

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.73 Quantum Mechanics I Fall, 2002

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Problem Set #5

DUE: At the start of Lecture on Friday, October 18.

Problems:

1. A. Use the \mathbf{a} , \mathbf{a}^\dagger algebra introduced at the end of Lecture #13 to organize the matrix elements of \mathbf{x}^3 and \mathbf{x}^4 according to selection rules:

$$\langle n | \mathbf{x}^3 | n+3 \rangle$$

$$\langle n | \mathbf{x}^3 | n+1 \rangle$$

$$\langle n | \mathbf{x}^4 | n+4 \rangle$$

$$\langle n | \mathbf{x}^4 | n+2 \rangle$$

$$\langle n | \mathbf{x}^4 | n \rangle$$

- B. Use non-degenerate perturbation theory to express the energy levels of

$$V(x) = kx^2/2 + ax^3 + bx^4$$

$$E(v)/hc = E_0/hc + \omega_e(v+1/2) \pm \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3$$

where ω_e , $\omega_e x_e$, and $\omega_e y_e$ are traditional vibrational constants. Express E_0 , ω_e , $\omega_e x_e$, and $\omega_e y_e$ in terms of m , k , a , and b . This is an extremely complicated and tedious algebraic nightmare. Maybe you can get your computer to do the algebra.

2. You are going to approach the following potential energy curve using a variety of methods, including the Discrete Variable representation (DVR) and Perturbation Theory:

$$V(x) = kx^2/2 - |a|x^3 + |b|x^4.$$

When $|a| > [(16/9)k|b|]^{1/2}$, $V(x)$ has two minima, at

$$x_{\min 1} = 0 \quad [V(0) = 0]$$

and

$$x_{\min 2} = \frac{3|a| + [9|a|^2 - 16k|b|]^{1/2}}{8|b|}$$

and a maximum at

$$x_{\max} = \frac{3|a| - [9|a|^2 - 16k|b|]^{1/2}}{8|b|}.$$

When $|a| < [(16/9)k|b|]^{1/2}$ the second minimum disappears. Let

$$m = 1.000 \times 10^{-2}$$

$$k = 1.000 \times 10^4$$

$$|a| = 1980$$

$$|b| = 200$$

in appropriate units.

- A. Find the energy of the local maximum of $V(x)$, $V(x_{\max})$, and use the WKB quantization condition to find the total number of bound levels at energy below the top of the potential hump. Also use WKB quantization to estimate the number of levels that *the inner well alone* would bind at $E \leq V(x_{\max})$.
- B. Use DVR to solve for the energies of the lowest n levels of this well, where n is twice the total number of levels bound below $V(x_{\max})$. Use a 500×500 matrix.
- C. Use the expectation value of x to apportion the levels you found below $V(x_{\max})$ into those bound primarily in the left (deeper) well and those bound in the right (shallower) well. Note that you can use the eigenvectors from DVR (because these are expressed in the harmonic oscillator basis set) to calculate $\langle x \rangle$ for each eigenstate.
- D. Fit the 5 lowest energies of those levels that you found in part C to be localized in the left (deeper) well to a power series in $v + 1/2$

$$\frac{E(v)}{hc} = \frac{E_0}{hc} + \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3$$

where ω_e , $\omega_e x_e$, and $\omega_e y_e$ are the traditional names for the vibrational expansion coefficients. Note that if you had attempted to fit all of the energy levels below $V(x_{\max})$ to this sort of power series, you would have required many more constants to obtain an acceptable fit and the fitted values of ω_e , $\omega_e x_e$, and $\omega_e y_e$ would not agree well with the values from perturbation theory.

- E. Compare the results you obtained in 1B to those you obtained in 2D.
3. Return to Problem #2 on Problem Set #3, using perturbation theory this time.

$$V_1(x) = \infty \quad |x| > L/2$$

$$V_2(x) = a[\delta(x - L/6) + \delta(x + L/6)]$$

Let $\mathbf{H}^{(0)} = \mathbf{P}^2/2m + V_1(x)$

$$E_n^{(0)} = \frac{h^2}{8mL^2} n^2 \quad n = 1, 2, \dots$$

$$\Psi_n^{(0)} = [2/L]^{1/2} \cos[n\pi(x + L/2)/L]$$

$$\mathbf{H}^{(1)} = V_2(x)$$

- A. Find the first order corrections to all of the energy levels. Comment on the three classes of states with respect to their values of $E_n^{(1)}$. Do the $E_n^{(1)}$ depend on the sign of a ?
- B. Before you derive the second-order corrections to all of the energy levels it is necessary to consider the selection rules on $\langle n | \mathbf{H}^{(1)} | m \rangle$. What are these selection rules?
- C. Work out the $E_n^{(2)}$ second-order energy corrections. Do the $E_n^{(2)}$ depend on the sign of a ?
- D. Use perturbation theory to address the question of when there will be zero and when there will be only one level at $E < 0$.
- E. Reconsider the two-sided correlation diagram proposed in 2E of Problem Set #3. Show that, for the three classes of levels, the energy levels are described by

$$E_n = E_n^{(0)} + aA_n + a^2B_n.$$

For which classes of levels is $A_n = 0$? For which classes of levels is $B_n = 0$?