Example of Application of Variational Principle

The steps in applying the variational method to a problem are:

1. Select a trial function, $\psi_{trial}\,(x;\,\alpha)$, a function of the variables (x) and the parameter (α)
2. Evaluate $<E(\alpha)>_{trial}$

$$\langle E(\alpha)\rangle_{trial} \equiv \widetilde{E}(\alpha) = \int \Psi^{*}_{trial}(x;\alpha)\,\hat{H}\,\Psi_{trial}(x;\alpha)dx \geq E_0 \;(true\,lowest\,eigenvalue)$$

3. Find the optimum values of the parameters:

$$Solve\,the\,equation\;\; \frac{\partial \tilde{E}(\alpha)}{\partial \alpha} = 0 \qquad for\;\alpha_{optimum}$$

4. Find the value $<E(\alpha_{opt})>$
5. Either "rest assured" that $<E(\alpha_{opt})> \geq E_0$ if you don't know E_0 (usual situation)

   or

   demonstrate $<E(\alpha_{opt})> \geq E_0$ for sample examples where we have applied a variational treatment to a problem where we have already been able to solve exactly for ψ_0 and E_0

Worked Example In Atomic Units

(see pp. 4-6 for example retaining MKS)

$$For\ the\ hydrogen\ atom\ Hamiltonian$$

$$\psi_{trial}(r,\theta,\phi;\alpha) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2}$$

$$\left(note\ this\ is\ best\ Gaussian;\ prob\ HW\ \#\ 32\ is\ best\ exponential\ \approx\ e^{-\alpha r};\ \mathbb{EASIER!}\right)$$

$$\tilde{E}(\alpha) \equiv \langle E(\alpha)\rangle_{trial} = \int \psi^*_{trial}\, \hat{H}\, \psi_{trial}\, d\tau$$

$$\hat{H} = -\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial^2\phi}\right] - \frac{Z}{r}$$

Evaluating $\mathcal{H}\psi_{\mathbf{trial}}$

$$to\ evaluate\ \hat{H}\,\psi_{trial}\ one\ can\ first\ forget\ the\ \partial\text{'}\ s\ with\ respect\ to\ \theta\ and\ \phi,\ since\ \psi_{trial}\ is\ spherically\ symmetric$$

$$\begin{aligned}
\hat{H}\, e^{-\alpha r^2} &= -\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\right] e^{-\alpha r^2} - \frac{Z}{r}\, e^{-\alpha r^2} \\
&= -\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2\right]\left(-2\,\alpha r e^{-\alpha r^2}\right) - \frac{Z}{r}\, e^{-\alpha r^2} \\
&= -\frac{1}{2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(-2\alpha r^3\, e^{-\alpha r^2}\right)\right] - \frac{Z}{r}\, e^{-\alpha r^2} \\
&= -\frac{1}{2}\left[\frac{1}{r^2}\left(-6\alpha r^2 e^{-\alpha r^2} + 4\,\alpha^2 r^4 e^{-\alpha r^2}\right)\right] - \frac{Z}{r}\, e^{-\alpha r^2} \\
&= \frac{1}{2}\left[\left(6\alpha - 4\,\alpha^2 r^2\right)\right] e^{-\alpha r^2} - \frac{Z}{r}\, e^{-\alpha r^2}
\end{aligned}$$

Substituting $\mathcal{H}\psi_{\mathbf{trial}}$ into <E(α)>

$$\tilde{E}(\alpha) = \int_0^\infty r^2\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2}\, \hat{H}\left[\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2}\right]$$

$$\tilde{E}(\alpha) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}} \int_0^\infty r^2 e^{-2\alpha r^2}\left\{\frac{1}{2}\left[\left(6\alpha - 4\,\alpha^2 r^2\right)\right] - \frac{Z}{r}\right\} dr\, \underbrace{\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi}_{4\pi}$$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}} \int_0^\infty e^{-2\alpha r^2}\left\{\frac{1}{2}\left[\left(6\alpha r^2 - 4\,\alpha^2 r^4\right)\right] - Zr\right\} dr$$

