Homework 9

Due: 11:59 PM, Tuesday, November 3. Submit your homework via Canvas.

Grading: 30 points required for full credit. 30 points are possible.

10 points **Problem 1:** Consider two coupled and distinguishable spin-$\frac{1}{2}$ particles with Hamiltonian

$$H = b_1 \frac{2S_{1z}}{\hbar} + b_2 \frac{2S_{2z}}{\hbar} + \frac{4\epsilon}{\hbar^2}\left(S_{1z}S_{2z} + S_{1x}S_{2x}\right). \tag{1}$$

Assume that ϵ is perturbatively small, and $b_1 \neq b_2$.

(a) Find the eigenvalues of H when $\epsilon = 0$.

(b) Calculate the eigenvalues and eigenvectors of H to first order in ϵ.

(c) Use second order perturbation theory to calculate the eigenvalues of H to second order in ϵ.

Problem 2 (Dissociation of the hydrogen molecule): We stated earlier in this class that the harmonic oscillator could be a good approximation for a chemical bond in a diatomic molecule, such as H_2. Consider the following oscillator model for such a bond:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - \gamma x^3 + \cdots \tag{2}$$

We solved this problem exactly when $\gamma = 0$. Now, let us solve this problem with perturbation theory when γ is "small".

5 points (a) Use dimensional analysis to determine the SI units of the parameter γ. Build a quantity with the same units as γ out of m, $\hbar$ and ω: i.e. $m^a\hbar^b\omega^c$ (what are a, b, c?). Then estimate how small γ must be for perturbation theory to be a sensible approximation method.

10 points (b) Use first and second order perturbation theory to show that the n^{th} energy level of H is approximately[1]

$$E_n \approx \hbar\omega\left(n + \frac{1}{2}\right) - \frac{\hbar^2\gamma^2}{8m^3\omega^4}\left(11 + 30n + 30n^2\right) + \cdots \tag{3}$$

Is your argument from part (a) reasonable?

5 points (c) The result of part (b) suggests that we can *estimate* the energy scale at which H_2 would break apart (the **dissociation energy**) by fitting the discrete energy levels E_n measured in the actual H_2 molecular bond to a quadratic function of the parameter n (treat it as continuous for this part), and looking for the maximum value of this fitting function. The energy levels of the H_2 bond are

$$E = 0.52, 1.00, 1.46, 1.89, 2.29, 2.67, 3.01, 3.33, 3.61, 3.86, 4.08, 4.25, 4.38, 4.46 \text{ eV}. \tag{4}$$

(The first entry in this list is E_0, the second is E_1, and so on.) Estimate the dissociation energy of this bond, and compare to the experimental value of 4.52 eV.

[1] *Hint:* First express x in terms of raising and lowering operators.