Physics 130 – Problem Set # 6

(due Wednesday, Feb. 27)

1. This problem discusses some properties of matrices relevant to the solution for eigenvalues and eigenvectors. In this problem, all quantities denoted by capital letters are square ($n \times n$) complex matrices.

   (a) The *trace* of a sqare matrix is the sum of diagonal elements:

   $$\mathrm{tr}[M] = \sum_i M_{ii}$$

   Show that $\mathrm{tr}[AB] = \mathrm{tr}[BA]$, and, more generally, that $\mathrm{tr}[ABC \cdots D] = \mathrm{tr}[BC \cdots DA]$, an identity called *cyclic invariance of the trace*.

   (b) Using part (a), show that, for a Hermitian matrix with eigenvalues λ_i,

   $$\mathrm{tr}[M] = \sum_i \lambda_i$$

   Hint: Write M as diagonalized by a unitary matrix.

   (c) The *determinant* of the matrix M is the antisymmetric product

   $$\det M = \epsilon_{ijk\cdots\ell} M_{1i} M_{2j} M_{3k} \cdots M_{n\ell}$$

   Show that $\det AB = \det A \cdot \det B$.

   (d) Show that, for a Hermitian matrix

   $$\det M = \prod_i \lambda_i$$

   (e) Use the identities above to find the eigenvalues of the matrix

   $$M = \begin{pmatrix} a & b \\ b^* & -a \end{pmatrix}$$

   (f) Show that an eigenvalue λ of a Hermitian matrix M satisfies the *characteristic equation*

   $$\det(M - \lambda \mathbf{1}) = 0$$

   (g) For a 3×3 Hermitian matrix, the characteristic equation is a cubic equation

   $$a + b\lambda + c\lambda^2 - \lambda^3 = 0$$

   The coefficients a, b, c can be written in terms of the eigenvalues of M. For example, $a = \det M = \lambda_1 \lambda_2 \lambda_3$. Find the corresponding expressions for b and c. The characteristic equation is invariant to unitary transformations $M \to V^\dagger M V$; therefore a, b, and c must be also.

2. The CO_2 molecule is a linear molecule described in chemistry as having double bonds that connect each O atom with the C. Here is a very rough way to view the bonding in this system: Put the C nucleus at $(0,0,0)$ and the two O atoms at $(0,0,\pm R)$. To minimize the energy, we first fill all of the 1S, 2S, and $2P_z$ states of the atoms. This uses up 18 of the 22 available electrons. To place the remaining 4 electrons in the molecule, we can hybridize the remaining 2P states. It is equivalent to treat these as the $2P_{m=1}$ and $2P_{m=-1}$ states, but the states are easier to draw and visualize if we take real linear combinations and speak of the $2P_x$ and $2P_y$ states. (I hope the notation is obvious; the $2P_x$ state is proportional to x, and the $2P_y$ is proportional to y.)

   (a) Using properties under the reflection $x \to -x$, $y \to -y$, show that all matrix elements of the Hamiltonian between a $2P_x$ state and a $2P_y$ state vanish.

   (b) Consider the problem of hybridizing the $2P_x$ states. In the 3-dimensional Hilbert space of $2P_x$ states, the Hamiltonian takes the form

$$H = \begin{pmatrix} E_O & -\Delta & 0 \\ -\Delta & E_C & -\Delta \\ 0 & -\Delta & E_O \end{pmatrix}$$

   where E_0, E_C, Δ are functions of the bond length R. Why must the four indicated off-diagonal elements be equal? (The matrix elements in the corners are not necessarily zero, but they are smaller than the nonzero elements indicated.)

   (c) Find the eigenvalues of the matrix in (b), following the logic: (i) First, show that

$$P = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

   which interchanges the O atoms, commutes with H. Since $P^2 = 1$, this matrix has eigenvalues ± 1. Show that P has one eigenvalue -1, and find the eigenvector. (ii) This vector must be an eigenvector of H. (Why?) Show this explicitly, and find the corresponding eigenvalue λ_-. (iii) Construct the characteristic equation for the matrix H. This is a cubic equation in λ, but it must have $(\lambda - \lambda_-)$ as a factor. (Why?) (iv) The remaining factor is a quadratic equation; solve it.

   (d) Sketch the forms of the three wavefunctions corresponding to the eigenvectors of H. In CO_2, the lowest level is a bonding orbital, the other two are anti-bonding.

   (e) Describe the solution of the problem of hybridizing the $2P_y$ states. Draw the bonding orbital in this case. It must have the same energy as that in the $2P_x$ case. Why?

   (f) Place the remaining 4 electrons into the eigenstates found in this problem.

3. In class, we discussed the solution of the two-state model of the ammonia molecule in an external electric field $\vec{E} = E\hat{z}$. We represented the Hamiltonian by a 2×2 matrix

$$H = E_0 + \begin{pmatrix} Ed & -\Delta \\ -\Delta & -Ed \end{pmatrix}$$

acting on the coefficients of the states $|\uparrow\rangle$ and $|\downarrow\rangle$. The constant E_0 played no role in the solution, so set $E_0 = 0$ in this problem.

(a) For $E > 0$, construct the eigenvectors of the matrix H. Call the two eigenvalues are $\pm\mathcal{E}$. Call the lower-energy eigenvector $|1\rangle$ and the higher energy eigenvector $|2\rangle$. Find the (simple) time evolution of these states, $|1(t)\rangle$ and $|2(t)\rangle$.

(b) Now add to the Hamiltonian a time-dependent electric field pointing in the $\hat{z}$ direction. In the original basis, this is

$$H_2 = -e\cos(\omega t)\begin{pmatrix} -d & 0 \\ 0 & d \end{pmatrix}$$

Write the Schrödinger equation for the Hamiltonian $H + H_2$.

(c) Look for a solution of the form

$$|\psi(t)\rangle = \alpha(t)\ |1(t)\rangle + \beta(t)\ |2(t)\rangle$$

Write the equations for $\dot{\alpha}(t)$ and $\dot{\beta}(t)$ explicitly. Notice that each term on the right-hand side is multiplied by an exponential $e^{i\overline{\omega}t}$.

(d) Consider first the case $\omega = 2\mathcal{E}/\hbar$ in which the time-dependent field is exactly resonant with the beat frequency between the two states of the ammonia molecule. In this case, some of the exponentials in (c) become equal to 1. The other terms oscillate rapidly. Drop those terms; then we obtain a set of two equations that are easy to solve. In this approximation, solve the equations with the initial condition

$$\alpha = 1 \qquad \beta = 0 \qquad \text{at } t = 0$$

and find $\alpha(t)$ and $\beta(t)$.

(e) Next, consider the more general case in which $|\omega - 2\mathcal{E}| \ll \mathcal{E}$. Keep the slowly oscillating terms and drop the rapidly oscillating terms. The equations are harder to solve in this case, but we can at least work out $\beta(t)$ in the approximation in which e is small and so $\alpha(t) \approx 1$. Using this set of approximations, find $\beta(t)$ as a function of ω. Notice that $\beta(t)$ grows without bound only at the resonant frequency.

(f) A curious aspect of the formulae is that the transition rates between $|1\rangle$ and $|2\rangle$ go to zero in the limit in which E is very large. Why?