$$using \int_0^\infty r^2\, e^{-2\alpha r^2}\, dr = \frac{\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{8\alpha^{\frac{3}{2}}} \quad , \quad \int_0^\infty r^4\, e^{-2\alpha r^2}\, dr = \frac{3\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{32\alpha^{\frac{5}{2}}} \quad , and \quad \int_0^\infty r^1\, e^{-2\alpha r^2}\, dr = \frac{1}{4\alpha}$$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}} \int_0^\infty e^{-2\alpha r^2}\left\{\frac{1}{2}\left[\ \left(6\alpha r^2\ -\ 4\,\alpha^2\,r^4\right)\ \ \right] - Zr\right\} dr$$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}}\left\{\frac{1}{2}\left[\left(\frac{6\,\alpha\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{8\alpha^{\frac{3}{2}}}\right) - \left(\frac{4\,\alpha^2\,3\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{32\,\alpha^{\frac{5}{2}}}\right)\right] - \frac{Z}{4\alpha}\right\}$$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{2\alpha^{\frac{1}{2}}}\left[\left(\frac{3}{4}\right) - \left(\frac{3}{8}\right)\right] - \frac{Z}{4\alpha}\right\}$$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\alpha}{2}\left[\left(\frac{3}{8}\right)\right] - \frac{Z\alpha^{\frac{1}{2}}}{4}\right\}$$

$$\tilde{E}(\alpha) = \left\{\frac{3}{2}\alpha - \left(\frac{8}{\pi}\right)^{\frac{1}{2}} Z\alpha^{\frac{1}{2}}\right\}$$

Evaluating dE(α)/ dα, and finding $\alpha_{\mathbf{optimum}}$

$$\tilde{E}(\alpha) = \left\{\frac{3}{2}\alpha - \left(\frac{8}{\pi}\right)^{\frac{1}{2}} Z\alpha^{\frac{1}{2}}\right\}$$

$$\frac{d\tilde{E}(\alpha)}{d\,\alpha} = \left\{\frac{3}{2} - \left(\frac{2}{\pi}\right)^{\frac{1}{2}} Z\alpha^{-\frac{1}{2}}\right\} = 0$$

$$thus$$

$$(\alpha_{optimum})^{\frac{1}{2}} = \left(\frac{2}{\pi}\right)^{\frac{1}{2}}\frac{2}{3}Z$$

$$(\alpha_{optimum}) = \frac{8}{9\pi}Z^2$$

Evaluating E($\alpha_{\mathbf{optimum}}$)

$$\tilde{E}(\alpha) = \left\{\frac{3}{a}\alpha\ -\ \left(\frac{8}{\pi}\right)^{\frac{1}{2}} Z\alpha^{\frac{1}{2}}\right\} = \left\{\frac{24}{18\pi}Z^2 - \frac{8}{3\pi}Z^2\right\} = \frac{4}{3\pi}Z^2 - \frac{8}{3\pi}Z^2 = -\frac{4}{3\pi}Z^2$$

$$for\ Z = 1\quad \tilde{E}(\alpha) = -\frac{4}{3\pi} = -\,0.\,4224$$

$$\mathbf{NOTE:\ In\,a.\,u.\ \ E_{H\,atom} = -\,0.\,5\,thus\,\tilde{E}(\alpha_{optimum})\ >\ E_0}$$

Worked Example In MKS units

$$For\ the\ hydrogen\ atom\ Hamiltonian$$

$$\psi_{trial}(r,\theta,\phi;\alpha) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2}$$

$$\big(note\ this\ is\ best\ Gaussian;\ HW\ prob\ \#\ 32\ is\ best\ exponential\ \approx\ e^{-\alpha r};\ \mathbb{EASIER}!\big)$$

$$\tilde{E}(\alpha) \equiv \langle E(\alpha)\rangle_{trial} = \int \psi^*_{trial}\,\hat{H}\,\psi_{trial}\,d\tau$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\,r^2\frac{\partial}{\partial r} + \frac{1}{r^2\,sin\,\theta}\frac{\partial}{\partial\theta}\,sin\theta\ \frac{\partial}{\partial\theta}\ + \frac{1}{r^2\,sin^2\,\theta}\frac{\partial^2}{\partial^2\phi}\right] - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$(note\ in\ last\ term\ \ e\ is\ electronic\ charge\ \textbf{not}\ exponential)$$

