\tau_1d\tau_2 = \int \int 1s'(1)1s'(2)\hat{H}1s'(1)1s'(2)dv_1dv_2
\]

(612)

due to the integration over spin is normalized and \( \hat{H} \) is spin-less. The Hamiltonian of the system is

\[
\hat{H} = \hat{h}(1) + \hat{h}(2) + \frac{1}{r_{12}}
\]

(613)

The integrals we need to evaluate is then

\[
\int \int 1s'(1)1s'(2)\hat{h}(1)1s'(1)1s'(2)dv_1dv_2 = \int 1s'(1)\hat{h}(1)1s'(1)dv_3
\]

(614)

\[
= (\zeta^2/2) - 2\zeta
\]

(615)
Which can be realized by rewritten the one-electron Hamiltonian as

$$\hat{h}(1) = -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} = -\frac{1}{2} \nabla_1^2 - \frac{\zeta}{r_1} + \frac{\zeta - 2}{r_1}$$

(616)

where the first two parts gives a Hamiltonian which together with the 1s' is the same as the hydrogen-like Schrödinger equation with eigenvalues \(E = \frac{\zeta^2}{2}\).

Similarly, for the integral over the second electron

$$\int \int 1s'(1)1s'(2)\hat{h}(1)1s'(1)1s'(2)dv_1dv_2 = \int 1s'(2)\hat{h}(2)1s'(2)dv_1$$

(617)

$$= (\zeta^2 / 2) - 2\zeta$$

(618)

The last integral we have already seen the solution to

$$\int \int 1s'(1)1s'(2)\frac{1}{r_{12}}1s'(1)1s'(2)dv_1dv_2 = \frac{5}{8}\zeta$$

(619)

The average energy is therefore

$$\langle E \rangle = 2[\frac{\zeta^2}{2} - 2\zeta] + \frac{5}{8}\zeta = \zeta^2 - \frac{27}{8}\zeta$$

(620)

Minimizing the energy with respect to \(\zeta\) gives

$$\frac{d \langle E \rangle}{d\zeta} = 2\zeta - \frac{27}{8} = 0$$

(621)

which gives

$$\zeta = \frac{27}{16} = 1.6875$$

(622)

which is smaller than 2 as expected. Let's check the average energy. For \(\zeta = 2\) the average energy give -2.75 a.u. and for \(\zeta = 1.6875\) we get the energy of -2.8477 a.u. The exact results is 2.9037 a.u. The un-optimized wavefunction therefore finds 95% of the total energy whereas the optimized wavefunctions find about 98% of the energy. However, the energy difference is still around 35 kcal/mol in error!
16.3 The linear variation method

Let’s assume that we have selected an appropriate set of basis functions \( \{ \phi_j \} \) which are linear independent but not necessarily orthonormal. We can then expand our trial wavefunction in a finite number of basis functions as

\[
\psi = \sum_j c_j \phi_j
\]

where the coefficients \( c_j \) are parameters to be determined by minimizing the variational integral. We will restrict the basis functions and coefficients to be real. The variation integral is then

\[
\langle E(\{ \phi_j, c_j \}) \rangle = \frac{\int \psi^\ast \hat{H} \psi d\tau}{\int \psi^\ast \psi d\tau}
\]

The normalization integral is

\[
\int \psi^\ast \psi d\tau = \sum_j c_j^2 \sum_k c_k^2 = \sum_j \sum_k c_j c_k \int \phi_j \phi_k d\tau = \sum_j \sum_k c_j c_k S_{jk}
\]

where we define the overlap integral \( S_{jk} \) as

\[
S_{jk} = \int \phi_j \phi_k d\tau
\]

Similarly, the expectation value integral is

\[
\int \psi^\ast \hat{H} \psi d\tau = \sum_j \sum_k c_j \hat{H} \phi_j \phi_k d\tau = \sum_j \sum_k c_j c_k \int \phi_j \hat{H} \phi_k d\tau = \sum_j \sum_k c_j c_k H_{jk}
\]

where we have introduced the matrix elements of the Hamiltonian

\[
H_{jk} = \int \phi_j \hat{H} \phi_k d\tau
\]

