

**Quantum Theory Seminar #11**

**Readings:**

Zettili - Chapter - 9 (pages 479-495)

Boccio - Chapter - 10 (pages 31-75)

This week we continue our study of time-independent perturbation theory and also look at the variational method.

**Presentations:**

**External Fields - Zeeman/Stark Effects**      Anna  
(Chapter 10 - pages 31-35)

**Spin-Orbit for the H-Atom - Part I**      Elizabeth  
(Chapter 10 - pages 35-41)

**Spin-Orbit for the H-Atom - Part II**      Emily  
(Chapter 10 - pages 41-49)

**Zeeman Effect for the H-Atom**      Nick  
(Chapter 10 - pages 49-53)

**Wigner-Eckart Theorem**      Markus  
(Chapter 10 - pages 53-57)

**Paschen-Bach effect;**      Dogus  
(Chapter 10 - pages 57-59)

**Spectroscopic notation and fine structure**      Bevan  
(Chapter 10 - pages 59-61)

**Stark Effect**      Erik  
(Chapter 10 - pages 61-64)

**Variational Method**      Karan  
(Chapter 10 - pages 72-75)

## Problems:

### 1. Z9-30 and Z9-34 Variational Method (Karan)

### 2. Perturbed Oscillators (Emily)

(a) A particle of mass  $m$  is moving in the 3-dimensional harmonic oscillator potential

$$V(x,y,z) = \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)$$

A weak perturbation is applied in the form of the function

$$\Delta V(x,y,z) = kxyz + \frac{k^2}{\hbar\omega}x^2y^2z^2$$

where  $k$  is a small constant.

Calculate the shift in the ground state energy to **second order in  $k$** .

(b) Now consider the system described by the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2\alpha}(1 - e^{-\alpha x^2})$$

(1) Calculate an approximate value for the ground state energy using first-order perturbation theory, perturbing the harmonic oscillator Hamiltonian

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2$$

(2) Calculate an approximate value for the ground state energy using the variational method with a trial function  $\psi = e^{-\beta x^2/2}$ . Assume that  $\alpha \ll m\omega / \hbar$

### 3. Helium from Hydrogen - 2 Methods (Markus)

(a) Using a simple hydrogenic wave function for each electron, calculate by perturbation theory the energy in the ground state of the He atom associated with the electron-electron Coulomb interaction. Use this result to estimate the ionization energy of Helium.

(b) Calculate the ionization energy by using the variational method with an effective charge  $\lambda$  in the hydrogenic wave function as the variational parameter.

(c) Compare (a) and (b) with the experimental ionization energy

$$E_{ion} = 1.807E_0 \quad , \quad E_0 = \frac{\alpha^2 mc^2}{2} \quad , \quad \alpha = \text{fine structure constant}$$

You will need

$$\psi_{1s}(r) = \sqrt{\frac{\lambda^3}{\pi}} \exp(-\lambda r) \quad , \quad a_0 = \frac{\hbar^2}{me^2} \quad , \quad \iint d^3r_1 d^3r_2 \frac{e^{-\beta(r_1+r_2)}}{|\vec{r}_1 - \vec{r}_2|} = \frac{20\pi^2}{\beta^5}$$

That last integral is very hard to evaluate from first principles.

**4. Hydrogen atom + xy perturbation(Bevan)** - An electron moves in a Coulomb field centered at the origin of coordinates. The first excited state ( $n=2$ ) is 4-fold degenerate. Consider what happens in the presence of a non-central perturbation

$$V_{pert} = f(r)xy$$

where  $f(r)$  is some function only of  $r$ , which falls off rapidly as  $r \rightarrow \infty$ . To first order this perturbation splits the 4-fold degenerate level into several distinct levels (some might still be degenerate).

- How many levels are there?
- What is the degeneracy of each?
- Given the energy shift, call it  $\Delta E$ , for one of the levels, what are the values of the shifts for all the others?

**5. Rigid rotators in electric and magnetic fields(Anna)**

- Suppose that the Hamiltonian of a rigid rotator in a magnetic field is of the form

$$\hat{H} = A\hat{L}^2 + B\hat{L}_z + C\hat{L}_y$$

Assuming that  $A, B \gg C$ , use perturbation theory to lowest nonvanishing order to get approximate energy eigenvalues.

- Consider a rigid body with moment of inertia  $I$ , which is constrained to rotate in the  $xy$ -plane, and whose Hamiltonian is

$$\hat{H} = \frac{1}{2I} \hat{L}_z^2$$

Find the eigenfunctions and eigenvalues (zeroth order solution).

Assume the rotator has a fixed dipole moment  $\vec{p}$  in the plane. An electric field  $\vec{E}$  is applied in the plane. Find the change in the energy levels to first and second order in the field.

**6. Perturbation with 2 Spins(Elizabeth)** - Let  $\vec{S}_1$  and  $\vec{S}_2$  be the spin operators of two spin-1/2 particles. Then

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

is the spin operator for this two-particle system.

