# MATH 333: Partial Differential Equations

## Project 7, Due Date: Mon., Oct. 30, 2006

Let $m$ be the mass of the electron in orbit around the proton of a hydrogen atom, $e$ its charge, and $h$ Planck's constant divided by $2\pi$. If $(0,0,0)$ represents the position of the proton, and $r = (x^2+y^2+z^2)^{1/2}$, then the motion of the electron is given by a "wave function" $\Psi(x,y,z,t)$ that satisfies Schrödinger's equation

$$-ih\Psi_t \;=\; \frac{h^2}{2m}\Delta\Psi + \frac{e^2}{r}\Psi. \tag{1}$$

The coefficient function $e^2/r$ is called the potential. If $D$ is any region in space, then

$$\int\!\!\int\!\!\int_D |\Psi|^2\,dx\,dy\,dz$$

is the probability of finding the electron in the region $D$ at time $t$, which means

$$\int\!\!\int\!\!\int_{\mathbb{R}^3} |\Psi|^2\,dx\,dy\,dz \;=\; 1,$$

implying that $|\Psi(\cdot,\cdot,\cdot,t)| \to 0$ as $r\to\infty$. (Note that, for complex-valued functions $f$ and $g$, the $L^2$ inner product is $\int f(x)\overline{g(x)}\,dx$ where, for a complex number $z = a+ib$, $\overline{z} = a - ib$ is known as its complex conjugate.)

Let us specialize Schrödinger's equation to one spatial dimension, so that we have

$$ih\Psi_t \;=\; -\frac{h^2}{2m}\Psi_{xx} + V(x)\Psi, \qquad x\in\mathbb{R},\;\; t>0. \tag{2}$$

(a) Assume separation of variables $\Psi(x,t) = y(x)\phi(t)$ to show that

$$\phi(t) \;=\; Ce^{-iEt/h},$$

where $E$ is a separation constant (interpreted as the allowable energy levels), and that $y$ satisfies

$$-\frac{h^2}{2m}y'' + [V(x)-E]y \;=\; 0. \tag{3}$$

(b) Show that $\displaystyle\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = \int_{-\infty}^{\infty} [y(x)]^2\,dx.$

(c) Assume that $h=1$, $m=1/2$ and $V(x)=x^2$. Show that the assumption that (3) has a solution of the form $y(x) = w(x)e^{-x^2/2}$ leads to *Hermite's differential equation*

$$w'' - 2xw' + (\lambda-1)w \;=\; 0. \tag{4}$$

(d) Because Hermite's DE has variable coefficients, it lies outside of the theory usually covered in MATH 231 (but the chapter—I believe it is Ch. 5—in Boyce & DiPrima on "Series Solutions of Second Order Linear Equations" is quite relevant). Assume that $w(\cdot)$ has a power series expansion

$$w(x) \;=\; \sum_{k=0}^{\infty} a_k x^k,$$

and plug this series (along with appropriate derivatives) into (4). Show that, when you match like powers of $x$, you get the 2nd-order recursion relation

$$(k+2)(k+1)a_{k+2} \;=\; (2k+1-E)a_k, \qquad k = 0, 1, 2, \ldots. \tag{5}$$

Such a relation does not determine $a_0$ nor $a_1$, which can be assigned values independently (for instance, setting $a_0 = 0$, $a_1 = 1$ yields an odd function; $a_0 = 1$, $a_1 = 0$ yields an even function).

(e) Show that, when $E = 2k+1$ where $k$ is an integer, then (5) shows $a_{k+2} = a_{k+4} = \cdots = 0$, and the resulting solution is a polynomial of degree $k$ that is even or odd depending on whether $k$ is even or odd. Such a solution is known as an Hermite polynomial $H_k(x)$ (with an appropriate normalization). The first 5 such polynomials are

$$\begin{array}{ll}
H_0(x) = 1 & (E = 1, a_1 = a_2 = 0) \\
H_1(x) = 2x & (E = 3, a_0 = a_3 = 0) \\
H_2(x) = 4x^2 - 2 & (E = 5, a_1 = a_4 = 0) \\
H_3(x) = 8x^3 - 12x & (E = 7, a_0 = a_5 = 0) \\
H_4(x) = 16x^4 - 48x^2 + 12 & (E = 9, a_1 = a_6 = 0).
\end{array}$$

Show that the solutions $\Psi_k$ to (2) corresponding to the values $E_k = 2k+1$ satisfy $\Psi_k(x,t) \to 0$ as $x \to \pm\infty$.

(f) Show that if $E \neq 2k+1$, any solution of Hermite's DE is a power series but not a polynomial. Deduce that, in this case, no solution of Hermite's DE can satisfy the condition at infinity. (Hint: Use (5) to find the behavior of $a_k$ as $k \to \infty$. Compare with the power series expansion of $e^{x^2}$. Deduce that $\Psi(x,t)$ behaves like $e^{x^2}$ as $|x| \to \infty$.)

You may earn an additional "project point" by investigating the full Schrödinger equation (1) further. In 1913, Neils Bohr observed that the energy levels of the electron in a hydrogen atom occur only at special values related to squares of integers. Show this mathematically, by taking $e = m = h = 1$, looking for solutions of the 3D (partial) differential equation corresponding to (2) that are spherically symmetric (i.e., $y(x,y,z) = R(r)$), assuming $R(0)$ is finite and that all eigenvalues $E$ are negative, and (eventually) arriving at the conclusion that the energy levels are $E = -1/n^2$, $n = 1, 2, \ldots$, verifying Bohr's experiments. This is not the end of the story, as there are eigenfunctions which possess angular dependence, and unbounded states that correspond to *continuous spectrum*. But such topics are beyond the scope foreseen in this project.