Practical Physics

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Chapter 1

Hamiltonian Mechanics

1.0.1 Simple Harmonic Oscillator (SHO)

Arguably the simplest classical system is conservative (energy doesn't leave/enter the system), has one degree of freedom and is linear. The SHO has passed into ubiquity as a model used to describe many physical systems, for example the vibration of a linear diatomic molecule. The SHO model is represented by a mass m on a spring with force constant k. The spring-mass system is extended and released; energy is stored in the spring when extended and subsequently converted between kinetic T (expressed in terms of momentum as $p^2/2m$) and potential energy V (in terms of the spring constant k, $\frac{k}{2}x^2$) when released. The Hamiltonian H is the total energy and is constant in a conservative system:

$$H = T + V = p^2/2m + \frac{1}{2}kx^2$$

Equations of motion are given by the partial derivatives:

$$\dot{p} = -\frac{\partial H}{\partial x}$$
$$\dot{x} = \frac{\partial H}{\partial p} \tag{1.1}$$

One may show that

$$x = A\sin(\omega t - \phi) \tag{1.2}$$

represents a general solution to the equation of motion, where A is a constant determined from initial conditions, $\omega = \sqrt{k/m}$ is the angular frequency and ϕ is the phase. In general, most systems aren't solvable exactly however one may always from phase space (a plot of p vs x) discuss qualitative aspects of the motion. Figure 1 illustrates the solution for x for the SHO, figure 2 (top) is the potential function $V(x)$ and below is phase space, for several constant values of energy (elliptical surfaces).

1.0.2 Classical Features

- Energy, momentum, displacement etc are all variables, continuously variable and commutative:

$$x.p - p.x = 0 \tag{1.3}$$

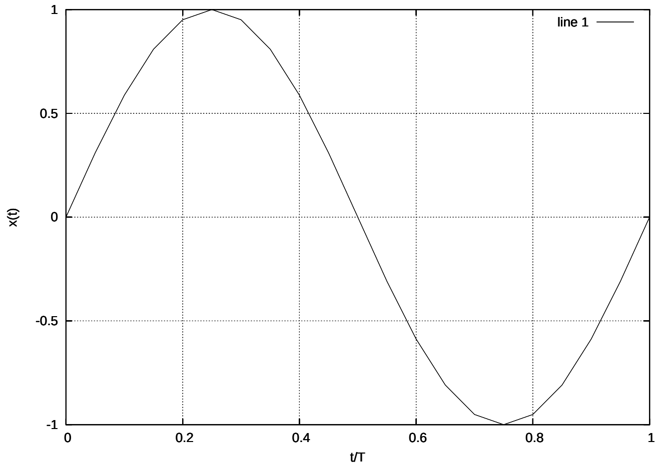


Figure 1.1: Amplitude as a function of time t divided by period T

- Given all the variables of the system, one may predict with certainty quantities like displacement, momentum etc, by solving equations of motion, or at least describe the salient features by studying orbits in phase space.
- The turning points of motion correspond to the case where $p = 0$ ie.,

$$x = \pm\sqrt{\frac{2H}{k}} \tag{1.4}$$

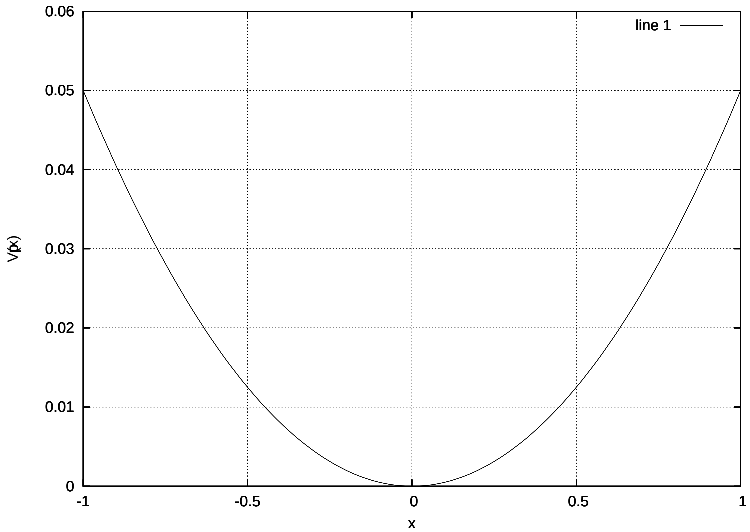
for the SHO and are proportional to energy. The displacement does not extend beyond these points, into the forbidden region.

1.0.3 Quantum Features

- Energy, momentum, displacement etc are all operators in Hilbert space, which has structure (a set of elements with defined operations and relationships). Operators may not commute, and if not, they may not both be measured with absolute certainty (cf Heisenberg uncertainty principle). The objects they 'operate' on may be functions or vectors. The dimension of Hilbert space for a given problem may be infinite (eg., SHO) or discrete (eg., nuclear spin levels) and is 'spanned' by orthogonal functions/vectors.
- The state of a system is given by the function ψ, which is described by the Schrodinger equation (eg., the 1D time independent version, position basis):

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x) \tag{1.5}$$

Given in this form, the amplitude of ψ corresponds to the probability for a particle to be found at a certain position. It is normalized ie., the probability for an object to be anywhere must be 1.
- There is often a non-zero probability for an object to be in the classically forbidden region.



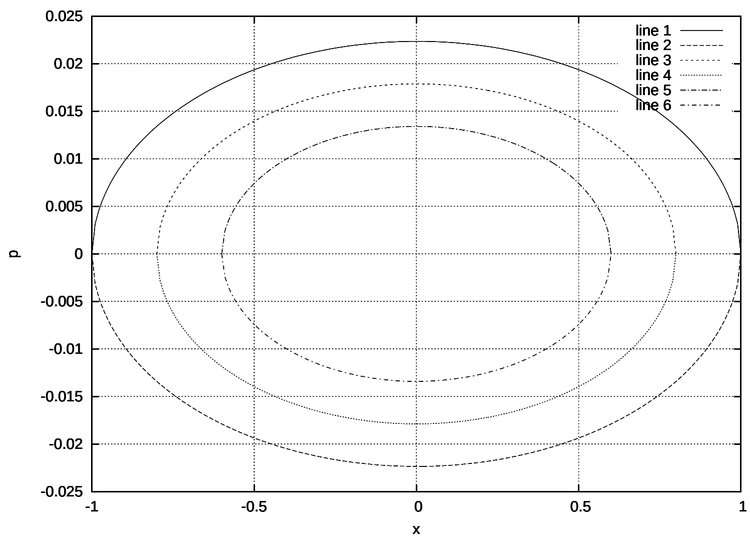


Figure 1.2: Top: Potential energy for SHO. Below: Phase space, constant energy contours for SHO

1.0.4 Quantum SHO

If we re-write the potential energy as $V(x) = 1/2m\omega^2x^2$ then one can show that the solution to Schrodinger's equation is given by:

$$\psi(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{m\omega x^2}{2\hbar}\right)H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \tag{1.6}$$

for $n = 0, 1, 2, ...$ The Hermite polynomials H_n, given by:

$$H_n(x) = (-1)^n e^{x^2}\frac{d^n}{dx^n}e^{-x^2}, \tag{1.7}$$

span an infinite dimensional space, since they are orthogonal and n may be any positive integer. They are therefore a basis for this system, and are referred to as eigenstates. Since the Schrodinger equation is linear, an arbitrary state may be prepared from a linear combination of eigenstates. Associated with each is a specific energy eigenvalue:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{1.8}$$

which reveals the discrete nature of QM; specific quantities of energy must be absorbed or emitted for a QM system to 'change states'. In addition, even if $n = 0$, there is a zero-point energy which exists, also in distinction to classical mechanics.

The first four energy eigenstates are illustrated in figures 3,4, by plotting $|\psi|^2$ versus x. Note that to begin with the particle is most likely near the origin, again in distinction to classical mechanics. As n increases, the probability distribution 'smears' out, and in the limit as $n \to \infty$, the classical result is reached. This overlap between QM and CM is referred to as the 'correspondence principle'. Note that one can show also that there is a (decreasingly) finite probability for the particle to be found in the classically forbidden region, an effect referred to as QM tunneling.

Notes: An arbitrary state as mentioned may be constructed as a linear combination of eigenstates. When a measurement of the system is taken, the wave function is said to 'collapse' and will thereafter (without further interruption) remain in a particular eigenstate. The mechanics and philosophy of the wave function collapse and measurement remain the subject of varied opinions and research.

QM stands in distinction to classical mechanics in that determinism is sacrificed in favor of a probabilistic interpretation of nature. The correspondence principle ensures overlap of the two pictures of nature in the appropriate limit. In general too many degrees of freedom prevent the Schrodinger equation from being of much practical benefit. One makes recourse to Statistical Mechanics and the Density Operator approach in NMR, for instance.

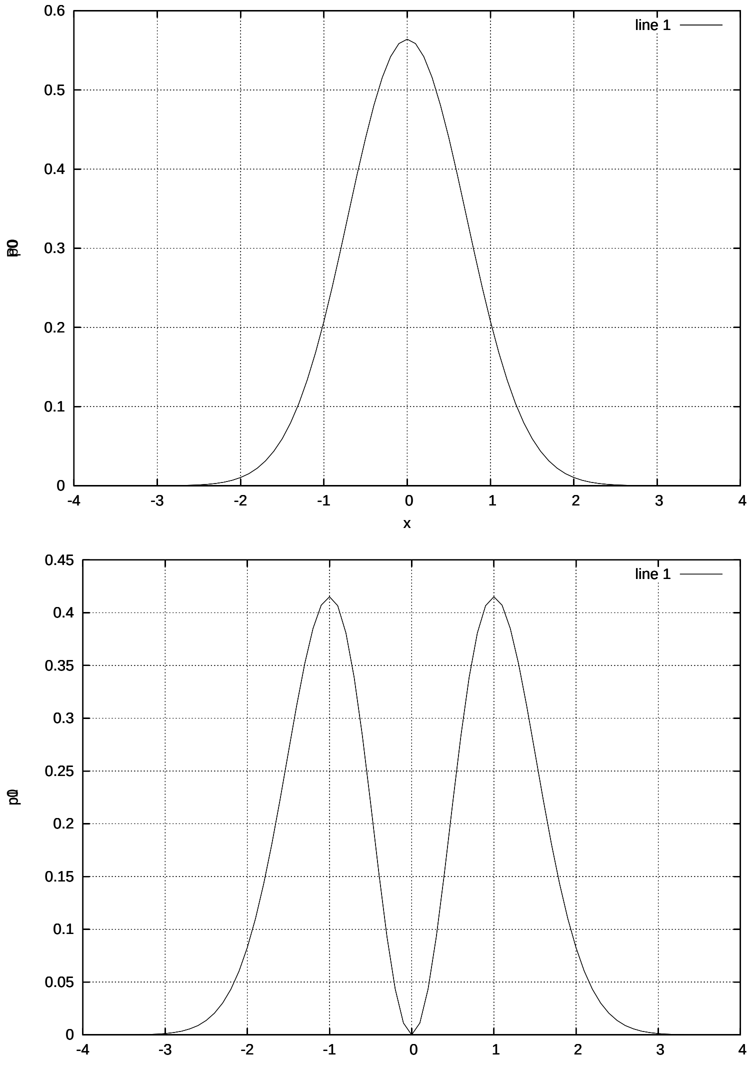


Figure 1.3: $|\psi|^2$ for zeroth (top) and first (below) energy eigenstates, SHO

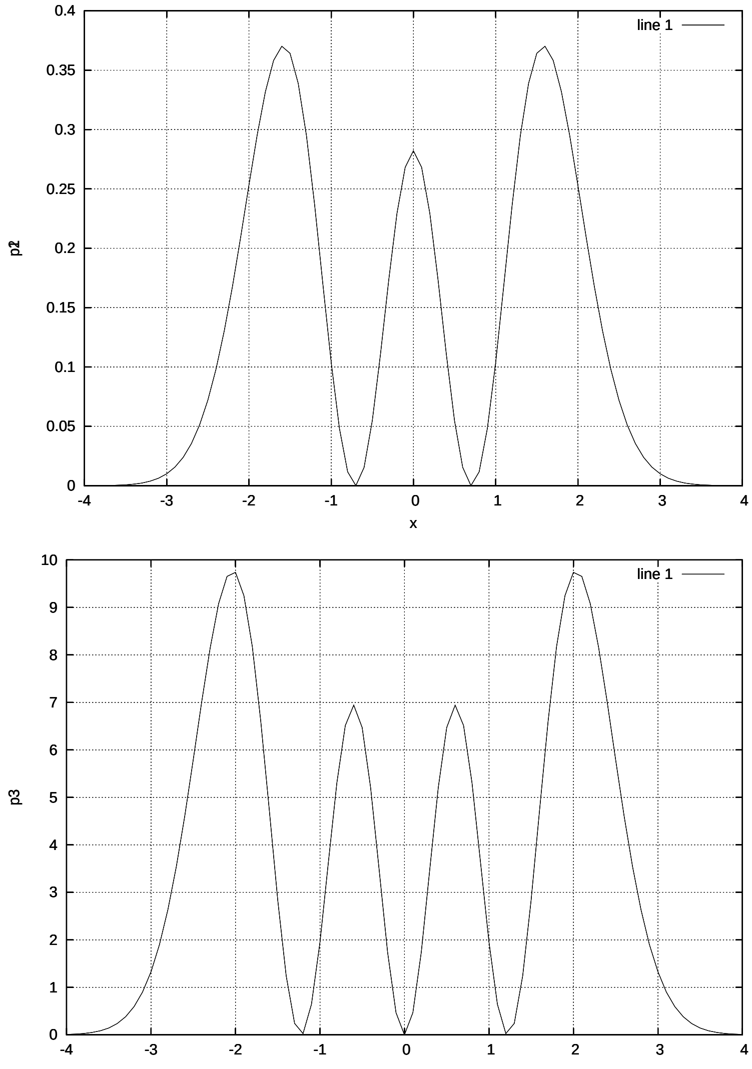


Figure 1.4: $|\psi|^2$ for second (top) and third (below) energy eigenstates, SHO

Chapter 2

Hilbert Space

2.0.5 Linear Algebra and Vector Spaces

The elements and operations of Hilbert space provides the machinery for quantum mechanics. Simply put, functions are viewed as vectors in a vector space. To begin with, examples of the inner product, completeness and orthonormality for vectors may be expressed in terms of R^3 co-ordinate space basis as:

$$(a, 0, 0) \cdot \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} = a^2 \tag{2.1}$$

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = a. \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + b. \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + c. \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{2.2}$$

$$(0, 1, 0) \cdot \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 1; (1, 0, 0) \cdot \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0 \tag{2.3}$$

In general, equation 1) is too exclusive, and a more flexible expression for complex vector spaces is:

$$(x, y) = \sum_{i=1}^{n} \xi_i^* \eta_i \tag{2.4}$$

which lends meaning to the idea of 'projection' of the 'dual' space vector x onto y ($x \neq y$) and 'length' or 'norm' ($x = y$), the latter written as $||x||$. A vector space which includes the inner product definition is referred to as an inner product space. By Schwarz's inequality, if x, y are vectors in this space, then

$$|(x, y)| \leq ||x||.||y|| \tag{2.5}$$

In 2), the basis is given implicitly and is said to 'span' R^3; an arbitrary vector in this space may always be expressed as a linear combination of these vectors. In 3) orthonomality is demonstrated using the basis. A set of vectors is orthonormal if each vector is orthogonal to every other in the set and normalized in unit length. Using an orthonormal set, a linear transformation can be represented as a matrix.

