Chem 249 Problem Set 3
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Spring 2020

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 generalized TLS H = H_0 + W where:

H_0 = {{h1, 0}, {0, h2}} and

W = {{w11, w12}, {w12, w22}}

a) find the two eigenvalues, E1 and E2, and the two eigenvectors {a1, b1} and {a2, b2} for the case where h1 = h2.

b) find the two eigenvalues, E1 and E2, and the two <u>Normalized</u> eigenvectors {a1, b1} and {a2, b2} for the case where h1 = h2 = 1000, w11 = w22 = 0 and w12 = 10

c) find the two eigenvalues, E1 and E2, and the two <u>Normalized</u> eigenvectors {a1, b1} and {a2, b2} for the case where h1 = h2 = 1000, w11 = -w22 = 100 and w12 = 10.

d) For the case where h1 = h2 = 1000, w12 = 10, and w11 = -w22 = Δ where Δ can vary from zero to 100, and plot in Igor a1/b1 and a2/b2 as a function of Δ.

3. Consider the simple harmonic oscillator with the following Hamiltonian:

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

a) express the operators x and p in terms of the raising and lowering operators a and a^+ (Find the definition of a and a^+ in the first QM pdf handout).

b) show that you can re-express H in terms of the raising and lowering operators a and a^+

$H = \hbar\omega(a^+a + ½)$

Hint: you also need to know that $[x,p] = i\hbar$.

4. 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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5. 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.