(a) Consider the Hamiltonian

$$\hat{H}_0 = \alpha(\hat{S}_x^2 + \hat{S}_y^2 - \hat{S}_z^2) / \hbar^2$$

Determine its eigenvalues and eigenvectors.

(b) Consider the perturbation  $\hat{H}_1 = \lambda(\hat{S}_{1x} - \hat{S}_{2x})$ . Calculate the eigenvalues in first-order perturbation theory.

Now consider a system with the unperturbed Hamiltonian

$$\hat{H}_0 = -A(\hat{S}_{1z} + \hat{S}_{2z})$$

with a perturbing Hamiltonian of the form

$$\hat{H}_1 = B(\hat{S}_{1x}\hat{S}_{2x} - \hat{S}_{1y}\hat{S}_{2y})$$

(c) Calculate the eigenvalues and eigenvectors of  $H_0$ .

(d) Calculate the exact eigenvalues of  $H_0 + H_1$ .

(e) By means of perturbation theory, calculate the first- and the second-order shifts of the ground state energy of  $H_0$ , as a consequence of the perturbation  $H_1$ . Compare these results with those of (d).

### Electric and Magnetic Fields as Perturbations

**7. Spherical cavity with electric/magnetic fields(Nick)** -

Consider a spinless particle of mass  $m$  and charge  $e$  confined in spherical cavity of radius  $R$ , that is, the potential energy is zero for  $r < R$  and infinite for  $r > R$ .

(a) What is the ground state energy of this system?

(b) Suppose that a weak uniform magnetic field of strength  $B$  is switched on. Calculate the shift in the ground state energy.

(c) Suppose that, instead a weak uniform electric field of strength  $\mathcal{E}$  is switched on. Will the ground state energy increase or decrease? Write down, but do not attempt to evaluate, a formula for the shift in the ground state energy due to the electric field.

(d) If, instead, a very strong magnetic field of strength  $B$  is turned on, approximately what would be the ground state energy? **8**

**8. Hydrogen in electric and magnetic fields(Dogus)** - Consider the  $n=2$  levels of a hydrogen-like atom. Neglect spins. Calculate to lowest order the energy splittings in the presence of both electric and magnetic fields  $\vec{B} = B\hat{e}_z$  ,  $\vec{E} = E\hat{e}_x$  .

**9.  $n=3$  Stark effect in Hydrogen(Erik)** - Work out the Stark effect to lowest nonvanishing order for the  $n=3$  level of the hydrogen atom. Obtain the energy shifts and the zeroth order eigenkets.

**10. Perturbation of the  $n=3$  level in Hydrogen - Spin-Orbit and Magnetic Field corrections(FINAL #1 - This is a big, messy problem which will tell me whether you know all aspects of time-independent perturbation theory - I expect all details to be carried out, however messy they are!)** - In this problem we want to calculate the 1st-order correction to the  $n=3$  unperturbed energy of the hydrogen atom due to spin-orbit interaction and magnetic field interaction for arbitrary strength of the magnetic field. We have  $\hat{H} = \hat{H}_0 + \hat{H}_{so} + \hat{H}_m$  where

$$\hat{H}_0 = \frac{\vec{p}_{op}^2}{2m} + V(r) \quad , \quad V(r) = -e^2 \left( \frac{1}{r} \right)$$

$$\hat{H}_{so} = \left[ \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \right] \vec{S}_{op} \cdot \vec{L}_{op}$$

$$\hat{H}_m = \frac{\mu_B}{\hbar} (\vec{L}_{op} + 2\vec{S}_{op}) \cdot \vec{B}$$

We have two possible choices for basis functions, namely,

$$|n\ell s m_\ell m_s\rangle \quad \text{or} \quad |n\ell s j m_j\rangle$$

The former are easy to write down as direct-product states

$$|n\ell s m_\ell m_s\rangle = R_{n\ell}(r) Y_\ell^{m_\ell}(\theta, \phi) |s, m_s\rangle$$

while the latter must be constructed from these direct-product states using addition of angular momentum methods.

The perturbation matrix is not diagonal in either basis.

The number of basis states is given by

$$\sum_{\ell=0}^{n-1=2} (2\ell+1) \times 2 = 10 + 6 + 2 = 18$$

All the 18 states are degenerate in zero-order. This means that we deal with an 18 x 18 matrix (mostly zeroes) in degenerate perturbation theory.

Using the direct-product states

- (a) Calculate the nonzero matrix elements of the perturbation and arrange them in block-diagonal form.
- (b) Diagonalize the blocks and determine the eigenvalues as functions of  $B$ .
- (c) Look at the  $B \rightarrow 0$  limit. Identify the spin-orbit levels. Characterize them by  $(\ell s j)$ .
- (d) Look at the  $B \rightarrow \text{large}$  limit. Identify the Paschen-Bach levels.
- (e) For small  $B$  show the Zeeman splittings and identify the Lande  $g$ -factors.
- (f) Plot the eigenvalues versus  $B$ .