The Variational Method

An Example

Let us try to solve the hydrogen atom problem using the variational method, using the trial function \( \varphi(r) = Ne^{-br} \) for the ground state, where \( N \) is the normalization constant and \( b \) is the adjustable variational parameter. The Hamiltonian for the ground state \( (l = 0) \), in atomic units, is

\[
\hat{H} = -\frac{1}{2} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right] - \frac{1}{r}.
\]  

(1)

If the trial function is normalized, the variational energy \( W \) is given by

\[
W = \int_0^\infty \varphi^* \hat{H} \varphi r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi.
\]  

(2)

Let us first determine the normalization constant by requiring that

\[
\int_0^\infty \varphi^* \varphi r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi = 1,
\]

or

\[
1 = 4\pi |N|^2 \int_0^\infty r^2 e^{-2br} dr,
\]

where we have evaluated the integrals over the angles \( \theta \) and \( \phi \) to get the factor of \( 4\pi \). Now, from tables of standard integrals, we find that

\[
\int_0^\infty z^n e^{-ax} dz = \frac{n!}{a^{n+1}}; \ n > -1, \ a > 0.
\]  

(3)

Substituting \( z = r, \ n = 2 \) and \( a = 2b \), we get \( \int_0^\infty r^2 e^{-2br} dr = 1/(4b^3) \), which leads to

\[
4\pi |N|^2 \int_0^\infty r^2 e^{-2br} dr = \frac{\pi}{b^3}, \ \text{or}
\]

\[
N = \frac{1}{\sqrt{\pi}} b^{3/2}.
\]

The next step is to evaluate the integral in Eq. (2). We first find the result of the Hamiltonian operator acting on the trial function:

\[
\hat{H} \varphi = -\frac{1}{2} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right] - \frac{\varphi}{r}
\]

\[
= -\frac{b^{3/2}}{2\sqrt{\pi}} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \left(-be^{-br}\right) \right] - \frac{\varphi}{r}
\]

\[
= \frac{b^{3/2}}{2\sqrt{\pi}} \left[ \frac{b}{r^2} (2r - r^2 b) - \frac{1}{r} \right] e^{-br}
\]

\[
= \frac{b^{3/2}}{\sqrt{\pi}} \left[ \frac{b}{r} - \frac{b^2}{2} \right] e^{-br}.
\]
Now, we evaluate the integral in Eq. (2) using the result given in Eq. (3).

\[
W = 4\pi \int_0^\infty \phi^\ast \hat{H} \phi r^2 dr = 4b^3 \int_0^\infty \left[ \frac{b - 1}{r} - \frac{b^3}{2} \right] e^{-2br^2} r^2 dr
\]

\[
= 4b^3 \left[ (b - 1) \frac{1}{(2b)^2} - \frac{b^3}{2 (2b)^3} \right] \]

\[
= \frac{b^2}{2} - b. \tag{4}
\]

Recall that the next step in the variational method is to minimize \( W \) with respect to the adjustable (variational) parameters. Let us now plot \( W \) as a function of the parameter \( b \) to see where the minimum value of \( W \) lies.

![Plot of W as a function of the parameter b.](image)

It is clear that the value of \( b \) corresponding to the minimum in \( W \) is \( b = 1 \) (in atomic units). We can reach the same conclusion by requiring that \( \frac{\partial W}{\partial b} = 0 \), which gives us

\[
\frac{\partial}{\partial b} \left[ \frac{b^2}{2} - b \right] = b - 1 = 0, \quad \text{or} \quad b = 1.
\]

Comparing the trial function to the exact ground state wave function, we see that the parameter \( b \) is, in fact, \( Z \), the nuclear charge. Therefore, the result \( Z = 1 \) for hydrogen is to be expected. Corresponding to the optimum value of the parameter \( b = 1 \), we get \( W = -1/2 \) hartree, which is the exact ground state energy of the hydrogen atom. We get this result, of course, because we started with a trial function that had the exact form of the correct ground state wave function. If we had started with a Gaussian type function instead, say, \( \phi = Ne^{-br^2} \), we would obtain

\[
W = \frac{3b^2}{2} - 2 \left( \frac{2b}{\pi} \right)^{1/2}. \tag{5}
\]

As an exercise, find the optimum value of \( b \) and verify that \( W \geq E \), where \( E \) is the exact ground state energy of \(-1/2 \) hartree.