More precisely, let V be an $n-$dimensional vector space, with $X = \{x_1, x_2, ..., x_n\}$ a basis in V, and let A be a linear transformation mapping V into itself. Because any vector may be epxressed as a linear combination of the basis, we have

$$Ax_j = \sum_{i=1}^{n} a_{ij} x_i \text{ for } j = 1, ..., n \tag{2.6}$$

The n^2 scalars a_{ij} constitute the matrix elements of linear transformation A relative to the basis X. With any square matrix such as A is asscoiated a quantity referred to as the determinant, which may be defined as:

$$\det A = \sum_j A_{Jj} \operatorname{cof}(A_{Jj}) \tag{2.7}$$

for any row J. The cofactor (cof) of the element A_{Jj} is equal to $(-1)^{J+j}$ times the determinant of the $(n-1) \times (n-1)$ matrix obtained from A by eliminating the Jth row and jth column. This algorithm may be extended to columns:

$$\det A = \sum_j A_{jJ} \operatorname{cof} A_{jJ} \tag{2.8}$$

For example, if

$$A = a_{ij} = \begin{bmatrix} 1 & 3 & 5 \\ 4 & 3 & 2 \\ 1 & 3 & 2 \end{bmatrix} \tag{2.9}$$

the the determinant is (along the first row):

$$\Delta = 1.(3.2 - 3.2) - 3.(4.2 - 2.1) + 5.(4.3 - 3.1) = 27 \tag{2.10}$$

or equivalently, by the second method (along the first column):

$$\Delta = 1.(3.2 - 3.2) - 4.(2.3 - 5.3) + 1.(2.3 - 3.5) = 27 \tag{2.11}$$

The determinant has a number of useful properties, including:

1. A common factor of each element of a row (or column) may be factored out as a multiplicative constant

2. An all zero row or column implies that det=0

3. det(AB)=det$A$.det$B$

The linear transformation A has an inverse with a matrix representation which depends on the determinant. For the previous example, the inverse is given by:

$$[A^{-1}]_{ij} = \frac{1}{\det A} [\text{adj} A]_{ij}$$

$$= \frac{1}{27} \begin{bmatrix} (-1)^{1+1} \det \begin{pmatrix} 3 & 2 \\ 3 & 2 \end{pmatrix} & (-1)^{2+1} \det \begin{pmatrix} 3 & 5 \\ 3 & 2 \end{pmatrix} & (-1)^{3+1} \det \begin{pmatrix} 3 & 5 \\ 3 & 2 \end{pmatrix} \\ (-1)^{1+2} \det \begin{pmatrix} 4 & 2 \\ 1 & 2 \end{pmatrix} & (-1)^{2+2} \det \begin{pmatrix} 1 & 5 \\ 1 & 2 \end{pmatrix} & (-1)^{3+2} \det \begin{pmatrix} 1 & 5 \\ 4 & 2 \end{pmatrix} \\ (-1)^{1+3} \det \begin{pmatrix} 4 & 3 \\ 1 & 3 \end{pmatrix} & (-1)^{2+3} \det \begin{pmatrix} 1 & 3 \\ 1 & 3 \end{pmatrix} & (-1)^{3+3} \det \begin{pmatrix} 1 & 3 \\ 4 & 3 \end{pmatrix} \end{bmatrix}$$

$$= \begin{bmatrix} 0 & \frac{1}{3} & -\frac{1}{3} \\ -\frac{2}{9} & -\frac{1}{9} & \frac{2}{3} \\ \frac{1}{3} & 0 & -\frac{1}{3} \end{bmatrix} \tag{2.12}$$

where the adjoint (adj) matrix A_{ij} is equal to $\mathrm{cof}(A_{ji})$. If the determinant is zero, then the matrix is said to be singular and no inverse exists. This may correspond physically to the case where the matrix elements are the coefficients in a set of linear equations which are not linearly independent. In this case there is insufficient information to determine to unknowns precisely.

Exercise: show that $AA^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = I$

In general numerical methods are far more expedient in calculating the inverse. Also, one is at liberty to choose the basis which the elements of A are expressed with respect to. If in another basis the same transformation is C, then if there exists an invertible matrix B such that;

$$C = B^{-1}AB \tag{2.13}$$

then C is related to A by a similarity transformation. Similar matrices also share the same eigenvalues; a scalar λ is an eigenvalue and a nonzero vector x is an eigenvector of a linear transformation A if

$$Ax = \lambda x \tag{2.14}$$

Re-writing this as $(A - \lambda I)x = 0$, the only non-trivial solution for x dictates that $(A - I\lambda)$ be singular, ie.,

$$\det(A - \lambda I) = \det \begin{bmatrix} a_{11} - \lambda & a_{12} & \ldots & a_{1n} \\ a_{21} & a_{22} - \lambda & \ldots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \ldots & a_{nn} - \lambda \end{bmatrix} = 0 \tag{2.15}$$

For instance, if

$$A = \begin{bmatrix} 1 & -3 & 2 \\ -3 & 2 & 1 \\ 2 & 1 & 3 \end{bmatrix} \tag{2.16}$$

then by the previous procedure, this yields characteristic equation:

$$-\lambda^3 + 6\lambda^2 + 3\lambda - 42 = 0 \tag{2.17}$$

with solutions $\lambda = -2.4188, 3.6132, 4.8056$.
Exercise: The Hamilton-Cayley theorem states that a matrix obeys it's own characteristic equation; show this for the previous example

One may write the corresponding eigenvectors as columns of a matrix P,

$$\begin{bmatrix} -0.725619 & -0.038605 & 0.687013 \\ -0.577350 & 0.577350 & -0.577350 \\ 0.374359 & 0.815583 & 0.441225 \end{bmatrix} \tag{2.18}$$

which is said to diagonalize A, since:

$$P^{-1}AP = \begin{bmatrix} -2.41883 & 0 & 0 \\ 0 & 3.61323 & 0 \\ 0 & 0 & 4.80560 \end{bmatrix} \tag{2.19}$$

In this example, all the eiganvalues (the 'spectrum') of the matrix A were real. While not stated explicitly, the matrix A given in the example is Hermitian. That is:

$$A = A\dagger \tag{2.20}$$

or in other words, a hermitian matrix is one that is equal to the transpose (rows and columns are interchanged) of it's complex conjugate (the two features of transpostion and conjugation indicated by †). This ensures that the roots of the characteristic equation and hence eigenvalues are real. In quantum mechanics, the eignenvlaues of an operator correspond to the result of a measurement. Therefore, observables must be hermitian in nature. In addition, eignevalues may have two types of multiplicity;

1. geometric multiplicity, meaning the number of linearly independent eigenvectors belonging to λ.
2. algebraic multiplicity, meaning the number of times λ appears as a root to the characteristic equation.

The physical implications in quantum mechanics are discussed in the appropriate section.

2.0.6 Sturm Liouville Systems

By analogy with the elements of linear algebra, one may produce similiar definitions for functions, ie., the inner product:

$$(f_1, f_2) \equiv \int_a^b f_1^*(x) f_2(x) dx \tag{2.21}$$

completeness (Riesz-Fischer Theorem):

> Let the functions $f_1(x), f_2(x), ...$ be the elements in function space. If
>
> $$\lim_{n,m\to\infty} ||f_n - f_m||^2 \equiv \lim_{n,m\to\infty} \int_a^b |f_n(x) - f_m(x)|^2 dx = 0, \tag{2.22}$$
>
> there exists a square (Lebesgue) integral function $f(x)$ to which the sequence $f_n(x)$ converges 'in the mean'; ie., there exists an f such that:
>
> $$\lim_{n\to\infty} \int_a^b |f(x) - f_n(x)|^2 dx = 0 \tag{2.23}$$

and orthonormality:

$$(f_n, f_m) \equiv \int_a^b f_i^*(x) f_j(x) dx = \delta_{ij} \tag{2.24}$$

The implication is that an arbitrary (albeit continuous) function (by analogy to vectors) may be 'built up' as a linear combination of basis functions, these functions having the properties of completeness and orthonormality. This possibility is expressed in Weierstass's theorem for polynomials (eg., Hermite, Legendre etc), extended to trigonometric functions.

The functions (eg., Hermite, Legendre etc) of Hilbert Space may each be viewed as special solutions to a more general system. All the functions are solutions to an equation of the form

$$Lu = \lambda u \tag{2.25}$$

where

$$L = \alpha(x)\frac{d^2}{dx^2} + \beta(x)\frac{d}{dx} + \gamma(x) \tag{2.26}$$

λ is a constant and α, β, γ are real functions of x. The operators L are hermitian:

$$(Lf, g) \equiv \int_{-\infty}^{\infty} (Lf(x))^* g(x) w(x) dx = \int_{-\infty}^{\infty} (f(x))^* (Lg(x)) w(x) dx \equiv (f, Lg) \tag{2.27}$$

(where $w(x)$ is a weight function) iff:

$$[w\alpha(f^* g' - g f^{*\prime})]_{-\infty}^{\infty} = 0$$

$$(w\alpha)' = w\beta \tag{2.28}$$

The last equation may be solved to give:

$$w\alpha = C \cdot \exp\left[\int \frac{\beta}{\alpha} dx\right] \tag{2.29}$$

Equation may be re-written as:

$$\frac{d}{dx}\left[w\alpha\frac{du}{dx}\right] + (\gamma - \lambda) w u \tag{2.30}$$

and with the boundary condition () comprise a Sturm-Liouville (SL) system. One may show that eigenfunctions asscoiated with distinct eignevalues are orthogonal. *Exercise:* Show this, ie., that:

$$(u_m, u_n) = \int_{-\infty}^{\infty} u_m^*(x) u_n(x) w(x) dx = 0 \tag{2.31}$$

The polynomial SL systems are special cases of the following polynomial coefficients:

$$\alpha(x) = \alpha_0 x^2 + \alpha_1 x + \alpha_2 \tag{2.32}$$

$$\beta(x) = \beta_0 x^2 + \beta_1 \tag{2.33}$$

$$\gamma(x) = \gamma_0 \tag{2.34}$$

Their properties are summarized in table 1. In addition, the operator L for these solutions also satisfies:

Model signal as:

Name	Differential Equation	$\alpha_0, \alpha_1, \alpha_2$	β_0	β_1	$w\alpha$	w	$[a, b]$
Jacobi	$(1-x^2)u'' + [-(p+q+2)x + (q-p)]u' + n(n+p+q+1)u = 0$	-1, 0, 1	$-(p+q+2)$	$q-p$	$(1-x)^{p+1}; (1+x)^{q+1}$	$(1-x)^p; (1+x)^q$	$[-1, 1]$
Jacobi	$(x-x)u'' + [-(p+q+2)x + (p+1)]u' + n(n+p+q+1)$u=0	-1,1,0	$-(p+q+2)$	$p+1$	$x^{p+1}(1-x)^{q+1}$	$x^p(1-x)^q$	$[0, 1]$
Gegenbauer	$(1-x^2)u''-2(m+1)xu'+n(n+2m+1)u = 0$	-1,0,1	$-2(m+1)$	0	$(1-x^2)^{m+1}$	$(1-x^2)^m$	$[-1, 1]$
Tschebycheff	$(1-x^2)u'' - xu' + n^2u = 0$	-1,0,1	-1	0	$(1-x^2)^{1/2}$	$(1-x^2)^{-1/2}$	[-1,1]
Legendre	$(1-x^2)u'' - 2xu' + n(n+1)u = 0$	-1,0,1	-2	0	$1-x^2$	1	[-1,1]
Laguerre	$xu'' - [x-(s+1)]u' + nu = 0$	0,1,0	-1	$s+1$	$x^{s+1}e^{-x}$	$x^s e^{-x}$	$[0, \infty]$
Hermite	$u'' - 2xu' + 2nu$	0,0,1	-2	0	e^{-x^2}	e^{-x^2}	$[-\infty, \infty$

Table 2.1: Sturm-Liouville systems

$$f(x) = \begin{cases} 2.5 + 3e^{-2x} \sin 9x & 0 \le x \le \pi \\ -2.5 - 3e^{-2\pi-2x} \sin 9x & -\pi \le x \le 0 \end{cases} \tag{2.35}$$

