

Chem. 540  
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### Variational Principle – Problem 2

The variational principle derived in class applies to the ground state energy only. In general, it is not easy in practice to use variational theories for excited states; but at least in principle it is possible to formulate such a theory. Show that if the trial function is orthogonal to the true ground state wavefunction, then the expectation value of the Hamiltonian will be greater than or equal to the energy of the first excited state. The practical difficulty lies in finding such a trial function, since in general one does not know the true ground state of the system.

As an illustration, find the expectation value of a harmonic oscillator Hamiltonian with a trial function of the type

$$\Psi(x) = cxe^{-\lambda x^2}.$$

Show that this trial function is orthogonal to the true ground state wavefunction of this Hamiltonian. Next, find the value of  $\lambda$  that minimizes the energy, and show that with this choice you recover the exact energy of the first excited state. This happens here because the trial function happens to have the same form as the exact wavefunction.