5.73 Problem Set 4

Due Friday, Oct. 21

1. Consider a molecular system with three low-lying electronic states: $|\psi_0\rangle, |\psi_a\rangle, |\psi_b\rangle$. $|\psi_0\rangle$ is the ground state and $|\psi_a\rangle$ and $|\psi_b\rangle$ are two degenerate excited states of the molecule. In this basis, the Hamiltonian and two important observables ($\hat{X}$ and $\hat{Y}$) are given by:

$$\mathbf{H} \equiv \begin{pmatrix} E_0 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_1 \end{pmatrix} \quad \mathbf{X} \equiv \begin{pmatrix} 0 & x & 0 \\ x & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{Y} \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & iy \\ 0 & -iy & 0 \end{pmatrix}$$

At time $t = 0$ the system is in the state

$$\vec{c} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}$$

   a. At $t = 0$, determine the average value of the energy. If one performs many, many experiments on this system, what are the possible observed values of the energy and what is the probability of each outcome?
   b. At $t = 0$, what are the possible outcomes if we measure $\hat{X}$ and what is the probability of each outcome?
   c. Calculate $\vec{c}(t)$, the state vector at time $t \neq 0$. What are the possible outcomes if we observe $\hat{X}$ at time t and what is the probability of each outcome?
   d. Calculate $\langle \hat{X}(t) \rangle$ and $\langle \hat{Y}(t) \rangle$, the average values of $\hat{X}$ and $\hat{Y}$ at time t. Is there anything interesting here?

2. Consider an anharmonic potential of the form

$$V(q) = \tfrac{1}{2}kq^2 - \alpha q^3 + \beta q^4$$

   a. Determine the stationary points of this potential. Assume m, k, α, β are all positive. Compute the value of the potential at each stationary point.
   b. Now, consider the particular case where, in natural units ($\hbar = m = k = 1$), the anharmonicities are given by $\alpha = .045$ and

$\beta = .00107$. Plot this potential and note any important features.

c. Use DVR to determine the lowest 25 eigenvalues of this potential. Note that you will probably need many more than 25 states to ensure that the lowest 25 eigenvalues are accurate.

d. Determine which of the 25 eigenstates are located to the left and right of the barrier. This may be done by examining appropriate average values (e.g. $\langle\psi_n|\hat{q}|\psi_n\rangle, \langle\psi_n|\hat{q}^2|\psi_n\rangle$, etc.) for each state. How well-localized are the states to the right of the barrier?

e. Fit the energies of the lowest several states localized on the left to a standard vibrational expansion:

$$E(n) = E_0 + \omega_e\left(n+\tfrac{1}{2}\right) - \omega_e x_e\left(n+\tfrac{1}{2}\right)^2 + \omega_e y_e\left(n+\tfrac{1}{2}\right)^3$$

where n is the quantum number that numbers the levels. What happens if you try to fit all 25 of the lowest states to this expansion?

3. This problem shows how more complicated (but still exactly solvable) problems often turn out to be the Harmonic Oscillator in disguise. These ideas arise from a field called supersymmetric quantum mechanics. Consider the generalized creation and destruction operators:

$$\hat{A} = \left(f(\hat{q}) + i\tfrac{1}{\sqrt{2}}\hat{p}\right) \quad \text{and} \quad \hat{A}^\dagger = \left(f(\hat{q}) - i\tfrac{1}{\sqrt{2}}\hat{p}\right)$$

a. Compute the commutator $\left[\hat{A}^\dagger, \hat{A}\right]$.

b. Construct the harmonic oscillator-like Hamiltonian $\hat{H}^+ = \hat{A}^\dagger\hat{A}$. Show that the effective potential is given by:

$$V^+(q) = f^2(q) - \frac{1}{\sqrt{2}}\frac{df(q)}{dq}.$$

c. Construct the related Hamiltonian $\hat{H}^- = \hat{A}\hat{A}^\dagger$. What is the effective potential in this case? $\hat{H}^+$ and $\hat{H}^-$ are said to be supersymmtric partners.

d. Denote the eigenstates of $\hat{H}^+$, $\hat{H}^-$ by

$$\hat{H}^+\left|\psi_n^+\right\rangle = E_n^+\left|\psi_n^+\right\rangle \quad \text{and} \quad \hat{H}^-\left|\psi_n^-\right\rangle = E_n^-\left|\psi_n^-\right\rangle$$

Show that $\hat{A}^\dagger\left|\psi_n^-\right\rangle$ is proportional to an eigenfunction of $\hat{H}^+$. What does this imply about the eigenvalues of $\hat{H}^-$?

What is the normalization constant for $\hat{A}^\dagger|\psi_n^-\rangle$? [Hint: you will want to exploit the analogy with the Harmonic oscillator]

e. Consider the specific case $f(\hat{q}) = \alpha e^{-\beta\hat{q}} + \gamma$. Plot the effective potentials for $\hat{H}^+$ and $\hat{H}^-$. Could either of these be useful? Show that:

$$V^+(\hat{q};\alpha,\beta,\gamma) = V^-(\hat{q};\alpha',\beta',\gamma') + R(\alpha,\beta,\gamma)$$

That is, show that $\hat{H}^+$ and $\hat{H}^-$ are of the same form, just with the parameters α,β,γ changed and a constant, R, added. This property is called shape invariance, and is crucial to determining the eigenvalues of $\hat{H}^+$ and $\hat{H}^-$.

f. Use the results of parts d. and e. to determine the lowest two eigenvalues of $\hat{H}^+(\alpha,\beta,\gamma)$ in the following way: Use part d. and the analogy with the Harmonic oscillator to determine the ground state energy of $\hat{H}^+(\alpha,\beta,\gamma)$. Next, use part e. to determine the ground state energy of $\hat{H}^-$, which will be related to an *excited state energy* of $\hat{H}^+$.

g. Determine the lowest two eigenvalues of the Morse Hamiltonian:

$$\hat{H}^+ = \frac{\hat{p}^2}{2} + D\left(1 - \exp(-\beta(q - q_0))\right)^2$$

by showing that the Morse potential corresponds to a particular choice of α,β,γ. Put your results in the standard vibrational form:

$$E(n) = \omega_e\left(n + \tfrac{1}{2}\right) - \omega_e x_e\left(n + \tfrac{1}{2}\right)^2.$$

What is the relationship between α,β,γ and ω_e, x_e?