Physics 492: Quantum Mechanics II
Problem Set #9
Due: Thursday, April 22, 2004

Problem 1: Lennard-Jones Encore (15 points)

In Problem Set #2 we studied the validity of the harmonic approximation to various binding potentials. Here we examine corrections via perturbation theory. In particular, consider again the "Lennard-Jones" potential used to model the binding of two atoms into a molecule,

$$V(r) = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6},$$

which has a stable equilibrium point at $r_0 = \left(2C_{12}/C_6\right)^{1/6}$. For small displacements $x = r - r_0$ the potential is harmonic. Including the first anharmonic correction,

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

where $\frac{1}{2}m\omega^2 = V''(r_0)$ and $\xi = \frac{1}{6}V'''(r_0)$ (units E/L^3). Let us thus write,

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \text{ where } \hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \text{ and } \hat{H}_1 = \xi\hat{x}^3.$$

(a) What is the small parameter of the perturbation expansion?
(b) Show that the first energy shift *vanishes* (hint: use symmetry).
(c) Show that the second order shift (first nonvanishing correction) is

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

(d) Show, $\left(\hat{a}+\hat{a}^\dagger\right)^3 = \hat{a}^3 + \hat{a}^{\dagger 3} + 3\left(\hat{N}+1\right)\hat{a} + 3\hat{N}\hat{a}^\dagger$.
(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 $C_{12} = 2.4\times10^4$ eV Å^{12}. Plot the potential and the energy levels from the ground to second excited state including the anharmonic shifts.

Problem 2: Perturbation Theory in a Two-Dimensional Hilbert Space (15 points)

Consider a spin-1/2 particle in the presence of a static magnetic field along the z and x directions, $\mathbf{B} = B_z \mathbf{e}_z + B_x \mathbf{e}_x$.

(a) Show that the Hamiltonian is, $\hat{H} = \hbar\omega_0 \hat{\sigma}_z + \frac{\hbar\Omega}{2}\hat{\sigma}_x$, where $\hbar\omega_0 = \mu_B B_z$ and $\hbar\Omega = 2\mu_B B_x$.

(b) If B_x=0, the eigenvectors are $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$ with eigenvalues $\pm\hbar\omega_0$ respectively. Now turn on a weak x field with $B_x \ll B_z$. Use perturbation theory to find the new eigenvectors and eigenvalues to lowest order in B_x / B_z.

(c) Suppose now B_z=0. What are the eigenvectors and eigenvalues in terms of $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$. Relate this to degenerate perturbation theory.

(d) This problem can actually be solved *exactly*. Find the eigenvectors and eigenvalues for *all* **B**. Show that these agree with your results in parts (b) and (c) by the appropriate limits.

(e) Plot the two energy eigenvalues as a function of B_z for a fixed B_x. Label the eigenvectors on the curves when B_z=0, $B_z \to -\infty$, and $B_z \to +\infty$.