Use the Fourier expansion:

$$f(x) = a_0 + \sum_n^\infty a_n \cos nx + \sum_n^\infty b_n \sin nx \tag{2.36}$$

where

$$a_0 = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) dx \tag{2.37}$$

$$a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos nx dx \tag{2.38}$$

$$b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin nx dx \tag{2.39}$$

Applying Eq(), one finds:

$$a_0 = \frac{1}{\pi} \int_0^\pi 2.5 dx + \frac{3}{\pi} \int_0^\pi e^{-2x} \sin 9x dx - \frac{1}{\pi} \int_{-\pi}^0 2.5 dx - \frac{3}{\pi} e^{-2\pi} \int_{-\pi}^0 e^{-2x} \sin 9x dx \tag{2.40}$$

now

$$\int_0^\pi e^{-2x} \sin 9x dx = -\frac{1}{2} e^{-2\pi} \sin 9x \Big|_0^\pi + \frac{9}{2} \int_0^\pi e^{-2x} \cos 9x dx \tag{2.41}$$

$$= -\frac{9}{4} e^{-2x} \cos 9x \Big|_0^\pi - \frac{81}{4} \int_0^\pi e^{-2x} \sin 9x dx \tag{2.42}$$

$$= -\frac{9}{85} e^{-2x} \cos 9x \Big|_0^\pi \tag{2.43}$$

$$= \frac{9}{85} \left[e^{-2\pi} + 1 \right] \tag{2.44}$$

$$= -e^{-2\pi} \int_{-\pi}^0 e^{-2x} \sin 9x dx \tag{2.45}$$

$$\tag{2.46}$$

and since the first and third integrals of Eq() cancel, one finds:

$$a_0 = \frac{54}{85\pi} \left[e^{-2\pi} + 1 \right] \tag{2.47}$$

Now $a_n =$

$$\frac{1}{\pi} \int_0^\pi 2.5 \cos nx dx + \frac{3}{\pi} \int_0^\pi e^{-2x} \sin 9x \cos nx dx$$
$$- \frac{1}{\pi} \int_{-\pi}^0 2.5 \cos nx dx - \frac{3}{\pi} e^{-2\pi} \int_{-\pi}^0 e^{-2x} \sin 9x \cos nx dx \tag{2.48}$$

Using the identity,

$$\cos nx \sin \beta x = \frac{1}{2} \sin(\beta + n)x + \frac{1}{2} \sin(\beta - n)x \tag{2.49}$$

we may write:

$$\frac{3}{\pi}\int_0^\pi e^{-2x}\sin 9x\cos nx dx = \frac{3}{2\pi}\int_0^\pi e^{-2x}\sin(9+n)x dx + \frac{3}{2\pi}\int_0^\pi e^{-2x}\sin(9-n)x dx \tag{2.50}$$

Let $9 \pm n = \alpha$;

$$\frac{3}{2\pi}\int_0^\pi e^{-2x}\sin\alpha x dx \tag{2.51}$$

$$= -\frac{3}{4\pi}e^{-2x}\sin\alpha x\Big|_0^\pi \rightarrow 0 + \frac{3\alpha}{4\pi}\int_0^\pi e^{-2x}\cos\alpha x dx \tag{2.52}$$

$$= -\frac{3\alpha}{8\pi}e^{-2x}\cos\alpha x\Big|_0^\pi - \frac{3\alpha^2}{8\pi}\int_0^\pi e^{-2x}\sin\alpha x dx \tag{2.53}$$

$$= -\frac{3\alpha}{2\pi(4+\alpha^2)}e^{-2x}\cos\alpha x|_0^\pi \tag{2.54}$$

$$\tag{2.55}$$

and since the first and third integrals of Eq() cancel, we may write:

$$a_n =$$

$$-\frac{3(9+n)}{2\pi(4+(9+n)^2)}\left(e^{-2x}\cos(9+n)x|_0^\pi\right) - \frac{3(9-n)}{2\pi(4+(9-n)^2)}\left(e^{-2x}\cos(9-n)x|_0^\pi\right)$$

$$+e^{-2\pi}\frac{3(9+n)}{2\pi(4+(9+n)^2)}\left(e^{-2x}\cos(9+n)x|_{-\pi}^0\right) + e^{-2\pi}\frac{3(9-n)}{2\pi(4+(9-n)^2)}\left(e^{-2x}\right. \tag{2.56}$$

There are two cases to consider; when n is odd, one finds that:

$$\cos(9\pm n)x|_0^\pi \text{ and } \cos(9\pm n)x|_{-\pi}^0 = 0 \tag{2.57}$$

When n is even, one finds:

$$e^{-2x}\cos(9\pm n)x\Big|_0^\pi = -[1+e^{-2\pi}] = -e^{-2\pi}\left(e^{-2x}\cos(9\pm n)x\Big|_{-\pi}^0\right) \tag{2.58}$$

Therefore,

$$a_n(n = \text{even}) =$$

$$\left(\frac{3(9+n)}{\pi(4+(9+n)^2)} + \frac{3(9-n)}{\pi(4+(9-n)^2)}\right)\left[e^{-2\pi}+1\right] \tag{2.59}$$

Now $b_n =$

$$\frac{1}{\pi}\int_0^\pi 2.5\sin nx dx + \frac{3}{\pi}\int_0^\pi e^{-2x}\sin 9x\sin nx dx$$

$$-\frac{1}{\pi}\int_{-\pi}^0 2.5\sin nx dx - \frac{3}{\pi}e^{-2\pi}\int_{-\pi}^0 e^{-2x}\sin 9x\sin nx dx \tag{2.60}$$

For the first and third integrals (which are non-zero for n=odd) one finds:

$$\frac{-2.5}{n\pi}\cos nx\Big|_0^\pi + \frac{2.5}{n\pi}\cos nx\Big|_{-\pi}^0 = \frac{10}{n\pi} \tag{2.61}$$

Using the identity,

$$\sin nx \sin \beta x = \frac{1}{2}\cos(\beta - n)x - \frac{1}{2}\cos(\beta + n)x \tag{2.62}$$

we may write:

$$\frac{3}{\pi}\int_0^{\pi} e^{-2x}\sin 9x \sin nx dx = \frac{3}{2\pi}\int_0^{\pi} e^{-2x}\cos(9-n)x dx - \frac{3}{2\pi}\int_0^{\pi} e^{-2x}\cos(9+n)x dx \tag{2.63}$$

Let $9 \pm n = \alpha$;

$$\frac{3}{2\pi}\int_0^{\pi} e^{-2x}\cos \alpha x dx \tag{2.64}$$

$$= -\frac{3}{4\pi}e^{-2x}\cos \alpha x\Big|_0^{\pi} - \frac{3\alpha}{4\pi}\int_0^{\pi} e^{-2x}\sin \alpha x dx \tag{2.65}$$

$$= -\frac{3}{4\pi}e^{-2x}\cos \alpha x\Big|_0^{\pi} + \frac{3}{8\pi}e^{-2x}\sin \alpha x\Big|_0^{\pi} \to 0 \tag{2.66}$$

$$-\frac{\alpha^2}{8\pi}\int_0^{\pi} e^{-2x}\cos \alpha x dx \tag{2.67}$$

$$= \frac{6}{2\pi(4+\alpha^2)}\left(e^{-2x}\cos \alpha x\Big|_0^{\pi}\right) \tag{2.68}$$

Based on previous on the previous result for $e^{-2x}\cos \alpha x|_0^{\pi}$ one finds:

$$b_n(n = \text{ even }) =$$

$$\left(\frac{6}{\pi(4+(9+n)^2)} + \frac{6}{\pi(4+(9-n)^2)}\right)\left[e^{-2\pi}+1\right] \tag{2.69}$$

and thus the fourier expansion for $f(x)$ is:

$$\frac{54}{85\pi}\left[e^{-2\pi}+1\right] + \sum_{n=2,4,6..}^{\infty}\left(\frac{3(9+n)}{\pi(4+(9+n)^2)} + \frac{3(9-n)}{\pi(4+(9-n)^2)}\right)\left[e^{-2\pi}+1\right]\cos nx$$

$$\sum_{n=1,3,5..}^{\infty}\frac{10}{n\pi}\sin nx + \sum_{n=2,4,6..}^{\infty}\left(\frac{6}{\pi(4+(9+n)^2)} + \frac{6}{\pi(4+(9-n)^2)}\right)\left[e^{-2\pi}+1\right]\sin nx \tag{2.70}$$

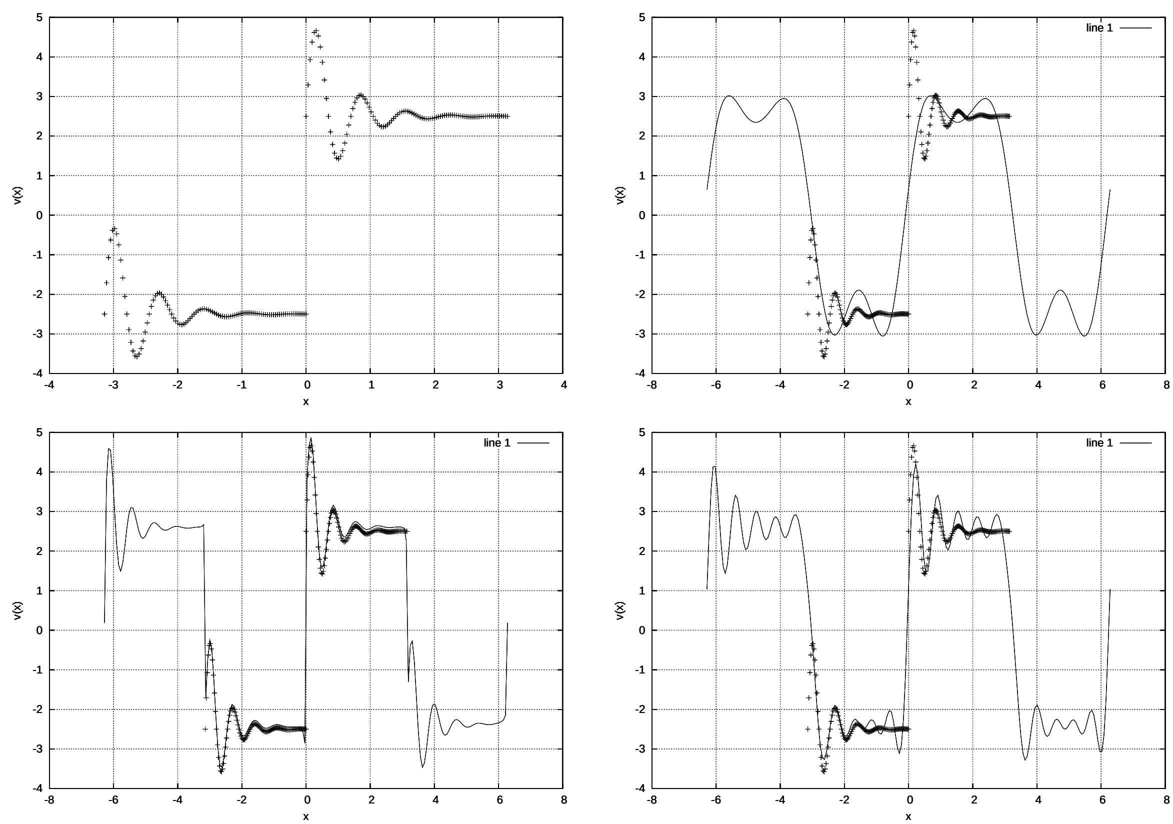


Figure 2.1: (Clockwise from top left): Signal due to ringdown after 74AC240 line buffer, Fourier series after 5 terms, 10 terms and 100 terms

Chapter 3

Statistical Mechanics

3.0.7 Ensembles

Within a classical mechanics framework the evolution of a single system of N particles may be determined from the $6N$ variables, if p and q for each are known as functions of time. The quantities of interest for a system (eg., energy, pressure etc) in theory may be determined as time averages. Gibbs proposed the ensemble idea, where averages take place over a group of similar systems, each a snapshot of the state the system may assume over time. The time average of a variable for a single system and the ensemble average are considered equivalent.
Exercise: Figure 1 is a plot of the running average of dice roll outcomes versus time. Show that the time and the ensemble average are equivalent.

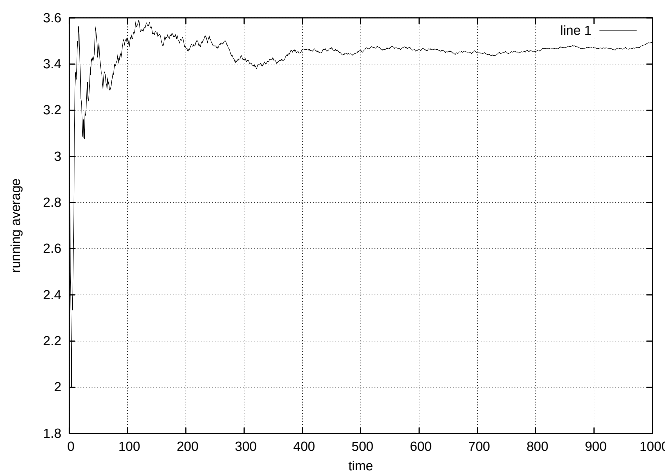


Figure 3.1: Running average of dice roll outcomes versus time

An ensemble may be specified by the number of systems

$$P(\mathbf{p},\mathbf{q})d\mathbf{p}d\mathbf{q} \tag{3.1}$$

in the volume element $d\mathbf{p}d\mathbf{q}$ of phase space, where for N particles

$$d\mathbf{p} = dp_1 dp_2 ... dp_{3N}$$

$$d\mathbf{q} = dq_1 dq_2 ... dq_{3N} \tag{3.2}$$

The ensemble average is defined as:

$$\langle A \rangle = \frac{\int A(\mathbf{p}, \mathbf{q}) P(\mathbf{p}, \mathbf{q}) d\mathbf{p} d\mathbf{q}}{\int P(\mathbf{p}, \mathbf{q}) d\mathbf{p} d\mathbf{q}} \tag{3.3}$$

The validity of this expression rests on the composition of the ensemble being constant, and therefore satisfies the equation of continuity ie.,

$$\frac{\partial P}{\partial t} + \text{div } (P\mathbf{v}) = 0 \tag{3.4}$$

which states that the time rate of change of P is balanced by flow into and out of the volume element of phase space. Using Hamilton's equations of motion, one can produce Liouville's theorem:

$$\frac{\partial P}{\partial t} + \sum_i \left[\frac{\partial P}{\partial q_i} \dot{q}_i + \frac{\partial P}{\partial p_i} \dot{p}_i \right] \equiv \frac{dP}{dt} = 0 \tag{3.5}$$

which states that the time rate of change of P along a flowline is zero.
Exercise: Show this
An ensemble for which:

$$P(E) = \begin{cases} \text{Constant (for energy in } \delta E \text{ at } E_0) \\ = 0 \text{ Otherwise} \end{cases} \tag{3.6}$$

is referred to as a microcanonical ensemble. To introduce the concept of temperature, it is necessary to first define entropy, which in a classical sense is:

$$\sigma = \log \Delta\Gamma \tag{3.7}$$

where $\Delta\Gamma$ is the volume of phase space accessible to the system, with dimension for N particles (momentum$\times$length)^{3N}=action^{3N}. This volume is interpreted as a measure of the lack of definitive knowledge of the system. The additive property of entropy follows easily, in the case where phase space consists of the products of individual subsystems.There are two fundamental assumptions made in conjunction with phase space and entropy:

1. The equilibrium condition of a system is given by the most probable condition
2. The entropy of a closed system has its maximum when the system is in the equilibrium condition.

