Problem Set PS03

ISSUED: 1/24/02 **Due: 1/31/02**

Prof. Darin J. Ulness   Name ______________________________

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. The matrix

$$\begin{bmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{bmatrix}$$

is call the rotation matrix.

   (a) Lets say we start with the vector $\vec{x} = (x, y)$ in the xy–plane. Apply the rotation matrix to $\vec{x}$ to form a new vector $\vec{x}' = (x', y')$. How are the new (primed) coordinates related to the old coordinates?

   (b) Start with the vector $(1, 1)$ and apply a rotation by $\pi/4$. Also apply a rotation by $\pi/2$. Do this first by drawing a picture of the vector and using geometry to draw the other two rotated vectors. Then redo it using the rotation matrix.

Exercises

2. In problem set PS01 we saw the Pauli spin matrices. These are very handy when dealing with the spin two-level system. Last semester we simply wrote spin up as α and spin down as β and could not give them a functional form. Now we can represent these states as two dimensional vectors in spin space:

$$\alpha = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \qquad \beta = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

The components of the spin operator $\hat{S}$ can be represented using the Pauli spin matrices as

$$\hat{S}_x = \frac{\hbar}{2}\sigma_1, \quad \hat{S}_y = \frac{\hbar}{2}\sigma_2, \quad \hat{S}_z = \frac{\hbar}{2}\sigma_3.$$

Operate on α and β with each of the spin component operators. Are α and β eigenfunctions of any of these? For those operators in which α and β are not eigenfunctions one must find the expectation value (average). Do this. Does your result make sense? Finally verify that $\hat{S}^2\chi = s(s+1)\hbar\chi = \frac{3\hbar}{4}\chi$, where χ is either α or β.

3. Verify that the 'left' and 'right' states of a two level system are not eigenfunctions of the two level Hamiltonian unless the two levels are degenerate. That is, these states are not solutions of the *time independent* Schrödinger equation.

4. Now verify that the 'left' and 'right' states of a two level system are solutions of the *time dependent* Schrödinger equation.

5. The Bohr frequency of a two level system is defined as $\omega_0 = \frac{E_2 - E_1}{\hbar}$. Write the final result of Eq. (12.116) in terms of the Bohr frequency (simplify as best you can). Does it make sense to say that the Bohr frequency gives the frequency with which a system oscillates from the 'left' to 'right' states.

6. A superposition of a two level system is prepared in the 'left' state at time zero. The probability of finding the system in state Ψ_R at time t is given by $|\int \Psi_L^*(t=0)\Psi_R(t)d\Omega|^2$. Evaluate this probability and comment on its time dependence. Why can the probability of finding the system in state 1 never be one or zero, but The probability of finding the system in state R can be one or zero?

7. Look at Table 1 of A. Amann "Structure, dynamics and spectroscopy of single molecules: A challenge to quantum mechanics" *J. Math. Chem.* **18**, 247 (1995).

   (a) What is the Bohr frequency in s^{-1} for the molecules listed in the table?

   (b) The ammonia inversion was actually the first system ever used to produce a laser beam. Actually at the time it was called a maser. Based in the level spliting for the ground and first excited states of ammonia, what do you think the "m" in maser stands for?

   (c) How many years would you expect to wait before aspartic acids changes its chirality? (The age of the universe is 10^{15}s.)

8. Two spin operators, $\hat{S}_+$ and $\hat{S}_-$, have the following properties:

$$\begin{aligned} \hat{S}_+\alpha &= 0 \\ \hat{S}_-\alpha &= \beta \\ \hat{S}_+\beta &= \alpha \\ \hat{S}_-\beta &= 0. \end{aligned}$$

   Build a single "spin flip" operator $\hat{S}_F$ out of $\hat{S}_+$ and $\hat{S}_-$. Your operator should have the following properties:

$$\begin{aligned} \hat{S}_F\alpha &= \beta \\ \hat{S}_F\beta &= \alpha. \end{aligned}$$

   That is, it changes a spin-up to a spin-down and vice versa.

9. Work out the ground state term symbol of chromium. Compare your answer with the handout.

Conceptual Problems

10. Under what circumstances is the $e^{\frac{iEt}{\hbar}}$ phase factor important and when is it unimportant.

11. Comparing the harmonic oscillator and particle in a box where $\triangle E$ for the harmonic oscillator is equal to $\triangle E_{1\to 2}$ for the particle in a box, let's say a superposition of the first ten states such that we have a fairly localized state in both the harmonic oscillator and particle in a box. Will the harmonic oscillator or the particle in a box wavepacket delocalize faster? Why?

