mpc2w5.tex
Week 5. 9.11.2011

Schrödinger Equation (Erwin SCHRÖDINGER (1887-1961) in 1926).

This postulates that a particle's motion is described by a *wave function* $\psi = \psi(\mathbf{x}, t)$ ($\mathbf{x} = (x_1, x_2, x_3)$, or (x, y, z)) satisfying a PDE

$$i\hbar\partial\psi/\partial t == \frac{\hbar^2}{2m}\Delta\psi + V\psi \qquad \text{(Schrödinger equation)}, \qquad (SE)$$

where V is the potential function (see Ch. VI for more on potentials), m is the mass, $\hbar := h/(2\pi)$, h is Planck's constant (Max PLANCK (1858-1947) in 1900) and Δ is the Laplacian. Writing $\psi(\mathbf{x}, t) = T(t)\Psi(\mathbf{x})$ to separate variables:

$$i\hbar\dot{T} = -\frac{\hbar^2}{2m}T\Delta\Psi + VT\Psi,$$

$$\frac{i\hbar\dot{T}}{T} = \frac{1}{\Psi}(-\frac{\hbar^2}{2m}\Delta\Psi + V\Psi) = const, \ E.$$

This constant E is the *energy.* So $T(t) = e^{i\hbar Et}T(0)$,

$$\psi(t, \mathbf{x}) = e^{i\hbar Et}T(0)\Psi(\mathbf{x}),$$

where $\Psi(\mathbf{x})$ satisfies the *time-independent Schrödinger equation*

$$-\frac{\hbar^2}{2m}\Delta\Psi + V\Psi - E\Psi = 0. \qquad (TISE)$$

Note. 1. The complex exponentials here have the form of sine (or cosine) *waves*. This is why Quantum Mechanics has "waves built into everything". As originally formulated by Heisenberg, everything was expressed in terms of *matrices* (see Ch. IV on Linear Algebra), and the resulting theory was called Matrix Mechanics. Schrödinger's theory was correspondingly called Wave Mechanics. Schrödinger then showed that the two were equivalent. Since physicists are used to waves, but were not then used to matrices (Heisenberg didn't know what a matrix was when he formulated his approach!), Wave Mechanics were preferred; the resulting theory became known as Quantum Mechanics.

2. The first person to suggest that "particles are waves" was Louis de BROGLIE (1892-1987) in 1924. But "particles are particles" also. So one

has a "wave-particle duality". This is true, not only for the particles, or quanta, of *matter* (e.g., electrons, protons, neutrons), but also of *radiation* (e.g., photons).

Recall that Newton (e.g. in his *Opticks*, 1704) advocated the *corpuscular theory of light*. This was opposed at the time by his contemporary Christiaan HUYGENS (1629-95), *Treatise on Light*, 1678, who advocated the *wave theory of light*. So too later did Thomas YOUNG (1773-1829) in 1803, and Augustin-Jean FRESNEL (1788-1827) in 1821. Albert EINSTEIN (1879-1955) discovered the *photoelectric effect* in 1905, thus identifying the quantum of light, later called the *photon* (he received the Nobel Prize for this work in 1921).

Separation of variables for Laplace's equation.

In spherical polars, take $u = u(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$. Then cancelling $1/r^2$ in the expression above for Δu, $\Delta u = 0$ is

$$\frac{\partial}{\partial r}(r^2 R'\Theta\Phi) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta.\Theta'.R\Phi) + \frac{1}{\sin^2\theta}.R\Theta\Phi'' = 0,$$

or dividing by $R\Theta\Phi$,

$$\frac{1}{R}\frac{\partial}{\partial r}(r^2 R') + \frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta.\Theta') + \frac{1}{\sin^2\theta}.\frac{\Phi''}{\Phi} = 0.$$

Take the first term to the RHS. Then the RHS depends only on r, the LHS only on θ, ϕ. So both are constant, by separation of variables.
RHS:

$$-\frac{1}{R}\frac{d}{dr}(r^2 R') = c.$$

Seek a trial solution r^ℓ. Then

$$R' = \ell r^{\ell-1}, \quad r^2 R' = \ell r^{\ell+1}, \quad d(r^2 R')/dr = \ell(\ell+1)r^\ell = \ell(\ell+1)R.$$

