Problem 1: The variational method

Let's consider the following very simple problems to see how good the variational method works.

(a) Consider the 1D harmonic oscillator. Take a Gaussian trial wave function \( \psi_a(x) = \exp(-\alpha x^2) \). Show that the variational approach gives the exact ground energy.

(b) Suppose for the trial, we took a Lorentzian, \( \psi_a = \frac{1}{x^2 + \alpha} \). Using the variational method, by what percentage are you off from the exact ground state energy?

(c) Consider the “double oscillator” \( V(x) = \frac{1}{2} m \omega^2 (|x| - a)^2 \).

Argue that a good choice of trial wave functions are,

\[
\psi_n^{(\pm)} = u_n(x-a) \pm u_n(x+a)
\]

where \( u_n(x) \) are the eigenfunctions for a harmonic potential at the origin.

(d) Using this show that the variational estimates of the energies are

\[
E_n^{(\pm)} = \frac{A_n \pm B_n}{1 \pm C_n}
\]

\[
A_n = \int dx \ u_n(x-a) H u_n(x-a), \quad B_n = \int dx \ u_n(x-a) H u_n(x+a), \quad C_n = \int dx \ u_n(x+a) u_n(x-a).
\]

(e) For \( a \) much larger than the ground state width, show that

\[
\Delta E_0 \equiv E_0^{(-)} - E_0^{(+)} = 2 \hbar \omega \sqrt{\frac{2V_0}{\pi \hbar \omega}} \exp\left(-\frac{2V_0}{\hbar \omega}\right), \quad \text{where} \quad V_0 = \frac{1}{2} m \omega^2 a^2.
\]

This is know as the ground “tunneling” splitting. Explain why.

(f) This approximation clearly breaks down as \( a \to 0 \). Think about the limits and sketch the energy spectrum as a function of \( a \).
Problem 2: Lennard-Jones Potential

Consider the “Lennard-Jones” potential used to model the binding of two atoms into a molecule, \( V(r) = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6} \), with \( C_{12} \) and \( C_6 \) real numbers.

(a) Near the minimum \( r_0 \), the potential looks, harmonic. Including the first anharmonic correction, show that up to a constant term,

\[
V(x) = \frac{1}{2} m\omega^2 x^2 + \xi x^3
\]

where \( r_0 = (2C_{12}/C_6)^{1/6} \) \( \frac{1}{2} m\omega^2 = V''(r_0) \) and \( \xi = \frac{1}{6} V'''(r_0) \).

Let us thus write, \( \hat{H} = \hat{H}_0 + \hat{H}_1 \), where \( \hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 \) and \( \hat{H}_1 = \xi \hat{x}^3 \).

(b) What is the small parameter of the perturbation expansion?

(c) Show that the first energy shift vanishes (hint: use symmetry).

(d) Show that the second order shift (first nonvanishing correction) is

\[
E_n^{(2)} = \frac{\xi^2 \hbar^2}{m^3 \omega^4} \left[ \frac{(n-2)(n-1)(n)}{3} + \frac{(n+3)(n+2)(n+1)}{-3} + \frac{9n^3}{1} + \frac{9(n+1)^3}{-1} \right]
\]

(e) Put these together to show that,

\[
E_n^{(2)} = \frac{\xi^2 \hbar^2}{m^3 \omega^4} \left[ \frac{15}{4} (n + 1/2)^2 + \frac{7}{16} \right]
\]

(f) Consider carbon C-C bonds take the Lennard-Jones parameters \( C_6 = 15.2 \text{ eV } \text{Å}^6 \) and \( C_{12} = 2.4 \times 10^4 \text{ eV } \text{Å}^{12} \). Plot the potential and the energy levels from the ground to second excited state including the anharmonic shifts.
Problem 3: Addition of spin and orbital angular momentum

Consider an electron with orbital angular momentum quantum number $l = 1$ and spin quantum number $s = 1/2$. The total angular momentum operator, is $\hat{\mathbf{j}} = \hat{\mathbf{l}} + \hat{\mathbf{s}}$.

(a) Find the simultaneous eigenvectors of $\hat{j}^2, \hat{j}_z, \hat{s}^2, \hat{l}^2$ in terms of the uncoupled representation by direct diagonalization of matrix for $\hat{j}^2$ in that basis.
Hint: Order your basis so that your matrices are block diagonal.

(b) Obtain the same results using the Clebsch-Gordan coefficients (use can use Mathematica, tables, or any other method).

(c) Find the matrix elements of $\hat{\mathbf{l}} \cdot \hat{\mathbf{s}}$ in the coupled basis. Hint: Consider $\hat{j}^2 = \left| \hat{\mathbf{l}} + \hat{\mathbf{s}} \right|^2$. 