Using these assumptions one can produce conditions for equilibrium, based on consideration of the two unit system, figure 2. A barrier which is initially fixed is removed; the approach to equilibrium involves exchange of internal energy U (thermal equilibrium), external variables x such as volume (mechanical equilibrium) and particles N_i (particle or chemical equilibrium). The system entropy or 'state function' is consequently a function of these variables. Restricting attention to the first case

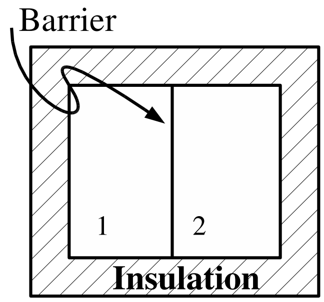


Figure 3.2: Two subsystems with different properties separated by a barrier

is sufficient to introduce the concept of temperature, eg., by the additive property of entropy, the differential change in the total at equilibrium is zero:

$$\delta\sigma = \left(\frac{\partial\sigma_1}{\partial U_1}\right)\delta U_1 + \left(\frac{\partial\sigma_2}{\partial U_2}\right)\delta U_2 = 0 \tag{3.8}$$

For a microcanonical ensemble, the total differential for energy is the sum of the parts and is equal to zero, ie.,

$$\delta U = \delta U_1 + \delta U_2 = 0 \tag{3.9}$$

thus

$$\delta\sigma = \left[\left(\frac{\partial\sigma_1}{\partial U_1}\right) - \left(\frac{\partial\sigma_2}{\partial U_2}\right)\right]\delta U_1 = 0 \tag{3.10}$$

and since δU_1 is arbitrary:

$$\frac{\partial\sigma_1}{\partial U_1} = \frac{\partial\sigma_2}{\partial U_2} \tag{3.11}$$

Then temperature τ is defined as,

$$\frac{1}{\tau} = \frac{\partial\sigma}{\partial U} \tag{3.12}$$

ie., the equilibrium condition in terms of temperature:

$$\tau_1 = \tau_2 \tag{3.13}$$

This is directly proportional to absolute temperature, $\tau = kT$, where the constant of proportionality is Boltzmann's constant $k = 1.38 \times 10^{-23} JK^{-1}$ An important quality of τ is revealed by considering the approach to equilibrium where initially $\tau_2 > \tau_1$, in which case

$$\delta\sigma > 0 \tag{3.14}$$

because the accessible region of phase space increases. One may determine that this implies $\delta U_1 > 0$ ie., energy passes from the system of high τ to the system of low τ. *Exercise:* Show this.

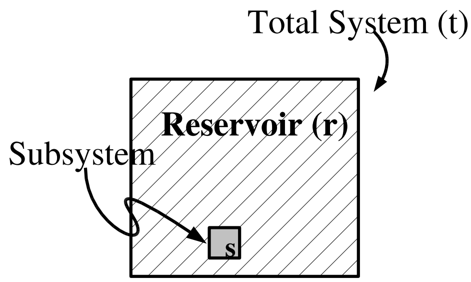


Figure 3.3: A system containing subsystem s and reservoir r, the latter which may/may not be comprised of other subsystems

The microcanonical ensemble is an impractical tool inasmuch as the volume of phase space (or for quantum systems the number of states accessible) is difficult to evaluate. While a microcanonical ensemble describes perfectly insulated systems, a canonical ensemble represents systems in thermal contact with a reservoir. More precisely, a system t is composed of subsystems, each which may exchange energy. From the perspective of one subsystem s, the remainder comprise a heat reservoir r.

By analogy with geometric probability, the probability that the total system is in an element $d\Gamma_t$ of phase space is:

$$dw_t = C d\Gamma_t \tag{3.15}$$

The total volume $d\Gamma_t$ may be considered as the product of the volumes for the subsystem and reservoir, ie.,

$$d\Gamma_t = d\Gamma_s d\Gamma_r \tag{3.16}$$

At this stage, the notion of the canonical ensemble is introduced by asking the probability dw_s that the subsystem is in $d\Gamma_s$, without knowledge of the condition of the reservoir. As before we express this indeterminacy using Δ:

$$dw_s = C d\Gamma_s \Delta\Gamma_r \tag{3.17}$$

The entropy of the reservoir is:

$$\sigma_r = \log \Delta\Gamma_r \text{ ie., } \Delta\Gamma_r = e^{\sigma_r} \tag{3.18}$$

Now the (total) system energy is equal to the sum of the parts $E_t = E_s + E_r$, but we assume that $E_t >> E_s$, hence when using a Taylor expansion for $\sigma_r(E_r)$, one finds:

$$\Delta\Gamma_r = \exp\{\sigma_r(E_t)\} \exp\left\{ -\frac{\partial \sigma_r(E_t)}{\partial E_t} E_s \right\} \tag{3.19}$$

or in other words, using the relation from earlier for temperature,

$$dw_s = A e^{-E_s/\tau} d\Gamma_s \text{ with } A = C e^{\sigma_r(E_t)} \tag{3.20}$$

or expressed another way, the probability density for the subsystem is given by the canonical ensemble:

$$\rho(E) = Ae^{-E/\tau} \tag{3.21}$$

From the nature of the probability density it is convention to define the classical:

$$Z \equiv \int e^{-E/t} d\Gamma \tag{3.22}$$

and quantum:

$$Z \equiv \sum_i e^{-E_i/\tau} \tag{3.23}$$

partition functions. To conclude we connect the canonical ensemble with thermodynamic functions, for instance the Helmholtz free energy in terms of the partition function:

$$F = -\tau \log Z \tag{3.24}$$

From which one may derive (for instance) the classical internal energy, eg.,

$$U = -\tau^2 \frac{\partial}{\partial \tau} \left(\frac{F}{\tau} \right)_V = \tau^2 \frac{\partial}{\partial \tau} \log Z = \frac{\int E e^{-E/\tau} d\Gamma}{\int e^{-E/\tau} d\Gamma} = \langle E \rangle \tag{3.25}$$

Exercise: For the classical 1D SHO, show that the average energy $\langle E \rangle$ is equal to $\tau/2$ using $\Gamma(3/2) = \sqrt{\pi}/2$ and $\Gamma(1/2) = \sqrt{\pi}$, where $\Gamma(x) = \int_0^\infty t^{x-1} e^{-t} dt$.

3.1 Monte Carlo

When studying systems with many degrees of freedom, the number of possible configurations quickly becomes intractable. We have seen that the Boltzmann factor $e^{-E/\tau}$ gives a measure of the probability for a system to be in a particular state. The Metropolis algorithm is based on this idea. More precisely, that as a system passes between two configurations in the approach to equilibrium (the minimum energy state), the relative probability

$$\frac{P(A)}{P(B)} = \frac{e^{-E_A/\tau}}{e^{-E_B \tau}} = e^{-(E_A - E_B)/\tau} \tag{3.26}$$

provides a pure number to be used in a numerical procedure:

1. Starting from an initial configuration A with energy E_A, change the configuration to$B$.

2. Compute E_B

3. If $E_B < E_A$ accept the move since it has a lower energy

4. If $E_A > E_B$ accept the new higher energy configuration with probability $e^{-(E_A - E_B)/\tau}$

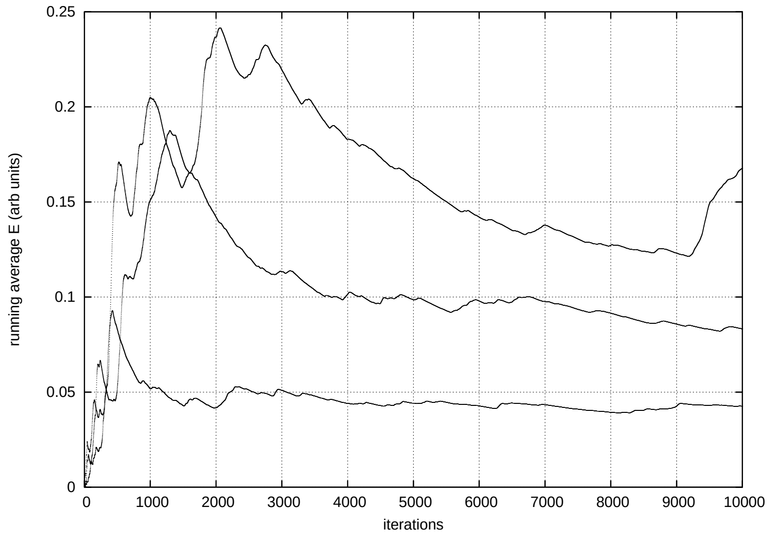


Figure 3.4: MC iterations (running average energy vs iterations) for the 1D SHO; (from low) $\tau = 0.1, 0.2, 0.4$

This last step is in keeping with thermal annealing where occasionally nature takes uphill climbs in approaching equilibrium. The following is Octave code for determining the average energy of a 1D SHO using MC. Note that as temperature increases (figure 4), the convergence worsens. This problem is dealt with using variance reduction techniques and/or quasi random number sequences.

```
   function [out]=mc_test(it, t);

%mc example; inputs iterations it, temp t
%outputs average energy with it's std dev for 1d sho
%WJB 04/26/06



   %displacement mag in one step
dxm=0.1;



   %statistics
f1=0;
f2=0;

%initial vals of displacement (x0) and energy (f0)
x0=0;
f0=x0*x0;

%top loop, cycles
for i=1:it
```

```
%update position and energy

xn=x0+(rand-0.5)*dxm;
fn=xn*xn;

w=fn-f0;

   %MC decision; accept move IF
%a) move has reduced energy OR
%b) boltzmann factor exceeds probability

if (w<0)||(exp(-w/t)>rand)

   x0=xn;
f0=fn;

   end


   %update statistics
f1=f1+f0;
f2=f2+f0*f0;

%store running statistics out(i,:)=[f1/i, sqrt((f2/i-(f1/i)^2)/i)];

end
%done
```

Chapter 4

The Density Operator

We return to the single spin system whose quantum state is described by ψ;

$$|\psi\rangle = \sum_n c_n |n\rangle.$$

For a particular spin I there exist $2I+1$ states $|I,-m\rangle, |I,-m+1\rangle, ..., |I,m-1\rangle, |I,m\rangle$ which span a $2I+1$ dimensional Hilbert space. They provide a convenient basis set since the Zeeman energy levels for a nuclei embedded in a magnetic field directly correspond to these eigenstates. The label m is the quantum number of the spin projection in the z-direction.

Physical observables correspond to the expectation value of some quantum mechanical operator, e.g., the x-component of the magnetization;

$$\langle M_x \rangle = \langle \psi | M_x | \psi \rangle = \sum_{n,m} c_m^* c_n \langle m | M_x | n \rangle \tag{4.1}$$

The sum over two quantum numbers constitutes a matrix equation and accordingly the terms $c_m^* c_n$ represent elements of the *quantum density operator*, defined as

$$\rho = |\psi\rangle\langle\psi| = \sum_{n,m} c_m^* c_n |n\rangle\langle m| \tag{4.2}$$

More generally we are concerned with a large number of spins, an ensemble of say N spins. We distinguish between *pure* and *mixed states*. An pure state is distinguished by having all spins in the same state $|\psi(t)\rangle$ and the density operator is defined as;

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)| = \sum_{i,j} \rho_{ij}(t) |i\rangle\langle j|$$

$$\rho_{ij}(t) = c_i(t) c_j^*(t) = \langle i | \rho(t) | j \rangle. \tag{4.3}$$

A mixed state contains various $|\psi_k(t)\rangle$ with weights $p_k, \sum_k p_k = 1$. The density operator is an average over all possible states;

$$\rho(t) = \sum_k^N p_k |\psi_k(t)\rangle\langle\psi_k(t)| = \sum_{i,j} \rho_{ij}(t) |i\rangle\langle j|,$$

$$\rho_{ij}(t) = \sum_k^N p_k c_{i(k)}(t) c_{j(k)}^*(t) = \langle i | \rho(t) | j \rangle. \tag{4.4}$$

To illustrate these ideas, consider an isolated spin 1/2 system, with basis functions:

$$|\alpha\rangle = |1/2, 1/2\rangle$$

$$|\beta\rangle = |1/2, -1/2\rangle$$

The system state is therefore:

$$|\psi\rangle = c_\alpha|\alpha\rangle + c_\beta|\beta\rangle$$

and hence the density operator:

$$\rho = \begin{pmatrix} c_\alpha c_\alpha^* & c_\alpha c_\beta^* \\ c_\beta c_\alpha^* & c_\beta c_\beta^* \end{pmatrix}, \tag{4.5}$$

where it is understood that the elements represent an average over the ensemble. A difference between the populations or diagonal elements, corresponds to a net longitudinal magnetization. The presence of coherences indicates transverse spin magnetization, a net spin perpendicular to the magnetic field. The coherences being complex have both magnitude and phase; the phase of the (-1) coherence is equal to the angle of the transverse magnetization with the x-axis. The off-diagonal elements $(i \neq j)$ correspond to states which are in a *coherent* superposition of basis states $|i\rangle$ and $|j\rangle$; for this condition to persist throughout the ensemble, the phase differences between different members must be constant. The order of coherence is defined by the difference between the z-angular momentum numbers for the basis states, $\Delta m_{ij} = m_i - m_j$. There is a strong distinction between a *single* $(\Delta m_{ij} = \pm 1)$ and *multiple quantum coherence* $(\Delta m_{ij} =\neq \pm 1)$. Due to the quantum mechanical selection rule for electromagnetic radiation, the single coherence elements represent dipole transitions (not to be confused with the dipole interaction between nuclear spins), which may be observed directly in experiment. Multiple quantum coherences involve higher order multipole transitions and can only be observed indirectly in magnetic resonance.

