CHM 3411 – Problem Set 2

Due date: Friday, January 25th (I've pushed the due date back due to the MLK holiday on Monday)

Do all of the following problems. Show your work.

1) For each of the following operators and functions, determine under what conditions (if any) the function is an eigenfunction of the operator. For those functions that are eigefunctions, find the corresponding eigenvalues.

a) $\hat{O} = d^2/dx^2$, $f(x) = \exp(ax)$, where a is a positive constant

b) $\hat{O} = d^2/dx^2$, $f(x) = \cos(ax)$, where a is a positive constant

c) $\hat{O} = x\,(d/dy) + y\,(d/dx)$, $f(x,y) = x^2 + y^2$

d) $\hat{O} = x\,(d/dy) + y\,(d/dx)$, $f(x,y) = xy$

e) $\hat{O} = \text{inv}$, $f(x) = x^2 + x$ (The inversion operator, inv, replaces x with –x everywhere it appears)

f) $\hat{O} = \text{inv}$, $f(x) = x^2 + 1$

2) Consider the following function

$$f(x) = Nx^2 \qquad -L \le x \le L\ ,\ L > 0$$

$$f(x) = 0 \qquad x < -L \text{ or } x > L$$

a) Find the value for N that makes f(x) a normalized function.

b) Would f(x) be an acceptable solution to some TISE? Why or why not? (Hint: Does f(x) satisfy all of the requirements for a wavefunction?)

3) There are a number of proofs in quantum mechanics that are both useful and surprisingly easy. Here we explore one of these.

Let f(x) be a "well behaved" normalized function. Because the functions ψ_n that are solutions to a particular TISE form a complete orthonormal set of functions (basis functions), we can say:

$$f(x) = c_1\,\psi_1(x) + c_2\,\psi_2(x) + c_3\,\psi_3(x) + \ldots$$

$$= \Sigma_{n=1}^{\infty}\, c_n\,\psi_n(x) \qquad (3.1)$$

a) Left multiply the left and right sides of eq 3.1 by ψ_j^*, the complex conjugate of the j^{th} solution to the TISE.

b) Integrate all of the terms from a over the region $-\infty < x < \infty$.

c) Using the orthonormality condition, find an expression for c_j, the coefficient for the j^{th} term in eq 3.1.

d) The result in part c takes on a particularly meaningful form if f(x) is a normalized function, that is, if

$$\int_{-\infty}^{\infty} f(x)^*\, f(x)\, dx = 1 \qquad (3.2)$$

Using your result from part c, show that if f(x) is a normalized function, it follows that

$$|c_1|^2 + |c_2|^2 + |c_3|^2 + \ldots = \Sigma_{n=1}^{\infty}\, |c_n|^2 = 1 \qquad (3.3)$$

where

$$|c_n|^2 = c_n^*\, c_n \qquad (3.4)$$

(Hint: Use the normalization condition (eq 3.2) as a starting point.)

The significance of this result is that if f(x) is the wavefunction for a state in a system, and if f(x) is a normalized function, then $|c_n|^2$ represents the probability of being in the ψ_n th eigenstate of the system.

Solutions.

1) a) $d^2/dx^2 \exp(ax) = d/dx\ a \exp(ax) = a^2 \exp(ax)$ YES; eigenvalue is a^2

b) $d^2/dx^2 \cos(ax) = -\ d/dx\ a \sin(ax) = -\ a^2 \cos(ax)$ YES; eigenvalue is $-a^2$

c) $[\ x\ d/dy + y\ d/dx\ ]\ (x^2 + y^2)$

$= [\ x\ d/dy + y\ d/dx\ ]\ x^2 + [\ x\ d/dy + y\ d/dx\ ]\ y^2$

$= 2xy + 2xy = 4xy$ NO; not an eigenfunction

d) $[\ x\ d/dy + y\ d/dx\ ]\ (xy)$

$= x\ d/dy\ (xy) + y\ d/dx\ (xy)$

$= x^2 + y^2$ NO; not an eigenfunction

e) $\text{inv}\ (x^2 + x) = (-x)^2 + (-x) = x^2 - x$ NO; not an eigenfunction

f) $\text{inv}\ (x^2 + 1) = (-x)^2 + 1 = x^2 + 1$ YES; eigenvalue is 1

2) a) Since the function is zero for $x < -L$ or $x > L$, we only have to integrate between $x = -L$ and $x = L$

$1 = \int_{-L}^{L} f(x)^* f(x)\ dx = \int_{-L}^{L} (Nx^2)\ (Nx^2)\ dx$

$= N^2 \int_{-L}^{L} x^4\ dx = N^2\ [\ (x^5/5)\ ]_{-L}^{L} = N^2\ [\ (L^5/5) - (\ -\ L^5/5)\ ] = N^2\ (2L^5/5)$

$N^2 = (5/2L^5)$ $\quad N = (5/2L^5)^{1/2}$

b) The function is discontinuous at $x = \pm L$ (it jumps from 0 to NL^2 at those two points). Since a solution to a TISE has to be continuous, $f(x) = Nx^2$ is not an acceptable wavefunction.

