

Second Year  
Long Vacation 2002  
Physical Chemistry  
Quantum Mechanics

Frank Schreiber

Please hand the work in to my pigeon hole in Wadham by Monday of the 1st week of Michaelmas Term 2002.

Literature

There are, of course, numerous books on the subject, and the choice is to some extent a matter of taste. Suitable books have been written by

Cohen-Tannoudji / Diu / Laloë  
Atkins / Friedman

Keywords

Perturbation theory  
- time-independent  
- time-dependent  
- degenerate vs. non-degenerate states  
Variational method  
Commutators and their meaning  
Angular momentum / operators / eigenfunctions / coupling of angular momenta / associated magnetic moments

**Revision and Background**

- 1) Write down *briefly* the definitions / most important facts / equations related to the above keywords.
- 2) Revise the tutorial material of weeks 1 and 2 of Trinity Term 2002
- 3) Submit your answers to the supplementary problems of these two tutorials in case you have not done so yet.

## Problem 1 Harmonic Oscillator, Anharmonicity, and Perturbation Theory

### 1. Unperturbed harmonic oscillator

Calculate the eigenfunctions and eigenenergies of the quantum mechanical harmonic oscillator with the Hamiltonian

$$H_0 = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2.$$

If you have difficulties solving the problem by yourself, you may consult a textbook and make yourself familiar with the solution strategy.

### 2. Variational method

Using  $\psi = Ae^{-Bx^2}$  as a trial function (with  $B > 0$ ), estimate the ground state energy of the harmonic oscillator using the variational method. Comment on the result.

### 3. Perturbation theory

Calculate the energy eigenvalues of the harmonic oscillator (as discussed above) with the perturbations  $H'$  given below. Use perturbation theory up to lowest non-vanishing order (i.e., if the energy correction is zero in first order, use second order). For

$$H = H_0 + H' = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2 + H'$$

analyse the following cases of small perturbations

- (a)  $H' = ax$
- (b)  $H' = bx^2$
- (c)  $H' = cx^3$
- (d)  $H' = dx^4$

Remarks:

- (i)  $a, b, c,$  and  $d$  are small, positive constants.
- (ii) Calculating integrals of the type  $\int_{-\infty}^{+\infty} \psi x^n \psi^* dx$  is easy when you remember the symmetry of  $\psi$  (even or odd function in  $x$  ?); then you may not need to calculate the integral explicitly.
- (iii) Comment on the sign of the energy correction in each case.
- (iv) Comment on the reliability of perturbation theory for the  $H' = cx^3$  case (Think about the condition (VIII.3) for the validity of perturbation theory).
- (v) Some of the Hamiltonians  $H$  may be solved exactly. If you see a way to solve it, do so, and compare the solution to that obtained from perturbation theory.

## Problem 2 Simple Potential Model - Potential Well

A very simple model for an interaction potential  $V(x)$  is given by the 1-dimensional potential well with

$$\begin{aligned} V(x) &= 0 && \text{for } x \geq a \\ V(x) &= -V_0 < 0 && \text{for } 0 < x < a \\ V(x) &= \infty && \text{for } x \leq 0 \end{aligned}$$

1. After inserting this potential into the Schrödinger equation, derive an equation, which determines the energies of bound states.
2. Discuss the solution of that equation.  
(You do not necessarily have to *solve* the equation, but you should sketch in a graph how the solution could be obtained graphically).

Remark:

Do not be confused; the problem is straight-forward. Solve the Schrödinger equation in each region separately and then match the solutions of the wavefunctions in different regions using the appropriate boundary conditions.

3. How large does  $V_0$  have to be for a given  $a$  to make bound states possible ?
4. How does the problem change if the potential is *spherical*, i.e. if the problem is not only 1-dimensional ? Can you write down the Schrödinger equation for this case ?  
(Note that in this case the angular momentum will come into play.)

### **Problem 3 Diatomic Molecules - Morse Potential**

The potential of a diatomic molecule including anharmonicity is frequently described by the (1-dimensional) Morse potential

$$V(x) = V_0(1 - e^{-\mu x})^2.$$

Find the eigenenergies.

Remark:

You may assume small oscillations, i.e.  $|\mu x| \ll 1$ .

### Problem 4 Rotation of Molecule in Electric Field - Perturbation Theory

Consider a molecule as a rigid rotator with a moment of inertia  $I$ . The molecule shall have a permanent electric dipole moment  $\vec{d}$ , and it shall be placed in a small electric field  $\vec{E}$ . By considering the energy in the field ( $-Ed \cos \phi$ ) as a small perturbation, calculate the first non-vanishing correction to the energy levels of the rotator.

Remarks:

1. The Schrödinger equation of the plane rigid rotator is

$$-\frac{\hbar^2}{2I} \frac{d^2 \Psi}{d\phi^2} = E \Psi$$

where  $\phi$  is the angle of rotation about the  $z$ -axis.

2. The energies are

$$E_m^{(0)} = \frac{\hbar^2 m^2}{2I}$$

The wavefunctions are

$$\psi_m^{(0)} = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

with  $m = 0, \pm 1, \pm 2, \dots$

3. From here on, use perturbation theory.

### **Problem 5 Angular Momentum**

1. Determine the commutators  $[\hat{L}_x, \hat{L}_y]$  and  $[\hat{L}_x, \hat{L}^2]$ .
2. Consider a hydrogen atom in the state  $n = 3$  and  $l = 2$ . Determine the possible values of the total angular momentum  $j$  and its  $z$  component  $m_j$ . For  $m_j = 3/2$  sketch a vector model of the angular momenta (two possibilities) and the corresponding magnetic moments.
3. Discuss briefly LS and jj coupling in atoms. Under which conditions do you expect one or the other type of coupling? What are the consequences of the different types of coupling?