12. Make a two level system out of the $1s$ and $2p_x$ states of the hydrogen atom. What is the Bohr frequency of this two level system. Make a qualitative sketch of the 'left' state and 'right' states. Make a qualitative series of pictures of a state which is initially equal to the 'left' state.

Computer Problems

13. Use MATHEMATICA to construct the 'left' and 'right' states of the previous problem. Plot the probability density of these wavefunctions. (See PS04 from last semester for information on how to plot the orbitals.)

Reflective Exercises

14. An important lesson to learn is that life is not fair. It might well be the case when you are in graduate school (or later in your career) that try as you might things are not working out like they should if life were fair. For example, you might be working twice as hard as one of your peers and yet not having the same level of success. Or, you might be treated unfairly by people with more power than you currently have.

    (a) Think how you have handled similar situations in the past.
    (b) Think about your character strengths that will help you in situations like this.
    (c) Think about areas where you can improve your skills at handling such situations.

15. Please read the following excerpt from "Fermat's Enigma" by Simon Singh.

    (a) Do you agree with this assessment?
    (b) Compare Euclid's first postulate: two points determine a line with the second law of thermodynamics of which "the amount of evidence [is] overwhelming" in support of it. Does the distinction between the mathematical and scientific proof remain in this case?
    (c) Compare a mathematical scientific theory like for example, quantum mechanics with non-mathematical scientific theory like for example, plate tectonics within the context of this excerpt.

> The story of Fermat's Last Theorem revolves around the search for a missing proof. Mathematical proof is far more powerful and rigorous than the concept of proof we casually use in our everyday language, or even the concept of proof as understood by physicists or chemists. The difference between scientific and mathematical proof is both subtle and profound, and is crucial to understanding the work of every mathematician since Pythagoras.

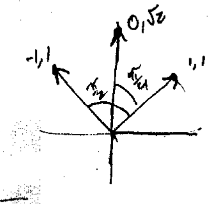
The idea of a classic mathematical proof is to begin with a series of axioms, statements that can be assumed to be true or that are self-evidently true. Then by arguing logically, step by step, it is possible to arrive at a conclusion. If the axioms are correct and the logic is flawless, then the conclusion will be undeniable. This conclusion is the theorem.

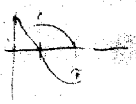
Mathematical theorems rely on this logical process and once proven true are true until the end of time. Mathematical proofs are absolute. To appreciate the value of such proofs they should be compared with their poor relation, the scientific proof. In science a hypothesis is put forward to explain a physical phenomenon. If observations of the phenomenon compare well with the hypothesis, this becomes evidence in favor of it. Furthermore, the hypothesis should not merely describe a known phenomenon, but predict the results of other phenomena. Experiments may be performed to test the predictive power of the hypothesis, and if it continues to be successful then this is even more evidence to back the hypothesis. Eventually the amount of evidence may be overwhelming and the hypothesis becomes accepted as a scientific theory.

However, the scientific theory can never be proved to the same absolute level of a mathematical theorem: It is merely considered highly likely based on the evidence available. So-called scientific proof relies on observation and perception, both of which are fallible and provide only approximations to the truth. As Bertrand Russell pointed out: "Although this may seem a paradox, all exact science is dominated by the idea of approximation." Even the most widely accepted scientific "proofs" always have a small element of doubt in them. Sometimes this doubt diminishes, although it never disappears completely, while on other occasions the proof is ultimately shown to be wrong. This weakness in scientific proof leads to scientific revolutions in which one theory that was assumed to be correct is replaced with another theory, which may be merely a refinement of the original theory, or which may be a complete contradiction.

①

⑨ $\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} \Rightarrow \begin{array}{l} x' = \cos\phi x - \sin\phi y \\ y' = \sin\phi x + \cos\phi y \end{array}$





$x' = \cos\frac{\pi}{4}(1) - \sin\frac{\pi}{4}(1) = 0$

$y' = \sin\frac{\pi}{4}(1) + \cos\frac{\pi}{4}(1) = \sqrt{2}$

$x' = \cos\frac{\pi}{2}(1) - \sin\frac{\pi}{2}(1) = -1$

$y' = \sin\frac{\pi}{2}(1) + \cos\frac{\pi}{2}(1) = 1$

②

$S_x\alpha = \frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix}0\\1\end{bmatrix}$ not eigenvector

$S_x\beta = \frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}0\\1\end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix}1\\0\end{bmatrix}$ not eigenvector

$S_y\alpha = \frac{\hbar}{2}\begin{bmatrix}0&-i\\i&0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix}0\\i\end{bmatrix}$ not eigenvector