3) a) If we left multiply the expression for $f(x)$ by ψ_j^*, we get

$\psi_j^*\ f(x) = \psi_j^*\ (c_1\ \psi_1) + \psi_j^*\ (c_2\ \psi_2) + \psi_j^*\ (c_3\ \psi_3) + \ldots$

b) If we integrate both sides of this equation from $-\infty$ to $+\infty$, we get

$\int_{-\infty}^{\infty} \psi_j^*\ f(x)\ dx = \int_{-\infty}^{\infty} \psi_j^*\ (c_1\ \psi_1)\ dx + \int_{-\infty}^{\infty} \psi_j^*\ (c_2\ \psi_2)\ dx + \int_{-\infty}^{\infty} \psi_j^*\ (c_3\ \psi_3)\ dx + \ldots$

$= c_1 \int_{-\infty}^{\infty} \psi_j^*\ \psi_1\ dx + c_2 \int_{-\infty}^{\infty} \psi_j^*\ \psi_2\ dx + c_3 \int_{-\infty}^{\infty} \psi_j^*\ \psi_3\ dx + \ldots$

All of the integrals where the two functions are different solutions are equal to zero (from orthogonality), and so all of the terms are equal to zero except for the term

$\int_{-\infty}^{\infty} \psi_j^*\ (c_j\ \psi_j)\ dx = c_j \int_{-\infty}^{\infty} \psi_j^*\ \psi_j\ dx = c_j$, since $\int_{-\infty}^{\infty} \psi_j^*\ \psi_j\ dx = 1$ by normality.

So $c_j = \int_{-\infty}^{\infty} \psi_j^*\ f(x)\ dx$

b) Assume f(x) is a normalized function. Then

$$1 = \int_{-\infty}^{\infty} f(x)^* f(x)\, dx = \int_{-\infty}^{\infty} [c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3 + \ldots]^* [c_1 \psi_1 + c_2 \psi_2 + c_3 \psi_3^* + \ldots]\, dx$$

where we have substituted the power series expansion for f(x).

$$1 = \int_{-\infty}^{\infty} (c_1 \psi_1)^* c_1 \psi_1\, dx + \int_{-\infty}^{\infty} (c_1 \psi_1)^* c_2 \psi_2\, dx + \int_{-\infty}^{\infty} (c_1 \psi_1)^* c_3 \psi_3\, dx + \ldots$$

$$\int_{-\infty}^{\infty} (c_2 \psi_2)^* c_1 \psi_1\, dx + \int_{-\infty}^{\infty} (c_2 \psi_2)^* c_2 \psi_2\, dx + \int_{-\infty}^{\infty} (c_2 \psi_2)^* c_3 \psi_3\, dx + \ldots$$

$$+ \int_{-\infty}^{\infty} (c_3 \psi_3)^* c_1 \psi_1\, dx + \int_{-\infty}^{\infty} (c_3 \psi_3)^* c_2 \psi_2\, dx + \int_{-\infty}^{\infty} (c_3 \psi_3)^* c_3 \psi_3\, dx + \ldots$$

$$+ \ldots$$

That's a lot of integrals! However, by orthonormality, the integrals are equal to zero if the two wavefunctions are different, and equal to 1 if the two wavefunctions are the same. So we get

$$1 = c_1^* c_1 + c_2^* c_2 + c_3^* c_3 + \ldots = |c_1|^2 + |c_2|^2 + |c_3|^2 + \ldots = \Sigma_{i=1}^{\infty} |ci|^2$$

Or, in terms of words, the sum of the squares of the coefficients c_i must be equal to 1.

Why is this useful? Well, we generally have a good idea of how the solutions to a TISE behave, and so if we can take an arbitrary "well behaved" function f(x) and express it in terms of the solutions of a TISE, it often becomes easier to describe the behavior of the function.