4.0.1 Time Evolution of the density operator

Quantum mechanics gives an expression for the density operator:

$$i\frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho] \tag{4.6}$$

In most realistic cases, the solution of the equation of motion is quite difficult. However for equilibrium, statistical mechanics gives for the density operator:

$$\rho_{eq} = \frac{\exp(-\hbar\hat{\mathcal{H}}_0/kT)}{\sum_k \langle k|\exp(\hbar\mathcal{H}_0/kT)|k\rangle} \tag{4.7}$$

where $\hat{\mathcal{H}}$ is the time independent portion of the Hamiltonian which can be used to derive the classical expression(s) for magnetization derived earlier.

In general spins are not isolated and interact, most importantly with their environment to take up or expel energy, change state and move toward equilibrium.

In NMR one usually deals with a reduced spin density operator σ, where all other degrees of freedom are relegated to a vestige ρ_R [**?**]. The total density operator is the product of both, but for the determination of spin properties we consider σ alone; the remaining degrees of freedom comprise the 'lattice'. It is the interactions with the lattice that allow the spin system to return to equilibrium. This process in NMR is called 'spin-lattice' relaxation and occurs with characteristic time T_1. Interactions between spins give rise to 'spin-spin' relaxation, with characteristic time T_2. This effect in NMR is attributed largely to the dipolar interaction, and in the solid state chemical shift and quadrupolar anisotropy provide addtional broadening. If we ignore the effects of the lattice which for small time scales is acceptable, we may write for the evolution of the density operator:

$$i\frac{d}{dt}(\sigma - \sigma_{eq}) = [\mathcal{H}, (\sigma - \sigma_{eq})] \tag{4.8}$$

Direct integration applying time ordering (T) gives the *Dyson* series, familiar from the interaction picture of quantum mechanics and time dependent perturbation theory [**?**];

$$\begin{aligned} \sigma(t) = \sigma(0) - iT\int_0^t [\mathcal{H}(t'), \sigma(0) - \sigma_{eq}]dt' \\ +(-i)^2 T\int_0^t dt' \int_0^{t'} dt''[\mathcal{H}(t), [\mathcal{H}(t''), \sigma(0) - \sigma_{eq}]] + ... \\ +(-i)^n T\int_0^t dt' \int_0^{t'} dt''... \int_0^{t(n-1)} dt(n) \\ \times[\mathcal{H}(t'), [\mathcal{H}(t''), [..., [\mathcal{H}(t^{(n)}), \sigma(0) - \sigma_{eq}...]]]] + ... \end{aligned} \tag{4.9}$$

One assumes that the time dependent Hamiltonian may be approximated by an average Hamiltonian $\bar{\mathcal{H}}(t_1, t_2)$, within a specific time interval $t_1 < t < t_2$. It may be derived through either diagonalization of the time evolution operator or Baker-Campbell-Hausdorff (or Magnus) expansion. We take $\mathcal{H}(t)$ to be piecewise constant in successive small time intervals;

$$\mathcal{H}(t) = \mathcal{H}_k \text{ for } (\tau_1 + \tau_2 + ... + \tau_{k-1}) < t < (\tau_1 + \tau_2 + ... + \tau_k) \tag{4.10}$$

The time dependence of the density operator,

$$\dot{\sigma} = -i[\mathcal{H}(t), \sigma] \tag{4.11}$$

may be integrated to give:

$$\sigma(t_c) = U(t_c)\sigma(0)U(t_c)^{-1} \tag{4.12}$$

where

$$\begin{aligned} U(t_c) = \exp(-i\mathcal{H}_n\tau_n)... \exp(-i\mathcal{H}_1\tau_1) \\ t_c = \sum_{k=1}^{n} \tau_k \end{aligned} \tag{4.13}$$

Continuing the process over successive intervals and remembering that the product of the unitary transformations, is itself a unitary transformation, one obtains:

$$U(t_c) = \exp\{-i\bar{\mathcal{H}}(t_c)t_c\} \tag{4.14}$$

The Baker-Campbell-Hausdorff relation

$$e^B e^A = \exp\{A + B + \frac{1}{2}[B, A] + \frac{1}{2}([B, [B, A]] + [[B, A,]A]) + ...\} \tag{4.15}$$

may be used for two sequential time intervals τ_1, τ_2 to give:

$$\begin{aligned}\bar{\mathcal{H}}(t_c) = \frac{i}{t_c}\{-i(\mathcal{H}_1\tau_1 + \mathcal{H}_2\tau_2) - \frac{1}{2}[\mathcal{H}_2\tau_2, \mathcal{H}_1\tau_1] \\ \frac{1}{12}(i[\mathcal{H}_2\tau_2, [\mathcal{H}_2\tau_2, \mathcal{H}_1\tau_1]] \\ +i[[\mathcal{H}_2\tau_2, \mathcal{H}_1\tau_1], \mathcal{H}_1\tau_1]) \\ +...\}\end{aligned} \tag{4.16}$$

The average Hamiltonian can be decomposed into different terms:

$$\bar{\mathcal{H}}(t_c) = H^0 + H^1 + H^2 + ... \tag{4.17}$$

For an interval composed of discrete time periods;

$$\begin{aligned}H^0 &= \frac{1}{t_c}\{_1\tau_1 + \mathcal{H}_2\tau_2 + ... + \mathcal{H}_n\tau_n\} \\ H^1 &= -\frac{i}{2t_c}\{[\mathcal{H}_2\tau_2, \mathcal{H}_1\tau_1] + [\mathcal{H}_3\tau_3, \mathcal{H}_1\tau_1] + [\mathcal{H}_3\tau_3, \mathcal{H}_2\tau_2] + ...\}, \\ H^2 &= -\frac{1}{6t_c}\{[\mathcal{H}_3\tau_3, [\mathcal{H}_2\tau_2, \mathcal{H}_1\tau_1]] + [[\mathcal{H}_3\tau_3, \mathcal{H}_3\tau_3, \mathcal{H}_2\tau_2], \mathcal{H}_1\tau_1] \\ &\frac{1}{2}[\mathcal{H}_2\tau_2, [\mathcal{H}_2\tau_2, \mathcal{H}_1\tau_1]] + \frac{1}{2}[[\mathcal{H}_2\tau_2, \mathcal{H}_2\tau_2, \mathcal{H}_1\tau_1], \mathcal{H}_1\tau_1] + ...\}\end{aligned} \tag{4.18}$$

In the infinitesimal limit as $\tau_k \to 0$ and allowing $\mathcal{H}$ to vary continuously, then we find:

$$U(t_c) = T\exp\left\{-i\int_0^{t_c} \mathcal{H}(\tau)d\tau\right\} = \exp(-i\bar{\mathcal{H}}t_c) \tag{4.19}$$

where T is the Dyson time ordering operator. Equating, one finds:

$$\begin{aligned}H^0 &= \frac{1}{t_c}\int_0^{t_c} \mathcal{H}(t_1)dt_1, \\ H^1 &= -\frac{i}{2t_c}\int_0^{t_c} dt_2 \int_0^{t_2} dt_1[\mathcal{H}(t_2), \mathcal{H}(t_1)], \\ H^2 &= -\frac{1}{6t_c}\int_0^{t_c} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1\{[\mathcal{H}(t_3), [\mathcal{H}(t_2), \mathcal{H}(t_1)]] \\ &+[[\mathcal{H}(t_3), \mathcal{H}(t_2)], \mathcal{H}(t_1)]\},\end{aligned} \tag{4.20}$$

the Magnus expansion.

Chapter 5

Greens Functions

Define the Green's function G corresponding to a point of discontinuity Q with coordinates α, β, δ in three dimensions as:

- a solution to Laplace's equation $\Delta G = 0$
- vanishing on a surface $S, G_S = 0$, and
- singular at Q eg., $G = \frac{1}{4\pi r_{pq}} + \omega$,

where ω is a harmonic function in the whole domain. The function G may be interpreted as a the steady state temperature due to a dirac delta function heat source, while the surface S is maintained at zero temperature. Alternatively, one may think of G as being due to a unit source of charge while the surface is conducting (and thus at zero potential). The harmonic function ω is that induced on the surface by the presence of the unit charge.

Consider two such greens functions with different singularities, eg.,

$$G = G_{pq} = \frac{1}{4\pi r_{pq}} + \omega; G' = G_{pq'} = \frac{1}{4\pi r_{pq'}} + \omega' \tag{5.1}$$

We apply Green's theorem:

$$\int\int\int (U\Delta V - V\Delta U) d\tau = \int\int (V\frac{\partial U}{\partial n} - U\frac{\partial V}{\partial n}) dS \tag{5.2}$$

while excluding the discontinuities to infinitessimal regions of integration, one finds:

$$\int\int (G\frac{\partial G'}{\partial n} - G'\frac{\partial G}{\partial n}) dS = 0 \tag{5.3}$$

On the surface G and G' vanish, therefore only the integrals over the infinitessimal spheres remain. Considering first the integral at point Q,

$$\int\int \frac{\partial G'}{\partial n} dS = 0 \tag{5.4}$$

since G' is harmonic inside. The function G behaves as $\frac{1}{4\pi r}$ thus

$$-\int\int \frac{\partial G}{\partial n} dS = 1 \tag{5.5}$$

and therefore in the limit:

$$G'(q) = G_{qq'} \tag{5.6}$$

On the sphere about Q'

$$\int\int \frac{\partial G}{\partial n} dS = 0 \tag{5.7}$$

while

$$\int\int \frac{\partial G'}{\partial n} dS = -1 \tag{5.8}$$

so that the limit is $-G(q') = -G_{q'q}$ and

$$G_{qq'} = G_{q'q} \tag{5.9}$$

Applying Greens theorem to Poisson's equation,

$$\Delta V = -f(x,y,z) \tag{5.10}$$

one finds:

$$\int\int\int (G\Delta V - V\Delta G) d\tau = -\int\int\int G f d\tau = \int\int \left(V\frac{\partial G}{\partial n} - G\frac{\partial V}{\partial n} \right) dS \tag{5.11}$$

Let G have the pole P, and allow the surface integral to be extended to the small sphere about P. Hence ($G_s = 0$)

$$-V_p + \int\int V\frac{\partial G}{\partial n} dS = -\int\int\int G\tau d\tau \tag{5.12}$$

Consider the case $f = 0$. Then V is harmonic inside S, and one finds

$$V_P = \int\int V\frac{\partial G}{\partial n} dS \tag{5.13}$$

5.1 Time dependence

Consider:

$$H\psi + \frac{\partial \psi}{\partial \tau} \tag{5.14}$$

Assume that H has a complete orthonormal set of eigenfunctions,

$$H\phi_m = \lambda_m \phi_m \tag{5.15}$$

and therefore

$$\psi(\mathbf{r}, \tau) = \sum_m A_m(\tau)\phi_m(\mathbf{r}) \tag{5.16}$$

Since $\psi(\mathbf{r})$ depends on τ, so will the coefficients A_m. Now

$$H\psi = H\left\{\sum_m A_m(\tau)\phi_m(\mathbf{r})\right\} = \sum_m A_m(\tau) H\phi_m(r) = \sum_m \lambda_m A_m(\tau)\phi_m(\mathbf{r}) \tag{5.17}$$

and

$$\frac{\partial \psi}{\partial \tau} = \sum_m \frac{\partial A_m}{\partial \tau} \phi_m(\mathbf{r}) = 0 \tag{5.18}$$

using completeness, one finds

$$A_m(\tau) = A_m(0) e^{-\lambda_m \tau} \tag{5.19}$$

therefore

$$\psi(\mathbf{r}, \tau) = \sum_m A_m(0) \phi_m(\mathbf{r}) e^{-\lambda_m \tau} \tag{5.20}$$

Boundary conditions:

$$\psi(\mathbf{r}, 0) = \sum_m A_m(0) \phi_m(\mathbf{r}) \tag{5.21}$$

completeness

$$A_n(0) = \int \phi_n^*(\mathbf{r}) \psi(\mathbf{r}, 0) d^3\mathbf{r} \tag{5.22}$$

thus

$$\psi(\mathbf{r}, \tau) = \sum_m e^{-\lambda_m \tau} \phi_m(\mathbf{r}) \int \phi_m^*(\mathbf{r}) \psi(\mathbf{r}', 0) d^3\mathbf{r}' \tag{5.23}$$

or

$$\psi(\mathbf{r}, \tau) = \int G_1(\mathbf{r}, \mathbf{r}', \tau) \psi(\mathbf{r}', 0) d^3\mathbf{r}' \tag{5.24}$$

where

$$G_1(\mathbf{r}, \mathbf{r}', \tau) = \sum_m \phi_m(\mathbf{r} \phi_m^*(\mathbf{r}) e^{-\lambda_m \tau} \tag{5.25}$$

note that

$$G_1(\mathbf{r}, \mathbf{r}', \tau) = sum_m \phi_m(\mathbf{r}) \phi_m^*(\mathbf{r}') = \delta^3(\mathbf{r}, \mathbf{r}') \tag{5.26}$$

and

$$\left(H + \frac{\partial}{\partial \tau} \right) G_1(\mathbf{r}, \mathbf{r}', \tau) = 0 \tag{5.27}$$

Therefore, G_1 is not strictly a Green's function but is in fact a solution to the equation. Note that the choice of time τ is arbitrary; one could put

$$\psi(\mathbf{r}, \tau) = \int G_1(\mathbf{r}, \mathbf{r}', \tau, \tau') \psi(\mathbf{r}', \tau') d^3\mathbf{r}' \tag{5.28}$$

where

$$G_1(\mathbf{r}, \mathbf{r}', \tau, tau') = \sum_m \phi_m(\mathbf{r}) \phi_m^*(\mathbf{r}') e^{-\lambda_m(\tau - \tau')} \tag{5.29}$$

The function G_1 propagates the function ψ in time from τ' to $\tau > \tau'$. In general one seeks a solution to the inhomogeneous equation:

$$H\psi + \frac{\partial \psi}{\partial \tau} = F(\mathbf{r}, \tau) \tag{5.30}$$

and we seek the Greens function to facilitate solution;

$$\psi(\mathbf{r}, t) = \psi_0(\mathbf{r}, \tau) + \int G(\mathbf{r}, \mathbf{r}', \tau, \tau') F(\mathbf{r}', \tau') d^3\mathbf{r}' \tau' \tag{5.31}$$