The variational integral is therefore

\[
\langle E(\{ \phi_j, c_j \}) \rangle = \bar{E} = \frac{\int \psi^\ast \hat{H} \psi d\tau}{\int \psi^\ast \psi d\tau} = \frac{\sum_j \sum_k c_j c_k H_{jk}}{\sum_j \sum_k c_j c_k S_{jk}}
\]
or

\[ \bar{E} \sum_{j}^{n} \sum_{k}^{n} c_j c_k S_{jk} = \sum_{j}^{n} \sum_{k}^{n} c_j c_k H_{jk} \]  \hspace{1cm} (630)

We will not minimize the energy with respect to the \( c_i \) coefficients

\[ \frac{\partial \bar{E}}{\partial c_i} = 0, \ i = 1, 2, \ldots, n \]  \hspace{1cm} (631)

where we assume the basis functions to be fixed (or pre-optimized). We can therefore differentiate partially with respect to each \( c_i \) and get \( n \) equations:

\[ \frac{\partial \bar{E}}{\partial c_i} \sum_{j}^{n} \sum_{k}^{n} c_j c_k S_{jk} + \bar{E} \frac{\partial}{\partial c_i} \sum_{j}^{n} \sum_{k}^{n} c_j c_k S_{jk} = \frac{\partial}{\partial c_i} \sum_{j}^{n} \sum_{k}^{n} c_j c_k H_{jk}, i = 1, 2, \ldots, n \]  \hspace{1cm} (632)

Let's consider the second term

\[ \frac{\partial}{\partial c_i} \sum_{j}^{n} \sum_{k}^{n} c_j c_k S_{jk} = \sum_{j}^{n} \sum_{k}^{n} \left[ \frac{\partial}{\partial c_i} (c_j c_k) \right] S_{jk} = \sum_{j}^{n} \sum_{k}^{n} \left[ c_k \frac{\partial c_j}{\partial c_i} + c_j \frac{\partial c_k}{\partial c_i} \right] S_{jk} \]  \hspace{1cm} (633)

Since all of the coefficients are independent variable we have

\[ \frac{\partial c_j}{\partial c_i} = \delta_{ij} \]  \hspace{1cm} (634)

Therefore, we have

\[ \frac{\partial}{\partial c_i} \sum_{j}^{n} \sum_{k}^{n} c_j c_k S_{jk} = \sum_{j}^{n} \sum_{k}^{n} c_k \delta_{ij} S_{jk} + \sum_{j}^{n} \sum_{k}^{n} c_j \delta_{ik} S_{jk} = \sum_{j}^{n} c_k S_{ik} + \sum_{j}^{n} c_j S_{ji} \]  \hspace{1cm} (635)

since we assumed real basis functions

\[ \frac{\partial}{\partial c_i} \sum_{j}^{n} \sum_{k}^{n} c_j c_k S_{jk} = \sum_{k}^{n} c_k S_{ik} + \sum_{j}^{n} c_j S_{ij} = \sum_{k}^{n} c_k S_{ik} + \sum_{j}^{n} c_j S_{ik} = 2 \sum_{k}^{n} c_k S_{ik} \]  \hspace{1cm} (636)

Replacing \( S_{jk} \) with \( H_{jk} \) we get

\[ \frac{\partial}{\partial c_i} \sum_{j}^{n} \sum_{k}^{n} c_j c_k H_{jk} = 2 \sum_{k}^{n} c_k H_{ik} \]  \hspace{1cm} (637)
where we have used that $H_{ji} = H_{ij}^* = H_{ij}$ since $\hat{H}$ is Hermitian and real functions. Collecting the terms gives up

$$2\bar{E} \sum_k^n c_k S_{ik} = 2 \sum_k^n c_k H_{ik}, \quad i = 1, 2, \ldots, n$$  \hspace{1cm} (638)$$

which gives us the following set on $n$ simultaneous linear homogenous equations

$$\sum_k^n [(H_{ik} - S_{ik} \bar{E})c_k] = 0$$  \hspace{1cm} (639)$$

For example for $n = 2$ we have

$$(H_{11} - S_{11} \bar{E})c_1 + (H_{12} - S_{12} \bar{E})c_2 = 0$$  \hspace{1cm} (640)$$

$$(H_{21} - S_{21} \bar{E})c_1 + (H_{22} - S_{12} \bar{E})c_2 = 0$$  \hspace{1cm} (641)$$