So r^ℓ is a solution if

$$\ell(\ell+1) = -c.$$

It turns out that we only need

$$\ell = n = 0, 1, 2, \ldots$$

Also, if $m = -n-1$, $m+1 = n$, so $m(m+1) = (-n)(-n-1) = n(n+1)$. Since both $\ell = n$ and $\ell = -n-1$ give the same value for $\ell(\ell+1) = -c$, we retain them both. So:

$$R(r) = r^n \quad \text{and} \quad r^{-n-1} \qquad (n = 0, 1, 2, \ldots).$$

LHS:

$$\frac{1}{\Theta \sin\theta} \frac{\partial}{\partial\theta}(\sin\theta.\Theta') + \frac{1}{\sin^2\theta}.\frac{\Phi''}{\Phi} = c = \ell(\ell+1) \qquad (\ell = n, -n-1):$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}(\sin\theta.\Theta') + \frac{\Phi''}{\Phi} = c\sin^2\theta; \qquad \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}(\sin\theta.\Theta') - c\sin^2\theta = -\frac{\Phi''}{\Phi}.$$

The RHS is a function of ϕ only, the LHS of θ only. So by separation of variables, both are constant, m^2 say:

$$-\Phi''/\Phi = m^2, \qquad \Phi'' = -m^2\Phi, \qquad \Phi(\phi) = \cos m\phi \quad \text{or} \quad \sin m\phi.$$

It turns out that only $m = 0, 1, 2, \ldots, n$ are needed. So: for $m = 0, 1, \ldots, n$, $n = 0, 1, 2, \ldots$, solutions of $\Delta u = 0$ are

$$u = r^n[r^{-n-1}].\cos[\sin]m\phi P_n^m(\theta),$$

where $\Theta = P_n^m$ satisfies

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}(\sin\theta.\Theta') - n(n+1)\sin^2\theta = m^2,$$

or

$$\sin\theta\frac{d}{d\theta}(\sin\theta.\Theta') - m^2\Theta - n(n+1)\sin^2\theta.\Theta = 0.$$

The solutions P_n^m of this ODE (linear, 2nd order) in Θ are called *Legendre functions.*

By linearity (superposition): sums

$$\sum_{n=0}^{\infty}\sum_{m=0}^{n} c_{mn} r^n \cos m\phi P_n^m(\theta)$$

are solutions of Laplace's equation, and similarly for r^{-n-1} and $\sin m\phi$.

These functions form a "complete orthonormal system" (CONS); see Ch. V on Fourier methods, and are called *spherical harmonics.*

IV. LINEAR ALGEBRA

In general, we expect to be able to solve 2 simultaneous linear equations in 2 unknowns, x and y say, uniquely in x and y. Usually we can. E.g.,

$$\begin{aligned} x + y &= 1, \\ x + 2y &= 5. \end{aligned}$$

Subtract: $y = 4$. Back-substitute: $x = -3$. Check (always!).
Sometimes we cannot. E. g.

$$\begin{aligned} x + y &= 1, \\ x + y &= 2. \end{aligned}$$

These equations are *incompatible*, and have NO solution.
Sometimes there are infinitely many solutions. E. g.

$$\begin{aligned} x + y &= 1, \\ 2x + 2y &= 2. \end{aligned}$$

The second equation is now it redundant – duplicates the first equation. We can give either variable an arbitrary value, and then solve either equation uniquely for the other.

What discriminates between these three cases?
General case: n equations in n unknowns,

$$\begin{aligned} a_{11}x_1 + \ldots + a_{1n}x_n &= b_1, \\ \vdots &= \vdots \\ a_{1n}x_1 + \ldots + a_{nn}x_n &= b_n. \end{aligned}$$

We re-write this more compactly as

$$Ax = b,$$

where x is a (column) *vector* of (n) unknowns, b is a (column) vector of constants, $A = (a_{ij})$ is a *matrix* - a *square* matrix of *order* n, or $n \times n$ (n *rows*, then n *columns*):

$$x = \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix}, \quad A = \begin{pmatrix} a_{11} & \ldots & a_{1n} \\ \vdots & \vdots & \vdots \\ a_{1n} & \ldots & a_{nn} \end{pmatrix}, \quad b = \begin{pmatrix} b_1 \\ \vdots \\ b_n \end{pmatrix}.$$

We can also write

$$\sum_{j=1}^{n} a_{ij}x_j = b_i \quad (i = 1, \ldots, n).$$

We can abbreviate this to

$$a_{ij}x_j = b_i,$$

using the *Einstein summation convention*: the summation over the *repeated* suffix is understood.