$\psi_0(\mathbf{r}, \tau)$ is the solution to the homogeneous equation. Put

$$G(\mathbf{r}, \mathbf{r}', \tau, \tau') = G_1(\mathbf{r}, \mathbf{r}', \tau, \tau')\theta(\tau - \tau') \tag{5.32}$$

where θ is the step function:

$$\theta(\tau - \tau') = \begin{cases} 1 & \tau > \tau' \\ 0 & \tau < \tau' \end{cases} \tag{5.33}$$

$$\left(H + \frac{\partial}{\partial \tau}\right) G(\mathbf{r}, \mathbf{r}', \tau, \tau') = \theta(\tau-\tau')HG_1(\mathbf{r}, \mathbf{r}', \tau, \tau') + \theta(\tau-\tau')\frac{\partial}{\partial \tau} g_1)\mathbf{r}, \mathbf{r}', \tau, \tau') + G_1(\mathbf{r}, \mathbf{r}', \tau, \tau')\frac{\partial}{\partial \tau} \tag{5.34}$$

but

$$\left(H + \frac{\partial}{\partial \tau}\right) G_1(\mathbf{r}, \mathbf{r}', \tau, \tau') = 0,$$

therefore

$$\left(H + \frac{\partial}{\partial \tau}\right) G(\mathbf{r}, \mathbf{r}', \tau, \tau') = \delta^3(\mathbf{r} - \mathbf{r}') \tag{5.35}$$

using

$$\lim_{\tau \to \tau'} G_1(\mathbf{r}, \mathbf{r}', \tau, \tau') = \delta^3(\mathbf{r} - \mathbf{r}')$$

And hence:

$$\psi(\mathbf{r}, \tau) = \psi_0(\mathbf{r}, \tau) + \int d^3\mathbf{r}' \int_{-\infty}^{\tau} d\tau' G_1(\mathbf{r}, \mathbf{r}', \tau, \tau') R(\mathbf{r}, \tau') \tag{5.36}$$

5.2 Scattering, three dimensions

Integral equations are useful in introducting boundary conditions. Consider the Green's function for the Helmholtz equation;

$$(\nabla^2 + k^2)G_k(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}, \mathbf{r}') \tag{5.37}$$

This implies that the full solution is given by:

$$\psi(\mathbf{r}) = \int G_k(\mathbf{r}, \mathbf{r}')U(r')\psi(\mathbf{r}')d^3r' \tag{5.38}$$

Including the solution ϕ to the homogeneous equation, one may also write the general solution:

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) + \int G_k(\mathbf{r}, \mathbf{r}')U(r')\psi(\mathbf{r}')d^3r' \tag{5.39}$$

where for the moment we leave the complex nature of k undecided. We assume that G is a function of $|\mathbf{r} - \mathbf{r}'|$ only and write:

$$G_k(\mathbf{r}, \mathbf{r}') = \int e^{iq\cdot(\mathbf{r}-\mathbf{r}')} g_k(\mathbf{q}) \frac{d^3q}{(2\pi)^3} \tag{5.40}$$

After substitution one finds:

$$(k^2 - q^2)g_k(\mathbf{q}) \tag{5.41}$$

Chapter 6

Neural Networks

Seek to emulate biological memory and computation processes; deal with three things:

1. Architecture; network variables and their relationships
2. Activity rule; a function of weights
3. Learning rule; how weights change with time, longer time scale than activity, depends upon target values set by teacher

Rules may be specified explicitly or else derived from objective functions. A supervised net learns from teacher/target values. Unsupervised nets are given data and may perform memory functions or search for patterns.

A single neuron has a number of inputs x_i and weights w_i and one output y. In addition there may be a weight w_0; the overall device is *feedforward*.

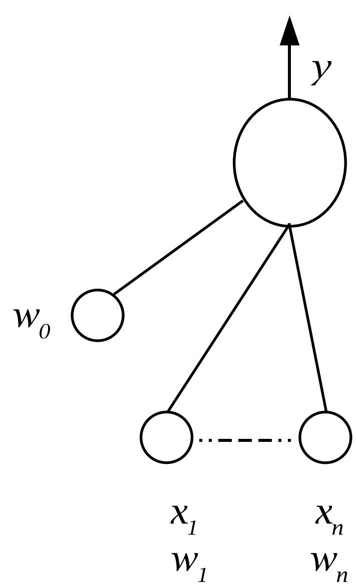


Figure 6.1: Single neuron

The activation is defined as:

$$a = \sum_i w_i x_i \tag{6.1}$$

and the output y is the function $f(a)$ of this activation. There are several popular choices:

1. $y(a) = a$
2. $y(a) = \frac{1}{1+e^{-a}}; y \in (0, 1)$
3. $y(a) = \tanh(a); y \in (0, 1)$
4. stochastic activation:

$$y(a) = \begin{cases} 1 \text{ with prob. } \frac{1}{1+e^{-1}} \\ \text{otherwise } -1 \end{cases} \tag{6.2}$$

6.0.1 dimension reduction for pixels

One begins by considering the binarized pixels as matrix data A. The operation $A^T A$ corresponds to a square matrix (the Grammian) whose eigenvalues may be used for measures in training a supervised network, a traditional choice in pattern recognition. The spectrum may be further expanded by using the QR decomposition B of the data matrix A. The trace of the Grammian provides normalization and finally the metrics used in OCR corresponded to the sixteen largest (sorted) values from the set S:

$$\{S\} = \frac{\text{eig}(B^T B)}{\text{tr}(B^T B)} \tag{6.3}$$

The normalized metrics derived in this manner are sufficient to create fairly well resolved decision regions, figure 4. This reduction in dimensionality [?] boasts little overhead.

The metrics are also independent of the absolute position of the intelligence in the data window being examined. Orthogonal characters may be treated identically without further processing since for any matrix A:

$$(A^T A)^T = AA^T = A^T A. \tag{6.4}$$

Finally, eigenvalues are fairly robust measures under distortions such as rotations. q

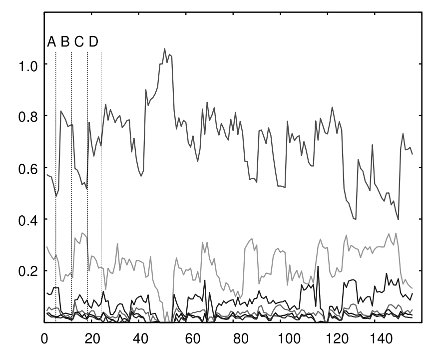


Figure 6.2: Largest six metrics for OCR displayed for Arial capital letters and various font sizes with the regions for A-D marked

Chapter 7

Pade Summation

The first few coefficients in the continued fraction expansion of Pade:

$$
\begin{aligned}
c_0 = &\ a_0 \\
c_1 = &\ -\tfrac{a_1}{c_0} \\
c_2 = &\ \tfrac{a_2}{c_0 c_1} - c_1 \\
c_3 = &\ -\tfrac{(c_1+c_2)^2}{c_2} - \tfrac{a_3}{c_0 c_1 c_2} \\
c_4 = &\ -2c_1 - 2c_2 - c_3 - \tfrac{(c_1+c_2)^3}{c_2 c_3} + \tfrac{a_4}{c_0 c_1 c_2 c_3} \\
c_5 = &\ -c_1 - c_2 - c_3 - c_4 - \tfrac{1}{c_4}\left[\tfrac{a_4}{c_0 c_1 c_2} - c_3 c_1 - \tfrac{c_1}{c_2}(c_1+c_2)^2 - \tfrac{a_4}{c_0 c_1 c_3} + \tfrac{a_4}{c_0 c_2 c_3} + \tfrac{a_5}{c_0 c_1 c_2 c_4}\right]
\end{aligned}
\tag{7.1}
$$

Chapter 8

FDM

Consider the Laplace equation:

$$\frac{\partial^2 u(x,y)}{\partial x^2} + \frac{\partial^2 u(x,y)}{\partial y^2} = u_{xx}(x,y) + u_{yy}(x,y) = 0 \tag{8.1}$$

One begins by seeking an approximation to u over the domain of interest, eg., the unit square. Presumably also on this square, there is a dirichlet boundary condition of the form:

$$u(x,y) = g(x,y) \tag{8.2}$$

We divide the interior by imposing a grid over the domain, where at each vertice we seek a numerical approximation to u. One such method of appoximation is the Taylor series in two variables:

$$u(x_0 \pm h, y_0) = u(x_0,y_0) \pm h u_x(x_0,y_0) + \frac{h^2}{2} u_{xx}(x_0,y_0) \pm \frac{h^3}{3!} u_{xxx}(x_0,y_0) + \frac{h^4}{4!} u_{xxxx}(x_0,y_0) \pm \ldots \tag{8.3}$$

$$u(x_0, y_0 \pm h) = u(x_0,y_0) \pm h u_y(x_0,y_0) + \frac{h^2}{2} u_{yy}(x_0,y_0) \pm \frac{h^3}{3!} u_{yyy}(x_0,y_0) + \frac{h^4}{4!} u_{yyyy}(x_0,y_0) \pm \ldots \tag{8.4}$$

The point (x_0, y_0) and it's four neighbors $(x_0 \pm h, y_0), (x_0, y \pm h)$ are within the unit square; rearranging and using the Laplace equation, one finds that to first order:

$$u(x_0,y_0) \approx \frac{1}{4}\{u(x_0+h,y_0) + u(x_0-h,y_0) + u(x_0,y_0+h) + u(x_0,y_0-h)\} \tag{8.5}$$

Referring to figure 1, if we refer to the approximations for $u_i; 1 \le i \le 4$ as w_i:

$$w_1 \approx u(1/3,2/3), w_2 \approx u(2/3,1/3), w_3 \approx u(2/3,2/3), w_4 \approx u(1/3,1/3) \tag{8.6}$$

then we may rewrite eq as a set of linear equations:

$$\begin{aligned} w_1 &= 1/4(w_3 + w_4 + g_1 + g_1 1) \\ w_2 &= 1/4(w_3 + w_4 + g_5 + g_7) \\ w_3 &= 1/4(w_1 + w_2 + g_2 + g_4) \\ w_4 &= 1/4(w_1 + w_2 + g_8 + g_1 0) \end{aligned} \tag{8.7}$$

where g_9 is the value of the BC at the origin. In matrix notation:

$$A\mathbf{w}\mathbf{k} \tag{8.8}$$

$$A = \begin{bmatrix} 1 & 0 & -1/4 & -1/4 \\ 0 & 1 & -1/4 & -1/4 \\ -1/4 & -1/4 & 1 & 0 \\ -1/4 & -1/4 & 0 & 1 \end{bmatrix}, \mathbf{w} = \begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \end{bmatrix}, \text{ and } \mathbf{k} = \frac{1}{4}\begin{bmatrix} g_1 + g_{11} \\ g_5 + g_7 \\ g_2 + g + 4 \\ g_8 + g_{10} \end{bmatrix} \tag{8.9}$$

We can rewrite the matrix A as $I - B$ where:

$$B = 1/4\begin{bmatrix} 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{bmatrix} \tag{8.10}$$

One may show that the matrix A has real, positive eigenvalues and especially where the equation is derived from self-adjoint, second order elliptic PDE's the inverse of A exists. Thus one is led to the consider the conditions on the convergence of matrix equation:

$$\mathbf{w}^{(m+1)} = B\mathbf{w}^{(m)} + \mathbf{k} \tag{8.11}$$

If one defines the error vector ϵ as the difference between the desired vector $\mathbf{w}$ and mth iterate as:

$$\epsilon^{(\mathbf{m})} = \mathbf{w}^{(m)} - \mathbf{w} \tag{8.12}$$

the via substitution into the earlier equation one may show that:

$$\epsilon^{(m)} = B^m \epsilon^{(0)} \tag{8.13}$$

Further, in order for the error to approach zero as the number of iterations increase, this requires:

$$\lim_{m\to\infty} B^m = 0 \tag{8.14}$$

Chapter 9

Number Theory

Repeated squaring algorithm

To compute a^n modulo m:

1. Write n as binary: $n = a_k 2^k + \ + a_1 2 + a_0$
2. Compute $a(\mod m), a^2(\mod m), , a^{2k}(\mod m)$
3. Calculate the product of these results mod m

Fermats Little Theorem

If p is prime, then it divides all the binomial coefficients $\binom{p}{k}, 1 \leq k \leq p-1$.Thus

$$(a+b)^p \equiv a^p + b^p (\mod p) \tag{9.1}$$

for any integers a, b. Further, by induction:

$$(a_1 + \ + a_k)^p \equiv a_1^p + \ + a_k^p (\mod p) \tag{9.2}$$

Linear Recurrence Relations

A recurrence relation:

$$s_{k+n} + a_0 s_n + a_1 s_{n+1} + \ + a_{k-1} s_{k+n-1}, n \geq 1 \tag{9.3}$$

is equivalent to the matrix equation

$$\begin{pmatrix} 0 & 1 & 0 & & 0 \\ 0 & 0 & 1 & & 1 \\ \vdots & & & & \\ 0 & 0 & & 0 & 1 \\ a_0 & a_1 & & & a_{k-1} \end{pmatrix} \begin{pmatrix} s_n \\ s_{n+1} \\ \vdots \\ s_{n+k-1} \end{pmatrix} = \begin{pmatrix} s_{n+1} \\ s_{n+2} \\ \vdots \\ s_{n+k} \end{pmatrix} \tag{9.4}$$

Evariste Galois used finite fields in the early 1800's to show the conditions under which algebraic equations have solutions in radicals. A field is a set F that has two binary operations, $+$ and $\cdot$, satisfying the following properties. For all $a, b, c \in F$, one finds [**?**]:

1. $a + b = b + a$

Table 9.1: Various representations for $GF(16)$

α power	polynomial	4-tuple
$-\infty$	0	0000
0	1	1000
1	x	0100
2	x^2	0010
3	x^3	0001
4	$1+x$	1100
5	$x+x^2$	0110
6	x^2+x^3	0011
7	$1+x+x^3$	1101
8	$1+x^2$	1010
9	$x+x^3$	0101
10	$1+x+x^2$	1110
11	$x+x^2+x^3$	0111
12	$1+x+x^2+x^3$	1111
13	$1+x^2+x^3$	1011
14	$1+x^3$	1001

2. $a \cdot b = b \cdot a$
3. $(a+b)+c = a+(b+c)$
4. $(a \cdot b)c = a(b \cdot c)$
5. $(a+b) \cdot c = a \cdot c + b \cdot c$
6. There is an element $1 \in F$ such that $a \cdot 1 = a$
7. There is an element $0 \in F, 0 \neq 1$ such that $a + 0 = a$
8. If $a \neq 0$ then there is an element, denoted a^{-1}, such that $a \cdot a^{-1} = 1$

The finite field is often denoted $GF(p)$ or $GF(p^k)$ with k an integer and p is necessarily a prime number. The elements for $GF(p)$ find a convenient representation in the integers $0, 1..., p-1$ where operations are taken modulo p. $GF(p^k)$ with $p = 2$ are of great importance to error correcting codes and the preservation of digital information. Representations for $GF(p^k)$ must take on a different form to the scalars and one such representation is in the form of n-tuples. Another popular representation involves the $p^k - 1$ roots of unity,

$$\alpha, \alpha^2, \alpha^3, ..., \alpha^{p^k-1} \tag{9.5}$$

or polynomials over the field $GF(p)$ taken modulo an irreducible polynomial $\pi(x)$ of degree k. The various representations for $GF(2^4)$, using $\pi(x) = 1 + x + x^4$ are listed in table 2 [?].

