Chem. 540
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Computer Assignment 4

The Variational Principle

In this assignment you will apply the variational principle to calculate approximations to the ground state energy of one-dimensional systems described by the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) .$$

Use the (un-normalized) trial function

$$\Psi_\lambda(x) = e^{-\lambda x^2}$$

For each of the potentials

(a) $V(x) = \frac{1}{2} m\omega^2 x^2$

(b) $V(x) = \frac{1}{2} x^4$

use a symbolic algebra program to calculate the expectation value of the Hamiltonian (the energy) with respect to this trial function, evaluate the first derivative of this expectation value with respect to the nonlinear variational parameter λ, and set this derivative equal to zero to find the optimal value of λ. To confirm that this is indeed a minimum, plot the energy as a function of λ. How does your energy compare to the exact result (in the case of the harmonic potential) or (in the case of the quartic potential) the result you obtained from the basis set expansion in the previous assignment? You may observe that the ground state energy from the present single-parameter trial function is comparable in accuracy to the result you obtained with several basis functions in the basis set calculation. Since the basis set calculation was an application of the Rayleigh-Ritz variational method, both results are based on the variational method. As you can see, the present nonlinear trial function converges more efficiently than the linear Rayleigh-Ritz expansion. What can you say about the wavefunction that minimizes the energy?