Chem. 540
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Computer Assignment 2

Eigenstates of Discrete Hamiltonians

The Hamiltonian operator for a two-state system has the form

$$\hat{H} = \varepsilon_1 |\phi_1\rangle\langle\phi_1| + \varepsilon_2 |\phi_2\rangle\langle\phi_2| - \hbar\Omega\left(|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|\right)$$

where $|\phi_1\rangle, |\phi_2\rangle$ are orthonormal states that form a complete set.

(a) Calculate the matrix of this Hamiltonian in the given basis.

(b) Using your symbolic algebra program, calculate the eigenvalues and eigenvectors of the Hamiltonian matrix.

(c) It's nicer to work with as few parameters as possible. Set $\varepsilon_1 = 0$, $\varepsilon_2 \equiv \varepsilon$. (Yes, you will lose an entire term in the Hamiltonian, but that's ok!) Again, calculate the eigenvalues and eigenvectors of the Hamiltonian.

(d) Substitute values in the Hamiltonian. Set $\hbar\Omega = 1$ and keep this fixed.
First, use $\varepsilon = 0$. What do the eigenvectors look like?
Next, try $\varepsilon = 5$. How do the eigenvectors change?
To get the complete picture, vary ε between 0 and 5. What happens to the eigenvalues and the eigenvectors?

(e) To investigate this more generally, expand the eigenvalues and eigenvectors from part (c) in the Taylor series in the ratio $\varepsilon / \hbar\Omega$ (i.e., consider this ratio to be a small parameter) and examine the leading terms of the eigenvectors. What do you observe? Next, assume $\varepsilon / \hbar\Omega >> 1$ and expand the eigenvalues and eigenvectors in the ratio $\hbar\Omega / \varepsilon$. Is there a qualitative change of the eigenvectors?

Tips

a) I trust this is straightforward, since this type of problem has appeared in homework and on the first exam; to input a matrix in Mathematica, here's an example: {{a, b}, {c, d}} represents a 2x2 matrix; hint: represent h*omega as "homega" without a space in between: Mathematica will treat h*omega as one variable instead of two, which will simplify derivations later;
b) Once you have written the Hamiltonian and put it into Mathematica, issue the Eigenvalues and Eigenvectors commands to get the eigenvalues and a set of eigenvectors, respectively. Mathematica will output the eigenvectors as "Mathematica lists" (entities corresponding, but not identical to, 1x2 matrices);
c) Pay close attention to the wording, though: Mathematica will output one set of eigenvectors, which will not always be normalized - you will have to check to make sure that they are normalized. One way to normalize them is to compute the norm of a vector, and divide the original eigenvector by this norm:
norm = Sqrt[Vector[[1]]^2 + Vector[[2]]^2]
VectorNormalized = Vector / norm

where Vector[[i]] is the ith element of a row vector called Vector in this example.

Make sure the new vectors are normalized by issuing:

FullSimplify[VectorNormalized[[1]]^2 + VectorNormalized[[2]]^2]

Obviously this number should be 1^2=1 for both vectors.

Now assign zero to epsilon1, and epsilon to epsilon2, and redo the Eigenvalues and Eigenvectors

d) To compute eigenvectors for several values of epsilon at the same time, use the command:

Table[MatrixForm[N[eigenvector]],{epsilon,0,5}]

This acts as a for-loop that constructs a table containing your eigenvectors, with epsilon taken from 0 to 5, in numerical form (hence the N[] command) displayed as neat 2x1 matrices (hence the command MatrixForm[]). The first 2x1 matrix in the table corresponds to epsilon = 0, the next to epsilon = 1, and so on. You should see the eigenvector entries "splitting" after epsilon = 1, and going towards (1 0) and (0 1). Plot them against epsilon and convince yourselves of this;

e) First retrieve your values for the eigenvectors before you assigned h omega to be 1. Now this is the more involving part of the homework the good newss is it can be solved without picking up a pen, as is the case for the entire homework. If you assume epsilon/(homega) is small, expand the eigenvector entries as Taylor series in epsilon. The command in Mathematica is

Series[function, {x, a, n}]

where you'd be expanding around x = a, up to order n. Don't worry if you see something like O[x]^(n+1) in the output that means "termss of order (n+1) or greater;"

Look at the output you should be able to associate an homega to each epsilon so as to get x = epsilon /(h omega) to order zero, one, two, etc. Right off the bat ignore the terms of power 2 or higher. You'll have to decide if to ignore the order one terms or not.

Second, for the expansion in (h omega)/epsilon, you must expand in a Taylor series around 1/epsilon. The Series command cannot take 1/epsilon as an expansion parameter so use

Series[(eigenvector /. epsilon â -> 1/epsilon) /. epsilon â -> f, {f, 0, n}]

This is a series of transformation rules: in the first, you replace epsilon by 1/epsilon, and in the second you rebrand the epsilon as a new variable f, around which you expand in a Taylor series. The two serial transformations are in effect equivalent to “express v[epsilon] = w[1/epsilon] = w[f],” or answering “what function w can I find such that if I plug in 1/epsilon into w, I get the function v[epsilon] that I started with?”•

Once you get the eigenvectors think of homega as “coupling terms.” What happens if these coupling terms tend to vanish, for instance? Or what would you expect if they were very large?