Evaluating $\mathcal{H}\psi_{\mathbf{trial}}$

$to\ evaluate\ \hat{H}\,\psi_{trial}\ one\ can\ first\ forget\ the\ \partial\text{'}\ s\ \ with\ respect\ to\ \theta\ and\ \phi,\ \ since\ \psi_{trial}\ is\ spherically\ symmetric$

$$\begin{aligned}
\hat{H}\,e^{-\alpha r^2} &= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\,r^2\frac{\partial}{\partial r}\ \right]e^{-\alpha r^2} - \frac{e^2}{4\pi\epsilon_0 r}\,e^{-\alpha r^2}\\
&= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\,r^2\ \right]\Big(-\,2\,\alpha r e^{-\alpha r^2}\Big) - \frac{e^2}{4\pi\epsilon_0 r}\,e^{-\alpha r^2}\\
&= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\Big(-\,2\alpha r^3\,e^{-\alpha r^2}\Big)\ \right] - \frac{e^2}{4\pi\epsilon_0 r}\,e^{-\alpha r^2}\\
&= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\ \Big(-\,6\alpha r^2 e^{-\alpha r^2}\ +\ 4\,\alpha^2\,r^4 e^{-\alpha r^2}\Big)\ \right] - \frac{e^2}{4\pi\epsilon_0 r}\,e^{-\alpha r^2}\\
&= \frac{\hbar^2}{2\mu}\big[\ \big(6\alpha\ -\ 4\,\alpha^2\,r^2\big)\ \ \big]\,e^{-\alpha r^2} - \frac{e^2}{4\pi\epsilon_0 r}\,e^{-\alpha r^2}
\end{aligned}$$

Substituting $\mathcal{H}\psi_{trial}$ into <E(α)>

$$\tilde{E}(\alpha) = \int_0^\infty r^2\,dr \int_0^\pi sin\,\theta\,d\theta \int_0^{2\pi} d\phi \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2}\,\hat{H}\left[\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2}\right]$$

$$\tilde{E}(\alpha) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}} \int_0^\infty r^2 e^{-2\alpha r^2}\left\{\frac{\hbar^2}{2\mu}\left[\ (6\alpha - 4\,\alpha^2\,r^2)\ \ \right] - \frac{e^2}{4\pi\varepsilon_0 r}\right\} dr \underbrace{\int_0^\pi sin\,\theta\,d\theta \int_0^{2\pi} d\phi}_{4\pi}$$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}} \int_0^\infty e^{-2\alpha r^2}\left\{\frac{\hbar^2}{2\mu}\left[\ (6\alpha r^2 - 4\,\alpha^2\,r^4)\ \ \right] - \frac{e^2\,r}{4\pi\varepsilon_0}\right\} dr$$

$$using \int_0^\infty r^2\,e^{-2\alpha r^2}\,dr = \frac{\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{8\alpha^{\frac{3}{2}}} \quad , \quad \int_0^\infty r^4\,e^{-2\alpha r^2}\,dr = \frac{3\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{32\alpha^{\frac{5}{2}}} \quad , and \quad \int_0^\infty r^1\,e^{-2\alpha r^2}\,dr = \frac{1}{4\alpha}$$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\hbar^2}{2\mu}\left[\left(\frac{6\,\alpha\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{8\alpha^{\frac{3}{2}}}\right) - \left(\frac{4\,\alpha^2\,3\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{32\,\alpha^{\frac{5}{2}}}\right)\right] - \frac{e^2}{4\pi\varepsilon_0\,4\alpha}\right\}$$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\hbar^2\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{2\mu\alpha^{\frac{1}{2}}}\left[\left(\frac{3}{4}\right) - \left(\frac{3}{8}\right)\right] - \frac{e^2}{4\pi\varepsilon_0\,4\alpha}\right\}$$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\hbar^2\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\alpha}{2\mu}\left[\left(\frac{3}{8}\right)\right] - \frac{e^2\alpha^{\frac{1}{2}}}{4(4\pi\varepsilon_0)}\right\}$$