Returning to the construction of the phase table over a finite field, $GF(2^4)$ will serve as a suitable example, or rather the integers (0,1,..14) corresponding to powers of α. The table length $2^4 - 1 = 15$ is composite and it is anticipated that there will be some degeneracy, owing to it's factorability. A conjecture has been established for suitable length (equation 9) and the desired CTP is expressed by the congruence equation 7. However the permutation of the integers to preserve the congruence for a small range of CTP's remains to be determined. Conversely, the choice of integers should produce phases for the various unwanted pathways which occur exactly once each, to preserve a total complex amplitude of zero. This statement is analogous to the ambiguity function problem of radar [**?**], and in that case the permutation of integers $z(n)$ to preserve this requirement is given by:

$$z(n+k) - z(n) \equiv z(n'+k) - z(n')(\text{mod } m) \tag{9.6}$$

where integers $n \not\equiv n'$ and $k \not\equiv 0$; here $m = 2^4 - 1 = 15$. These permutations are relatively easy to generate for $GF(p)$ and are given by the powers of the primitive roots of p. For the more general $GF(p^k)$, the Zech logarithm $z(n)$ defined by:

$$\alpha^{z(n)} = 1 + \alpha^n \tag{9.7}$$

where α is a primitive element of $GF(p^k)$, gives the required permutations. It may be shown that $rz(n)$ satisfies equation 11, where r is co-prime to $p^k - 1$ and therefore there exist $\phi(p^k - 1)$ such sequences. This immediately leads to another condition to be used in phase cycle design, in that p and k should be chosen according to:

$$\phi(p^k - 1) \geq l + 1 \tag{9.8}$$

Chapter 10

Optimization

In general data points overlap and the process of extracting coordinates becomes an optimization task, where one seeks individual identity, position and number of data points within a cluster of points. Simulated anneal is a suitable method for large optimization tasks, particularly where a problem may be posed in terms of combinatorics, eg., the traveling salesman problem. The method is analogous to the process in nature whereby a system on cooling anneals or reaches the minimum structural configuration by occasionally (as it cools) taking configurations which have higher energy than the previous step. Significant steps in this application include:

1. Image generation, composed of total number $p = M + N + ...$ of sub images, which is larger than anticipated. The identity of the image to be optimized is represented as:
$$A = \sum^{M} a_{ij}^{m} + \sum^{N} a_{ij}^{n} + ... \tag{10.1}$$
where a_{ij}^{m} etc represents both the sub image identity and offset i, j within the total image.

2. Indices i, j etc are randomly stepped and the cost E_f evaluated.

3. Moves in configuration space are accepted or rejected in the traditional simulated anneal scheme, using the probabilistic factor:
$$e^{-(E_f - E_i)/T} \tag{10.2}$$

4. Sub image numbers M, N etc are pruned on the basis of Euclidean distance; where two or more images of the same type almost overlap, one is successively removed, until such time as convergence is reached.

The cost function is a standard least squares sum, consisting of the difference between an image generated from identified, isolated points and the pixel region of overlapping points. Simulated anneal is also used in image processing for the tasks of deconvolution and image reconstruction.

For a 100×100 pixel region which contains 5 identical, overlapping points of size 30×30, there are approximately 2^{36} possible configurations, assuming a translation

Table 10.1: Experimental results for simulated anneal applied to the data point disambiguation problem. The temperature constant pertains to the annealing schedule, the underlying point types where either (A) a diamond or (B) a triangle, and the offsets refer to row and column indices within the total image matrix, respectively.

Trial #	Temp. const.	Type	Offset (orig.)	Offset (calc.)
1	0.3	A	(11,39)	(11,40)
			(35,19)	(34,20)
			(19,4)	(20,3)
		B	(21,35)	(22,35)
			(10,18)	(10,17)
2	0.3	A	(29,24)	(29,23)
			(22,9)	(21,9)
			(23,37)	(21,39)
		B	(2,39)	(2,39)
			(18,17)	(18,16)
3	0.05	A	(3,37)	(3,37)
			(22,1)	(21,1)
			(17,21)	(19,19)
		B	(20,38)	(20,39)
			(25,26)	(24,27)
			-	(15,24)

of 2 pixels between individual elements for adequate resolution. Despite the magnitude of configuration space for even this simple case, this is within the capabilities of simulated anneal, regularly applied to problems such as VLSI. Figure 5 gives an example of pixel regions containing overlapping data points and the corresponding machine learnt versions. The images were generated randomly using two data point types, a diamond (A) and triangle (B). Table 1 details the results of these experiments; for the first two examples convergence was reached in under 30k iterations. In the last case, convergence was reached in under 40k iterations. A slower annealing schedule and subsequently more iterations are required as the pixel region and number of possible different data points increases. The results are promising in that data which would be traditionally considered lost is recovered with fairly high accuracy.

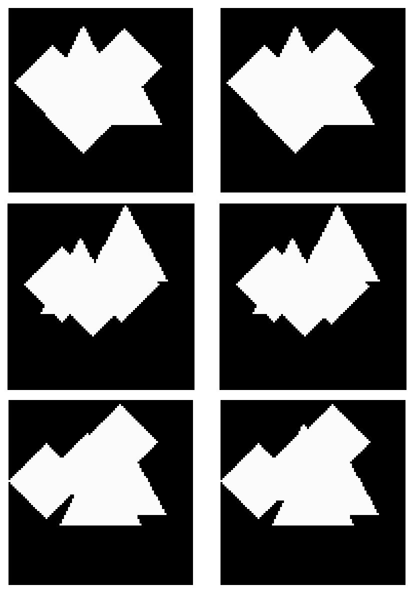


Figure 10.1: Examples of overlapping data points (left) and machine learnt versions (right)

Chapter 11

Data Processing

The following discussion gives the salient features of subsequent data processing after acquisition, using MATLAB/OCTAVE functions to perform the manipulations. Generally speaking, the data filename for data acquired on a Bruker Avance console is either `fid` or `ser` depending on whether the data is one dimension or multi-dimensional, respectively. To open up a datafile, the file type is `int32` and is for instance the machine used to acquire the data uses UNIX or big-endian byte ordering;

```
fid=fopen('fid',r,'ieee-be');
[A,count]=fread(fid,Inf,int32);
```

The string `fid` is the filename and the integer `fid` is the file ID. Data is stored in variable `A`, and the number of elements is `count`. Now the acquisition is usually of the form `real, imag, real ...` in which case one can reassemble the data with the commands:

```
for j=0:(count/2-1);
w(j+1)=A(2*j+1)+i*A(2*j+2)
end
```

At this point, it is usually prudent to study the FID to see if early points have been distorted by for instance the probe ring down. These x points are removed by performing a left shift:

```
w=w(x:count/2);
```

The effects of noise or inadvertent apodization of the signal may be reduced by zero filling (simply padding the dataset with zeros, usually to a power of 2) and exponential multiplication. Other data windows may be used, for instance sine bell or Gaussian.

```
x=0:dw:(count-1)*dw;
w=w.*exp(-x.*lb);
```

where lb is the exponential line broadening in hertz and dw is the dwell time. Following these steps, a Fourier transform is taken, using the FFT [?] algorithm:

```
z=fftshift(fft(z,1024));
f=-(512:511)/(1024*dw);
```

In this example the argument to `fft` transforms the data, which is padded with zeros to 1024 points. The command `fftshift` is necessary since by convention the zero frequency point is in the middle of the spectra, indicated in the construction of the frequency axis data `f`.Typically the frequency data is a mix of absorption and dispersion components. A linear phase correction is applied to produce a symmetric, pure absorption spectra for ease of interpretation:

```
z=z.*exp(i*(ph1.*f+ph0));
```

where `ph0` and `ph1` are the zeroth and first order phase corrections respectively. At this stage the baseline in the frequency domain is often not flat or worse has significant oscillation. This can be for a variety of reasons, the most prosaic due to a large bandwidth and subsequent loss of early data points due to mechanical limitations. A simple algorithm can search for the minima in the baseline, a result of the convolution between the desired signal and early truncation. Subsequently a fitted polynomial is subtracted leaving the desired information. After data has been adequately processed it may be examined by a variety of means. In the simplest cases, the frequency of a single peak (for instance from a high resolution liquid's spectra) may give sufficient information. However in Solid State NMR, the frequency spectra are usually complex functions of the interactions discussed thus far, and simulation is necessary in order to extract the useful information.

Chapter 12

Laplace Method

We begin by examining the effect of 2 harmonic boundaries on 1d fluid motion, under the low reynolds number approximation. The simplest case of constant, symmetric and anti-symmetric boundaries are solved first, and then using Duhammel's principle, time varying boundaries are introduced. This example will serve as a test for a 1D projection of the 3D numerical solver. Idealy, in 3D, rotational motion is induced in the azimuthal direction using a harmonic boundary with phase directly proportional to ϕ, ie.,

$$f(t) = \sin(\omega t + \phi)$$

and after vectoring thrust is produced along z. The low reynolds number approximate equation (stokes):

$$\rho \frac{\partial u}{\partial t} = \eta \frac{\partial^2 \phi}{\partial r^2} \tag{12.1}$$

2 boundaries, 2 harmonic conditions...BC's

$$u(-1, t) = 1$$

$$u(1, t) = 1 \tag{12.2}$$

and

$$u(r, 0) = 0; -1 \leq r \leq 1 \tag{12.3}$$

Take Laplace transform of diffusion equation $\mathcal{L}(u) \rightarrow U$:

$$\frac{d^2 U}{dr^2} - \frac{\rho}{\eta} s U = 0 \tag{12.4}$$

put $\alpha = \frac{\rho}{\eta}$

$$U = A \cosh(\sqrt{\alpha s} r) + B \sinh(\sqrt{\alpha s} r) \tag{12.5}$$

BC's

$$U(r = -1) = A \cosh(\sqrt{\alpha s}) - B \sinh(\sqrt{\alpha s}) = 1/s \tag{12.6}$$

$$U(r = 1) = A \cosh(\sqrt{\alpha s}) + B \sinh(\sqrt{\alpha s}) = 1/s \tag{12.7}$$

one finds that $B = 0$ and $A = 1/s\cosh(\sqrt{\alpha s})$ and hence:

$$U(r,s) = \frac{\cosh(\sqrt{\alpha s})r}{s\cosh(\sqrt{\alpha s})} \tag{12.8}$$

Invert using the Hadamard relationship:

$$\mathcal{L}^{-1}\left\{\frac{P(s)}{Q(s)}\right\} = \sum_{s_k}\frac{P(s_k)}{Q'(s_k)}e^{s_k t}; Q(s=s_k)=0 \tag{12.9}$$

One finds:

$$s_k = 0, -\frac{(2n+1)^2\pi^2}{4\alpha}; n = 0,1,2,3,.. \tag{12.10}$$

therefore

$$u(r,t) = \sum_{s_k}\frac{\cosh(\sqrt{\alpha s}r)}{\cosh(\sqrt{\alpha s}) + \sqrt{\alpha s}\sinh(\sqrt{\alpha s})}e^{s_k t} \tag{12.11}$$

$$= 1 + \frac{2}{\pi}\sum_{n=0,1,2,..}\frac{(-1)^n\cos(\frac{[2n+1]\pi}{2}r)}{2n+1}\exp\left[-\frac{(2n+1)^2\pi^2}{4\alpha}t\right] \tag{12.12}$$

new BC's; let

$$U(r=-1) = A\cosh(\sqrt{\alpha s}) - B\sinh(\sqrt{\alpha s}) = -1/s \tag{12.13}$$

$$U(r=1) = A\cosh(\sqrt{\alpha s}) + B\sinh(\sqrt{\alpha s}) = 1/s \tag{12.14}$$

one finds that $A = 0$ and $A = 1/s\sinh(\sqrt{\alpha s})$ and hence:

$$U(r,s) = \frac{\sinh(\sqrt{\alpha s})r}{s\sinh(\sqrt{\alpha s})} \tag{12.15}$$

One finds:

$$s_k = 0, -\frac{(n)^2\pi^2}{\alpha}; n = 0,1,2,3,.. \tag{12.16}$$

therefore

$$u(r,t) = \sum_{s_k}\frac{\sinh(\sqrt{\alpha s}r)}{\sinh(\sqrt{\alpha s}) + \sqrt{\alpha s}\cosh(\sqrt{\alpha s})}e^{s_k t} \tag{12.17}$$

$$= \frac{1}{\pi}\sum_{n=0,1,2,..}\frac{(-1)^n\sin(n\pi r)}{n}\exp\left[-\frac{(n)^2\pi^2}{\alpha}t\right] \tag{12.18}$$