Note. It took Einstein to think of this! But he needed it: the mathematics of General Relativity involves endless summations of this kind. Although it takes some getting used to, experience shows that the Einstein summation convention is very useful. When handling heavy mathematical manipulation (particularly all day, every day), strip the notation down to the bare functional minimum.

Determinants.

The *determinant det* A, or $|A|$, of a square matrix A of order n can bve defined as follows:

$n = 1$: $A = (a_{11})$, $|A! := a_{11}$ (1 term).

$n = 2$:

$$A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}, \quad |A| := a_{11}a_{22} - a_{21}a_{12}$$

($2 = 2!$ terms).

$n = 3$: $|A| := a_{11}|A_{11}| - a_{12}|A_{12}| + a_{13}|A_{13}|$ ($3! = 3.2!$ terms), where each A_{ij} is the submatrix (of order 2) obtained from A by deleting the row and column containing a_{ij} (the ith row and jth column).

$n = 4$: $|A| := a_{11}|A_{11}| - a_{12}|A_{12}| + a_{13}|A_{13}| + a_{14}|A_{14}|$ ($4! = 4 \times 3!$ terms), etc. Observe the *chessboard* (or chequerboard) *pattern* of signs, $\pm$. The determinant contains:

(i) $n!$ terms (following this pattern, or by induction);

(ii) each term is of the form

$$a_{1\sigma(1)}a_{2\sigma(2)} \ldots a_{n\sigma(n)},$$

where

$$\sigma = (\sigma(1), \ldots, \sigma(n))$$

is a *permutation* of $\{1, 2, \ldots, n\}$ – contains each value $1, 2, \ldots, n$ exactly once;

(iii) this term has + or -, according as the permutation is *even* or odd.

Imagine you had to rearrange the integers $\sigma(1), \ldots, \sigma(n)$ in increasing order $1, 2, \ldots, n$, being allowed only to interchange a pair at each step. Such a change is called a *transposition*. We quote from Algebra the fact that, although there are many ways of doing this for a given permutation, all such ways will have a number of transpositions of the same *parity* (odd or even). This is called the parity (or signum) of the permutation, $sgn(\sigma)$.

Combining, we have the general definition of the determinant of any order:

$$|A| := \sum_{\sigma} (-1)^{sgn(\sigma)} a_{1\sigma(1)} a_{2\sigma(2)} \ldots a_{n\sigma(n)}.$$

This method sketched out in (i) - (iii) above gives the expansion of the determinant *by its first row*. We may similarly define the expansion of the determinant by its first *column*, or by any row or column.

Matrix Transpose.

If $A = (a_{ij})$ (m rows, n columns) is a matrix, write A^T (or A') for the $n \times m$ matrix whose (i, j) element is a_{ji}:

$$A = (a_{ij}) \quad (m \times n): \qquad A^T = (a_{ji}) \quad (n \times m).$$

Properties of Determinants.

1. $|A| = |A^T|$
(transposing switches rows and columns, and we have seen that we can expand $|A|$ either by rows or by columns).

2. If we interchange two rows (or two columns), $|A|$ changes sign ($|A| \to -|A|$). For, this introduces an *extra transposition* into each permutation σ in the expansion of $|A|$, which changes its sign. So each term in the expansion changes sign, so the determinant does too.

3. If two rows (or two columns) coincide, $|A| = 0$. For, then interchanging these rows (or columns) has no effect, but it changes the sign of the determinant. So $|A| = -|A|$, so $|A| = 0$.

4. If we add a multiple c of a row (or column) i to any other row (or column) j, $|A|$ is unchanged.

For, expand by the new row (or column). We get $|A| + c|B|$, where B is the matrix with rows (or columns) i and j equal, so $|B| = 0$ by above, so we get $|A|$ as before.

We shall see that this has important consequences in helping us to solve simultaneous linear equations efficiently (Gaussian elimination).