Physics 531
Problem Set #1 – Due January 7, 2005

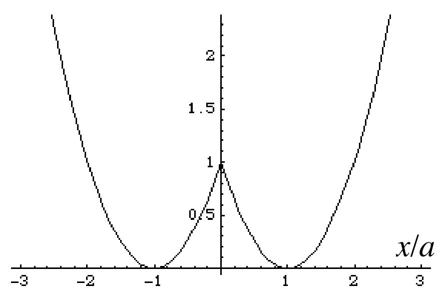
Problem 1: The variational method

Lets us 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, $\psi_a = \dfrac{1}{x^2+\alpha}$. Using the variational method, by what percentage are you off from the exact ground state energy?

(c) Consider the "double oscillator" $V(x) = \frac{1}{2}m\omega^2\left(|x|-a\right)^2$.



Argue that a good choice of trail 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

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

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

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

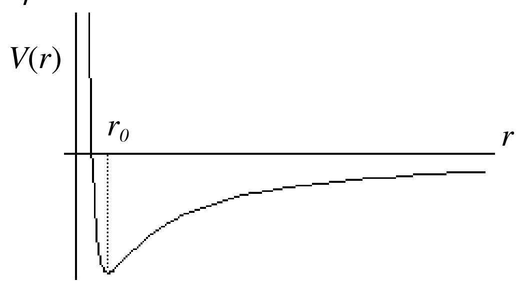
$$\Delta E_0 \equiv E_0^{(-)} - E_0^{(+)} \approx 2\hbar\omega\sqrt{\frac{2V_0}{\pi\hbar\omega}}\exp\left(-\frac{2V_0}{\hbar\omega}\right), \text{ where } V_0 = \frac{1}{2}m\omega^2 a^2.$$

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, $V(r) = \dfrac{C_{12}}{r^{12}} - \dfrac{C_6}{r^6}$, 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 $r_0 = (2C_{12}/C_6)^{1/6}$ $\dfrac{1}{2} m\omega^2 = V''(r_0)$ and $\xi = \dfrac{1}{6} V'''(r_0)$.

Let us thus write, $\hat{H} = \hat{H}_0 + \hat{H}_1$, where $\hat{H}_0 = \dfrac{\hat{p}^2}{2m} + \dfrac{1}{2} m\omega^2 \hat{x}^2$ 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

$$E_n^{(2)} = \frac{\xi^2 \left(\dfrac{\hbar}{2m\omega} \right)^3}{\hbar\omega} \sum_{m \pm n} \frac{\left| \langle m | \left(\hat{a} + \hat{a}^\dagger \right)^3 | n \rangle \right|^2}{n - m}$$

(e) Put these together to show that,

$$E_n^{(2)} = \frac{\xi^2 \hbar^2}{m^3 \omega^4} \left[\frac{(n-2)(n-1)(n)}{3} + \frac{(n+3)(n+2)(n+1)}{-3} + \frac{9n^3}{1} + \frac{9(n+1)^3}{-1} \right]$$
$$= -\frac{\xi^2 \hbar^2}{m^3 \omega^4} \left[\frac{15}{4} \left(n + 1/2 \right)^2 + \frac{7}{16} \right]$$

(f) Consider carbon C-C bonds take the Lennard-Jones parameters $C_6 = 15.2$ eV Å^6 and $C_{12} = 2.4 \times 10^4$ eV 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 $\hat{\vec{\mathbf{j}}} = \hat{\vec{\mathbf{l}}} + \hat{\vec{\mathbf{s}}}$.

(a) Find the simultaneous eigenvectors of $\hat{\mathbf{j}}^2, \hat{j}_z, \hat{\mathbf{s}}^2, \hat{\mathbf{l}}^2$ in terms of the uncoupled representation by direct diagonalization of matrix for $\hat{\mathbf{j}}^2$ 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 $\hat{\vec{\mathbf{l}}} \cdot \hat{\vec{\mathbf{s}}}$ in the coupled basis. Hint: Consider $\hat{\vec{\mathbf{j}}}^2 = \left|\hat{\vec{\mathbf{l}}} + \hat{\vec{\mathbf{s}}}\right|^2$.