Similar to what we know from degenerate perturbation theory, the only non-trivial solution is when

$$\text{det}(H_{ij} - S_{ij} \bar{E}) = 0$$  \hspace{1cm} (642)$$

The solution to this equation gives us $n$ roots which we can order

$$\bar{E}_1 \leq \bar{E}_2 \leq \cdots \leq \bar{E}_n$$  \hspace{1cm} (643)$$

Similar we can order the bound states of the real system as

$$E_1 \leq E_2 \leq \cdots \leq E_n \leq E_{n+1} \leq \cdots$$  \hspace{1cm} (644)$$

From variational theorem we know that $E_1 \leq \bar{E}_1$ and we prove that it holds for all states

$$E_1 \leq \bar{E}_1, E_2 \leq \bar{E}_2, \cdots, E_n \leq \bar{E}_n$$  \hspace{1cm} (645)$$

**Example:** Find the eigenvalues and normalized eigenvector of the following Hermitian matrix

$$A = \begin{pmatrix} 3 & 2i \\ -2i & 0 \end{pmatrix}$$  \hspace{1cm} (646)$$

The secular equation for the eigenvalues $\lambda$ is $\text{det}(a_{ij} - \delta_{ij}\lambda) = 0$ or

$$\begin{vmatrix} 3 - \lambda & 2i \\ -2i & \lambda \end{vmatrix} = 0, \quad \lambda^2 - 3\lambda - 4 = 0$$  \hspace{1cm} (647)$$
This gives us eigenvalues of \( \lambda_1 = 4 \) and \( \lambda = -1 \). For the first root the the set of simultaneous linear equations is

\[
(3 - \lambda_1) c_1^1 + 2 i c_2^1 = (3 - 4) c_1^1 + 2 i c_2^1 = -c_1^1 + 2 i c_2^1 = 0 \tag{648}
\]

\[
-2 i c_1^1 - \lambda_1 c_2^1 = -2 i c_1^1 - 4 c_2^1 = 0 \tag{649}
\]

using either of these give \( c_1^1 = 2 i c_2^1 \). Normalization gives

\[
1 = |c_1^1|^2 + |c_2^1|^2 = 4 |c_2^1|^2 + |c_2^1|^2 \tag{650}
\]

which gives \( c_2^1 = \sqrt{5} \) and \( c_1^1 = 2 i \sqrt{5} \). Similarly, for the second root we will get

\[
c_1^2 = -i / \sqrt{5}, c_2^2 = 2 / \sqrt{5} \tag{651}
\]

Checking that if we use the normalized eigenvectors we can diagonalize the Hermitian matrix

\[
C^{-1}AC = C^\dagger AC = 1/5 \begin{pmatrix} -2i & 1 \\ i & 2 \end{pmatrix} \begin{pmatrix} 3 & 2i \\ -2i & 0 \end{pmatrix} \begin{pmatrix} 2i & -i \\ 1 & 2 \end{pmatrix} \tag{652}
\]

\[
= 1/5 \begin{pmatrix} -2i & 1 \\ i & 2 \end{pmatrix} \begin{pmatrix} 8 & i \\ 4 & -2 \end{pmatrix} = 1/5 \begin{pmatrix} 20 & 0 \\ 0 & -5 \end{pmatrix} \tag{653}
\]

Find the eigenvalues of the following matrices

\[
A = \begin{pmatrix} 0 & -1 \\ 3 & 2 \end{pmatrix} \tag{654}
\]

Solution: \( \lambda = 1 + \sqrt{2}i, c_1 = -1/\sqrt{12} + i/\sqrt{6}, c_2 = \sqrt{3}/2 \) and \( \lambda = 1 - \sqrt{2}i, c_1 = -1/\sqrt{12} - i/\sqrt{6}, c_2 = \sqrt{3}/2 \)

\[
B = \begin{pmatrix} 2 & 0 \\ 9 & 2 \end{pmatrix} \tag{655}
\]

Solution: \( \lambda = 2, c_1 = 0, c_2 = 1, \) and \( \lambda = 2, c_1 = 1, c_2 = 0 \)

\[
C = \begin{pmatrix} 4 & 0 \\ 0 & 4 \end{pmatrix} \tag{656}
\]