Evaluating dE(α)/ dα , and finding $\alpha_{optimum}$

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\hbar^2\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\alpha}{2\mu}\left[\left(\frac{3}{8}\right)\right] - \frac{e^2\alpha^{\frac{1}{2}}}{4(4\pi\varepsilon_0)}\right\}$$

$$\frac{d\tilde{E}(\alpha)}{d\,\alpha} = 4\pi\left(\frac{2}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\hbar^2\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{2\mu}\left[\left(\frac{3}{8}\right)\right] - \frac{e^2\alpha^{-\frac{1}{2}}}{8(4\pi\varepsilon_0)}\right\} = 0$$

$$thus$$

$$(\alpha_{optimum})^{\frac{1}{2}} = \frac{e^2}{8(4\pi\varepsilon_0)}\left(\frac{16\mu}{3\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\hbar^2}\right)$$

$$(\alpha_{optimum}) = \frac{e^4}{64(4\pi\varepsilon_0)^2}\left(\frac{256\mu^2}{9\left(\frac{\pi}{2}\right)\hbar^4}\right) = \frac{8e^4\mu^2}{9\pi(4\pi\varepsilon_0)^2\hbar^4}$$

Evaluating E($\alpha_{optimum}$)

$$\tilde{E}(\alpha) = 4\pi\left(\frac{2}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\hbar^2\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\alpha}{2\mu}\left[\left(\frac{3}{8}\right)\right] - \frac{e^2\alpha^{\frac{1}{2}}}{4(4\pi\varepsilon_0)}\right\}$$

$$with$$

$$(\alpha_{optimum}) = \frac{e^4}{64(4\pi\varepsilon_0)^2}\left(\frac{256\mu^2}{9\left(\frac{\pi}{2}\right)\hbar^4}\right) = \frac{8e^4\mu^2}{9\pi(4\pi\varepsilon_0)^2\hbar^4}$$

$$gives$$

$$\tilde{E}(\alpha_{optimum}) = 4\pi\left(\frac{2}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\hbar^2\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{2\mu}\left[\left(\frac{3}{8}\right)\right]\left(\frac{8e^4\mu^2}{9\pi(4\pi\varepsilon_0)^2\hbar^4}\right) - \frac{e^2\left(\frac{8e^4\mu^2}{9\pi(4\pi\varepsilon_0)^2\hbar^4}\right)^{\frac{1}{2}}}{4(4\pi\varepsilon_0)}\right\}$$

$$simplifying\, with\, the\, Bohr\, radius\;\; a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

$$\tilde{E}(\alpha_{optimum}) = 4\pi\left(\frac{2}{\pi}\right)^{\frac{3}{2}}\left\{\frac{\hbar^2\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{2\mu}\left(\frac{3}{8}\right)\left(\frac{8e^2\mu}{9\pi(4\pi\varepsilon_0)\hbar^2 a_0}\right) - \frac{e^2\left(\frac{8}{9\pi}\right)^{\frac{1}{2}}}{4(4\pi\varepsilon_0)a_0}\right\}$$

$$\tilde{E}(\alpha_{optimum}) = 4\pi\left(\frac{2}{\pi}\right)^{\frac{3}{2}}\frac{e^2}{(4\pi\varepsilon_0)a_0}\left\{\left[\frac{\left(\frac{\pi}{2}\right)^{\frac{1}{2}}}{6\pi} - \frac{\left(\frac{8}{9\pi}\right)^{\frac{1}{2}}}{4}\right]\right\}$$

$$\tilde{E}(\alpha_{optimum}) = \frac{e^2}{(4\pi\varepsilon_0)a_0}\left\{\left[\frac{8}{6\pi} - \frac{8}{3\pi}\right]\right\}$$

$$\tilde{E}(\alpha_{optimum}) = \frac{e^2}{(4\pi\varepsilon_0)a_0}\left\{\left[-\frac{8}{6\pi}\right]\right\}$$

$$\tilde{E}(\alpha_{optimum}) = -\,0.4244\,\frac{e^2}{(4\pi\varepsilon_0)a_0}$$

$$NOTE\colon\, E_0\,,\, the\, acutal\, lowest\, eigenvalu\, of\, \widehat{H}\, is$$

$$E_0 = -\,0.5\,\frac{e^2}{(4\pi\varepsilon_0)a_0}$$

THUS: $\tilde{\mathbf{E}}(\alpha_{\mathbf{optimum}}) > \mathbf{E_0}$ **as required by the variation theorem!!!**