Chem 249 Problem Set 3
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Spring 2016

Basic Quantum Theory and Energy Levels in Spectroscopy

- Dirac Bra-Ket Notation
- Matrix Representation
- Two Level System
- Spin 1/2 Systems
- Simple Harmonic Oscillator
- Perturbed Harmonic Oscillator
- Time Independent Perturbation Theory

Handouts:

1. QM1: Basic Equations
2. QM2: Time Independent Perturbation Theory
3. CH1: Child Handout #1
4. CH2: Child Handout #2

Additional Readings:

1. Atkins, Quantum Mechanics
2. Cohen-Tannoudji, Quantum Mechanics
3. Schiff, Quantum Mechanics

Problems:

1. Find the eigenvalues and eigenvectors for the three Pauli matrices in the σ_Z basis. (See CT Complement A_{iv} for details)

2. Consider a TLS using the terminology from C-T complement B_{iv}. The eigenvalues and eigenvectors are described in terms of two angles, θ and ϕ. Assume ϕ=0 (H_{12} real). We define $E_{avg} = (H_{11} + H_{22})/2$; delE = $(H_{11}-H_{22})/2$.

a) What is the range of θ? How θ are and H_{12} related?

b) Plot the two eigenvalues E+ and E- over the range of the angle θ. (You can fix Eavg to 100 and delE to 10.

3. Consider an anharmonic oscillator with the following Hamiltonian:

$H = H_0 + W$

$H_0 = p^2/2m + kx^2/2$

$W = \alpha x^3$

a. Calculate the energies of H to first order in the perturbation W. Write out formally the first order correction to the eigenstate vector, and then list the states which contribute to the new ground state.

b. Determine the allowed transitions using electric dipole selection rules for the absorption of radiation from the ground state for (i) H_0 and (ii) H.

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4. Consider a three state system described by the following 3x3 matrix Ho:

E_1	0	0
0	E_2	0
0	0	E_3

Now consider three perturbations, W_1, W_2 and W_3:

W_1:

0	0	0
0	0	0
0	0	c

W_2:

0	0	a
0	0	0
a	0	0

W_3:

0	0	0
0	0	b
0	b	0

where the quantities a, b and c are assumed to be small.

a) Use perturbation theory to find the new energies for these three separate perturbations for the for (i) the general case and (ii) the case where E1 = 100, E2=200, E3= 210 and a = b = c = 10.

b) Diagonalize the 3 x 3 matrices directly (using Wolfram Alpha or Mathematica), and compare this exact solutions with that obtained from the results of part a).

c) Consider a combined system H = Ho + W_2 + W_3. Use Wolfram Alpha to find the new eigenstates and vectors for this system for the case E1 = 100, E2=200, E3= 200 and a = b = 10.