Solution: \( \lambda = 4, c_1 = 1, c_2 = 0, \) and \( \lambda = 4, c_1 = 0, c_2 = 1 \)

78
16.4 The hydrogen atom in an external electric field

Let's consider a hydrogen atom in an external electric along the z-axis. Since we polarize the wavefunction along the z direction an appropriate choice of the trial wavefunction would be

\[ \psi = c_1 1s + c_2 2p_z \] (657)

and the Hamiltonian for the system is

\[ \hat{H} = \hat{H}_{\text{hyd}} - F r \cos \theta = -\frac{1}{2} \nabla^2 - \frac{1}{r} - F r \cos \theta \] (658)

Since \( n = 2 \) we can write the secular equation as

\[
\begin{vmatrix}
H_{11} - \bar{E} S_{11} & H_{12} - \bar{E} S_{12} \\
H_{21} - \bar{E} S_{21} & H_{22} - \bar{E} S_{22}
\end{vmatrix} = 0
\] (659)

Since the hydrogen-like functions are orthonormal the evaluation of the overlap integrals is trivial and the secular equation reduces to

\[
\begin{vmatrix}
H_{11} - \bar{E} & H_{12} \\
H_{21} & H_{22} - \bar{E}
\end{vmatrix} = 0
\] (660)

We therefore need to consider the following integrals

\[ H_{11} = \langle 1s | \hat{H}_{\text{hyd}} | 1s \rangle - F \langle 1s | r \cos \theta | 1s \rangle = -\frac{1}{2} \] (661)

\[ H_{22} = \langle 2p_z | \hat{H}_{\text{hyd}} | 2p_z \rangle - F \langle 2p_z | r \cos \theta | 2p_z \rangle = -\frac{1}{8} \] (662)

and

\[ H_{12} = \langle 1s | \hat{H}_{\text{hyd}} | 2p_z \rangle - F \langle 1s | r \cos \theta | 2p_z \rangle = -F \langle 1s | r \cos \theta | 2p_z \rangle \] (663)

\[ -\frac{F}{2\sqrt{2}} \int_0^\infty r^4 \exp(-3r/2) dr \int_0^\pi \cos^2 \theta \sin \theta d\theta \] (664)

\[ = -\frac{F}{2\sqrt{2}} \left[ \frac{4!}{(3/2)^5} \right] \frac{2}{3} = -0.745F \] (665)

Therefore, the secular equation reduces to

\[
\begin{vmatrix}
-\frac{1}{2} - \bar{E} & -0.745F \\
-0.745F & -\frac{1}{8} - \bar{E}
\end{vmatrix} = 0
\] (666)
Expanding this gives
\[
(-\frac{1}{2} - \bar{E})(-\frac{1}{8} - \bar{E}) - 0.745^2F^2 = \bar{E}^2 + \frac{5}{8}\bar{E} - 0.745^2F^2 = 0
\] (667)
for which the solution to the quadratic equation gives
\[
\bar{E} = -\frac{5}{16} \pm \sqrt{\frac{9/64 + 2.22F^2}{2}}
\] (668)
Therefore, for \(F = 0\) we get
\[
\bar{E} = -\frac{5}{16} \pm \frac{0.202}{2} = -0.5145, -0.1105
\] (670)
which are the unperturbed solution as expected. For a field strength of \(F = 0.1Z\) we get
\[
\bar{E} = -\frac{5}{16} \pm 0.202 = -0.5145, -0.1105
\] (670)
Next we need to solve for the coefficients \(c_1\) and \(c_2\), the linear equations are
\[
(H_{11} - \bar{E})c_1 + H_{12}c_2 = 0
\] (671)
\[
H_{21}c_1 + (H_{22} - \bar{E})c_2 = 0
\] (672)
Substituting the solution for \(F = 0.1\) into the equation gives
\[
0.01425c_1 - 0.0745c_2 = 0
\] (673)
\[
-0.0745c_1 + 0.3893c_2 = 0
\] (674)
which gives us \(c_1 = 5.2275c_2\). Using the normalization constraints we get
\[
c_1^2 + c_2^2 = 1 = (5.2275^2 + 1)c_2^2, c_2 = \pm 0.1879
\] (675)
which for the positive root gives \(c_1 = 0.98219\)