$S_y\beta = \frac{\hbar}{2}\begin{bmatrix}0&-i\\i&0\end{bmatrix}\begin{bmatrix}0\\1\end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix}-i\\0\end{bmatrix}$ not eigenvector

$S_z\alpha = \frac{\hbar}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix}1\\0\end{bmatrix}$ eigenvector

$S_z\beta = \frac{\hbar}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}0\\1\end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix}0\\1\end{bmatrix}$ eigenvector

$\langle S_x \rangle_\alpha = \begin{bmatrix}1&0\end{bmatrix}\frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = 0$ same for $\langle S_x\rangle_\beta$ and $\langle S_y\rangle_\alpha$ and $\langle S_y\rangle_\beta$

$\hat{S}^2 = S_x^2 + S_y^2 + S_z^2$ $S_x^2 = \frac{\hbar^2}{4}\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}0&1\\1&0\end{bmatrix} = \frac{\hbar^2}{4}\begin{bmatrix}1&0\\0&1\end{bmatrix}$, $S_y^2 = \frac{\hbar^2}{4}\begin{bmatrix}1&0\\0&1\end{bmatrix}$ $S_z^2 = \frac{\hbar^2}{4}\begin{bmatrix}1&0\\0&1\end{bmatrix}$

$\hat{S}^2 = \frac{3\hbar^2}{4}\begin{bmatrix}1&0\\0&1\end{bmatrix}$

$\hat{S}^2\alpha = \frac{3\hbar^2}{4}\begin{bmatrix}1&0\\0&1\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = \frac{3\hbar^2}{4}\begin{bmatrix}1\\0\end{bmatrix}$ same for β.

③ See Quiz 01

④ $\Psi_L = \frac{1}{\sqrt2}\Psi_1 + \frac{1}{\sqrt2}\Psi_2 = \frac{1}{\sqrt2}\psi_1 e^{\frac{-iE_1 t}{\hbar}} + \frac{1}{\sqrt2}\psi_2 e^{\frac{-iE_2 t}{\hbar}}$

$i\hbar\frac{\partial \Psi}{\partial t} = i\hbar\frac{\partial}{\partial t}\left[\frac{1}{\sqrt2}\psi_1 e^{\frac{-iE_1 t}{\hbar}} + \frac{1}{\sqrt2}\psi_2 e^{\frac{-iE_2 t}{\hbar}}\right]$

$= \frac{E_1}{\sqrt2}\psi_1 e^{\frac{-iE_1 t}{\hbar}} + \frac{E_2}{\sqrt2}\psi_2 e^{\frac{-iE_2 t}{\hbar}}$

this is equal to $\hat{H}\Psi_L$ (see notes

similarly for Ψ_R

⑤ (12.116) $\left|\int \Phi^* \Phi\right|^2 = \frac{1}{2}\left(1 + \cos\frac{E_1 - E_2}{\hbar}t\right)$

$= \frac{1}{2}(1 + \cos(-\omega_0 t))$ $\cos(-a) = \cos a$

$= \frac{1}{2}(1 + \cos\omega_0 t)$

⑥ This is just eq (12.116) for the TLS

$P_L = \left|\int \psi_L^*(t=0)\psi_L\right|^2 = \frac{1}{2}(1 + \cos\omega_0 t)$

⑦ see solution set from last year

⑧ $\hat{S}_r = \hat{S}_+ + \hat{S}_-$

⑨ Cr: [Ar] $4s^1 3d^5$

↑ ↑ ↑ ↑ ↑ (2, 2, …) ↑

$M^{max} = ~~10~~, ~~8~~, ~~7~~, 6, 4, 0$
I G, S

I: $M_S^{max} = 1$ $g_s = 3$

G: $M_S^{max} = 3/2$ $g_s = 4$

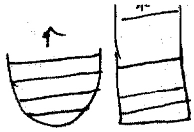
S: $M_S^{max} = 3$ $g_s = 7$

$^7S_3$

⑩ $(1s)^2 \to (2s)^2$ any state when the electrons are unpaired is a triplet state.

⑪ a) for superposition states

b) for eigenstates.

⑫ 

The box wavepacket would delocalize faster since the energy levels are more spread out.

⑬ $\psi_L = \frac{1}{\sqrt2}1s + \frac{1}{\sqrt2}2p_x$ $\Delta E = \frac{-R}{4} - \frac{-R}{1} = \frac{3}{4}R$

$\psi_R = \frac{1}{\sqrt2}1s - \frac{1}{\sqrt2}2p_x$ $\omega_0 = \frac{\frac{3}{4}R}{\hbar}$ Bohr frequency