PHY 246 Quantum Mechanics

Problem set 1; Due 9 Feb 2005, Wednesday

1. Find the eigenvalues and eigenvectors of the following matrices:

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + 0.001 \begin{pmatrix} 2 & 3 \\ 3 & 5 \end{pmatrix}. \tag{1}$$

In the last case, it is enough to find an answer accurate to three decimal places.

2. Find the eigenvalues and eigenvectors of the general complex 2×2 matrix

$$L = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \tag{2}$$

Show that the eigenvalues of such a hermitean matrix are real; and that the eigenvectors are orthogonal to each other for unequal eigenvalues.

3. Let V be the set of all complex valued functions of a real variable θ, that are periodic with period 2π. That is

$$u(\theta + 2\pi) = u(\theta), \text{for all } u \in V. \tag{3}$$

Define the inner product $< u|v >= \int_0^{2\pi} u^*(\theta)v(\theta)d\theta$. Define also the operator $P = -i\frac{d}{d\theta}$. Show that P is hermitean. Find its eigenvalues and eigenvectors.

Hint:

Show first that

$$< u|P|v >= -i \int_0^{2\pi} u^*(\theta) \frac{dv}{d\theta} d\theta. \tag{4}$$

and

$$< v|P|u >^* = i \int_0^{2\pi} v(\theta) \frac{du^*}{d\theta} d\theta. \tag{5}$$

An integration by parts will be useful.

4. Consider a system with hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + k|x|^n \tag{6}$$

where $k, n > 0$.

(i) Find an estimate of the ground state energy using the ansatz $\psi(x) = Ce^{-a|x|}$ where $a > 0$.

(ii) Compare with the exact answer for the case $n = 2$.

Hint $\int_0^\infty x^n e^{-x} dx = n!$

5. Consider a molecule whose rotational energy is determined by the hamiltonian

$$H = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_2} \tag{7}$$

i.e., the moments of inertia in the second and third directions are equal. What are the energy eigenvalues? If $I_1 > I_2$, what is the state of lowest energy? What if $I_1 < I_2$?

This is a single long hard problem, which will require to put together almost everything you know about quantum mechanics so far. You will get a flavor of what a real world problem in theoretical physics is like. Even if you can't solve the problem completely, just going as far as you can go will be itself a useful experience, so everyone should try.

Main Problem Calculate the ionization energy of the Lithium atom; i.e., the minimum energy it takes to remove an electron from the ground state of Lithium. Compare with experimental information. This can be split into two main parts:

6. Find the ground state energy of the Li^+ ion. (This is a twist on the calculation of the ground state energy of Helium).

7. Find the ground state energy of Lithium (this is the hard part!)

Hint Choose a variational approximation in which two of the electrons occupy the wavefunction $u(x) = Ce^{-a_1|x|}$ and the third electron is in the state $v(x) = B(1-b|x|)e^{-a_2|x|}$. Thus the ansatz for the wavefunction will be (ignoring spin)

$$\psi(x_1, x_2, x_3) = u(x_1)u(x_2)v(x_3) \tag{8}$$

where x_1, x_2, x_3 are the positions of the electrons.

The calculation can be split into several parts:

(i) Determine the constants C, B, b such that these wavefunctions u, v are of length one and are orthogonal to each other. The numbers a_1, a_2 are used as variational parameters.

(ii) Find the expectation value of the hamiltonian ignoring the repulsion between electrons, as a function of a_1, a_2. This is a variant of the hydrogenic ion.

(iii) Find the charge density and the electrostatic field created by the above wavefunction. The repulsion energy can now be calculated as a function of a_1, a_2 as the integral of their product. Use the calculation of the repulsive energy of helium as a model for this.

(iv) Now minimize the energy as a function of a_1 and a_2.

This last part can simplified by putting in a special relation between a_1 and a_2 based on the analogy with Helium and Hydrogen. For example, the outer electron should be in a wavefunction which is roughly the excited state of hydrogen (since the nucleus is shielded by the inner electrons) , while the inner electrons are roughly in the ground state of a hydrogenic ion of nuclear charge $Z = 3$.

You will see that choosing the right variational ansatz is an art: a compromise between generality and practicality. This is where your physical intuition matters most.