Introduce harmonic boundaries ($f(t) = \sin(\omega t); g(t) = \sin(\Omega t + \phi)$) s.t:

$$U(r=-1) = F(s) = A\cosh(\sqrt{\alpha s}r) - B\sinh(\sqrt{\alpha s}r) \tag{12.19}$$

$$U(r=1) = G(s) = A\cosh(\sqrt{\alpha s}r) + B\sinh(\sqrt{\alpha s}r) \tag{12.20}$$

one finds

$$A = \frac{F(s)+G(s)}{2\cosh(\sqrt{\alpha s})} = \frac{H(s)}{\cosh(\sqrt{\alpha s})} \tag{12.21}$$

$$B = \frac{G(s) - F(s)}{2\sinh(\sqrt{\alpha s})} = \frac{I(s)}{\sinh(\sqrt{\alpha s})} \tag{12.22}$$

ie.,

$$U(s,r) = H(s)s\frac{\cosh(\sqrt{\alpha s}r)}{s\cosh(\sqrt{\alpha s})} + I(s)s\frac{\sinh(\sqrt{\alpha s}r)}{s\sinh(\sqrt{\alpha s})} \tag{12.23}$$

One can use

$$\mathcal{L}[w_t] = sW - w(x,0) \tag{12.24}$$

to show that for a general function $u(x,t)$:

$$\begin{aligned} u(x,t) &= \mathcal{L}^{-1}\{F(s)\mathcal{L}[w_t]\} \\ &= \mathcal{L}^{-1}[F(s)] * [w_t] \\ &= \int_0^t f(\tau)w_\tau(x,t-\tau)d\tau \end{aligned}$$

$$\int_0^t w(x,t-\tau)f'(\tau)d\tau + f(0)w(x,t) \tag{12.25}$$

Can use solutions from earlier; need to evaluate following integral(s):

$$\begin{aligned} &\omega \int e^{-\beta(t-\tau)}\cos(\omega\tau)d\tau \\ &= \frac{\omega}{\beta} e^{\beta(\tau-t)}\cos(\omega\tau)\Big|_o^t + \frac{\omega^2}{\beta}\int_0^t e^{\beta(\tau-t)}\sin(\omega\tau)d\tau \\ &= \frac{\omega\beta}{\omega^2+\beta^2}\left[e^{\beta(\tau-t)}\cos(\omega\tau)\Big|_0^t + \frac{\omega}{\beta}e^{\beta(\tau-t)}\sin(\omega\tau)\Big|_0^t \right] \\ &= \frac{\omega\beta}{\omega^2+\beta^2}\left[\cos(\omega t) - e^{-\beta t} + \frac{\omega}{\beta}\sin(\omega t)\right] \end{aligned}$$

$$\begin{aligned} &\Omega \int e^{-\beta(t-\tau)}\cos(\Omega\tau+\phi)d\tau \\ &= \frac{\Omega}{\beta} e^{\beta(\tau-t)}\cos(\Omega\tau+\phi)\Big|_o^t + \frac{\Omega^2}{\beta}\int_0^t e^{\beta(\tau-t)}\sin(\Omega\tau+\phi)d\tau \\ &= \frac{\Omega\beta}{\Omega^2+\beta^2}\left[e^{\beta(\tau-t)}\cos(\Omega\tau+\phi)\Big|_0^t + \frac{\Omega}{\beta}e^{\beta(\tau-t)}\sin(\Omega\tau+\phi)\Big|_0^t \right] \\ &= \frac{\Omega\beta}{\Omega^2+\beta^2}\Big[\cos(\Omega t+\phi) - e^{-\beta t}\cos(\phi) \\ &+ \frac{\Omega}{\beta}\{\sin(\Omega t+\phi) - e^{-\beta t}\sin(\phi)\}\Big] \end{aligned}$$

$$\mathcal{L}^{-1}H(s) = \frac{f(t)+g(t)}{2} \tag{12.26}$$

$$\mathcal{L}^{-1}I(s) = \frac{g(t) - f(t)}{2} \tag{12.27}$$

Let $u(r,t) = A + B$ and for simplicity, $\omega = \Omega$; A :

$$\frac{\sin(\omega t) + \sin(\omega t + \phi)}{2} + \frac{1}{\pi} \sum_{n=0,1,2,..} \frac{(-1)^n \cos(\frac{[2n+1]\pi}{2} r)}{2n+1} \times$$

$$\frac{\omega\beta}{\omega^2 + \beta^2} \Big[\cos(\omega t) + \cos(\omega t + \phi) - e^{-\beta t}(1 + \cos(\phi))$$

$$+ \frac{\omega}{\beta} \Big\{\sin(\omega t) + \sin(\omega t + \phi) - e^{-\beta t}\sin(\phi)\Big\}\Big]$$

$$+ \sin(\phi) + \frac{2\sin(\phi)}{\pi} \sum_{n=0,1,2,..} \frac{(-1)^n \cos(\frac{[2n+1]\pi}{2} r)}{2n+1} \exp\left[-\frac{(2n+1)^2\pi^2}{4\alpha} t\right] \tag{12.28}$$

where $\beta = \frac{(2n+1)^2\pi^2}{4\alpha}$. Similarly, for B, one finds:

$$\frac{1}{2\pi} \sum_{n=0,1,2,..} \frac{(-1)^n \sin(n\pi r)}{n} \times$$

$$\frac{\omega\beta}{\omega^2 + \beta^2} \Big[-\cos(\omega t) + \cos(\omega t + \phi) - e^{-\beta t}(\cos(\phi) - 1)$$

$$+ \frac{\omega}{\beta} \Big\{-\sin(\omega t) + \sin(\omega t + \phi) - e^{-\beta t}\sin(\phi)\Big\}\Big]$$

$$+ \frac{\sin(\phi)}{\pi} \sum_{n=0,1,2,..} \frac{(-1)^n \sin(n\pi r)}{n} \exp\left[-\frac{n^2\pi^2}{\alpha} t\right] \tag{12.29}$$

where $\beta = \frac{n^2\pi^2}{\alpha}$.

Chapter 13

Group Theory

In the last century, group theory has been applied with much success to problems concerning eigenstates of the Hamiltonian operator H. A seemingly intractable problem can be reduced in some cases to that which is easily assimilated and solved. This usually involves a consideration of the symmetry of H and subsequent application of group theory. The idea of symmetry and group theoretic principles applied to atomic structure allows an ambiguous assignment of atoms using a modicum of symbols.

An abstract group $\mathcal{G}$ is considered to be that set of elements $A, B, ...$ such that group multiplication is defined, so as to associate a third element with any ordered pair. More concisely, an abstract group is composed of elements which satisfy:

1. The product of any two elements is in the set; i.e., the set is closed under multiplication.
2. Association holds; $A(BC) = (AB)C$.
3. There exists a unit element E; $AE = EA = A$.
4. An inverse exists for each element; $AA^{-1} = A^{-1}A = E$

The multiplicative relationship between group elements may be represented by a multiplication table. Within that table each row and column contains each element only once. For example the covering operations of the square, group D_4. For any group element X one may form the period of X, or cyclic subgroup of order n, defined as:

$$X, X^2, X^3, ...X^n = E \tag{13.1}$$

where n is the order of the element X. Groups $\mathcal{G}$ of order h may consist of subgroups $\mathcal{S} = E, S_2, ...S_g$ of lower order g, where the order is the number of elements. The set of elements $EX, S_2X, ...S_GX$ is a right co set $\mathcal{S}X$ if X is not in $\mathcal{S}$. A left co set may be similarly defined. Co-sets don't constitute subgroups since the identity is absent. Further, one may show that left and right co sets of a subgroup are either identical or have no elements in common.

Elements are said to be conjugate if for instance:

$$B = XAX^{-1} \text{ or } A = X^{-1}BX \tag{13.2}$$

	E	A	B	C	D	F	G	H
E	E	A	B	C	D	F	G	H
A	A	E	G	H	F	D	B	C
B	B	G	E	F	H	C	A	D
C	C	F	H	E	G	A	D	B
D	D	H	F	G	E	B	C	A
F	F	C	D	B	A	G	H	E
G	G	B	A	D	C	H	E	F
H	H	D	C	A	B	E	F	G

Table 13.1: Proper covering operations of the group D_4.

where X is a member of the group. The arrangement of mutually conjugate elements constitutes a class, $\mathcal{C}$. For example D_4 has classes

$$\{A, B\}, \{C, D\}, \{F, H\}, \{G\}, \{E\}$$

. Physically speaking, class elements may be rotations of the same angle(s) performed about different axes, related by a group operation. If a subgroup consists entirely of classes, then it is referred to as an invariant subgroup or normal divisor. For instance, within D_4 there exists the following subgroups which are also normal divisors:

$$\{A, B, G, E\}; \{C, D, G, E\}; \{F, G, H, E\} \tag{13.3}$$

In general one is more concerned with *representations* Γ of group elements, isomorphic to the original group. This simply means that (for instance) one selects a group of square matrices whose multiplication properties are identical to the original abstract group. The dimensionality of a representation refers to the number of rows/columns, and if the representation is larger in dimension than needed to illicit the same properties, it is said to be *reducible*. Any representation by matrices with non-vanishing determinants is equivalent via a similarity transformation to a representation by unitary matrices. Schur's lemma gives a test of reducibility; if a (non-constant) commuting matrix exists for a any representation, then it is reducible. Stated another way, only a constant matrix commutes with an irreducible representation. Further, given two irreducible representations of the same group $\Gamma^{(1)}(A_i)$ and $\Gamma^{(2)}(A_i)$ of dimensionality l_1 and l_2 and if a rectangular matrix M exists such that

$$M\Gamma^{(1)}(A_i) = \Gamma^{(2)}(A_i)M \quad i = 1, 2, ...h \tag{13.4}$$

then either:

1. $l_1 \neq l_2$ and $M = 0$, or

2. $l_1 = l_2$ and $M = 0$, or at least $|M| \neq 0$, in which case M has an inverse and the representations are identical.

The previous results for matrices, representations are implicit to the great orthogonality theorem, which for all the inequivalent, irreducible, unitary representations of a group states that:

$$\sum_R \Gamma^{(i)}(R)^*_{\mu\nu}\Gamma^{(j)}(R)_{\alpha\beta} = \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha}\delta\nu\beta \tag{13.5}$$

where R covers all group elements and l_i is the dimensionality of $\Gamma^{(i)}$. This result may be used to give the dimensionality theorem:

$$\sum_i l_i^2 = h \tag{13.6}$$

Simply put, the sum of the squares of the irreducible representation's dimensions is equal to the order h of the group.

Since all matrices related to one another through unitary transformations are equivalent, an invariant to said transformation is often used, hence the *character* χ of a representation. The invariant quantity is the trace of a matrix; the character of the jth representation is the set of h numbers $\chi^{(j)}(E), \chi^{(j)}(A_2)..., \chi^{(j)}(A_h)$, where

$$\chi^{(j)}(R) = \mathrm{Tr}\Gamma^{(j)}(R) = \sum_{\mu=1}^{l_j}\Gamma^{(j)}(R)_{\mu\mu} \tag{13.7}$$

Naturally, all class members have the same character,

13.0.2 Angular Momentum

The addition of angular momentum may be in the simplest case simply the addition of spin and orbital angular momentum, or more typically the combination of one or more spins. Consider to begin with the addition of two angular momenta j_1 and j_2 with eigenfunctions $\psi_{j_1m_1}$ and $\psi_{j_2m_2}$. Then

$$J_1^2\psi_{j_1m_1} = j_1(j_1+1)\psi_{j_1m_1}; J_2^2\psi_{j_2m_2} = j_2(j_2+1)\psi_{j_2m_2}$$

$$J_{1z}\psi_{j_1m_1} = m_1\psi_{j_1m_1}; J_{2z}\psi_{j_2m_2} = m_2\psi_{j_2m_2} \tag{13.8}$$

The direct product $\psi_{j_1m_1}\psi_{j_2m_2}$ is referred to as the uncoupled representation, in which $J_1^2, J_{1z}, J_2^2, J_{2z}$ are diagonal. The total angular momentum operator J is defined by

$$J = J_1 + J_2 \tag{13.9}$$

We seek the coupled representation where $J^2, J_z, J_1^2 and J_2^2$ are diagonal with eigenvalues $j(j+1)$ and m respectively. The two representations are connected by a unitary transformation through:

$$\psi_{jm} = \sum_{m_1m_2} C(j_1j_2j; m_1m_2m)\psi_{j_1m_1}\psi_{j_2m_2} \tag{13.10}$$

The elements $C(..)$ comprise the Clebsch-Gordon coefficients. A simple manipulation shows:

$$(m - m_1 - m_2)C(j_1j_2j; m_1m_2m) = 0 \tag{13.11}$$

Which implies that $m = m_1 + m_2$ or else $C(j_1 j_2 j; m_1 m_2 m) = 0$; further

$$|j_1 - j_2| \leq j \leq |j_1 + j_2| \tag{13.12}$$

again, else $C(j_1 j_2 j; m_1, m - m_1) = 0$. The $C.C.$ coefficients obey various symmetry relations, including:

$$\begin{aligned} C(j_1 j_2 j_3; m_1 m_2 m_3) &= (-1)^{j_1+j_2-j_3} C(j_1 j_2 j_3; -m_1, -m_2, -m_3) \\ &= (-1)^{j_1+j_2-j_3} C(j_2 j_1 j_3; m_2 m_1 m_3) \\ &= (-1)^{j_1-m_1} \left(\frac{2j_3+1}{2j_2+1} \right)^{\frac{1}{2}} C(j_1 j_3 j_2; m_1, -m_3, m_2) \end{aligned} \tag{13.13}$$

with $j_3 = j; m_3 = m$. There exists various expressions for the co-efficients, Racah's the most popular:

$$\begin{aligned} C(j_1 j_2 j_3; m_1 m_2 m_3) &= \delta_{m_3, m_1+m_2} \\ \times \Bigg[(2j_3+1) &\frac{(j_1+j_2-j_3)!(j_3+j_1-j_2)!(j_3+j_2-j_1)!}{(j_1+j_2+j_3+1)!} \\ \times (j_1+m_1)!(j_1-m_1)!&(j_2+m_2)!(j_2-m_2)!(j_3+m_3)!(j_3-m_3)! \Bigg]^{\frac{1}{2}} \\ \times \sum_\nu \frac{(-1)^\nu}{\nu!} &[(j_1+j_2-j_3-\nu)!(j_1-m_1-\nu)!(j_2+m_2-\nu)! \\ &\times (j_3-j_2+m_1+\nu)!(j_3-j_1-m_2+\nu)!]^{-1} \end{aligned} \tag{13.14}$$

Recurrence relation:

Central to the quantum processes taking place at the heart of NMR is the rotation of some quantization axis. Under these conditions, simple considerations show that the square of the angular momentum operator remains unchanged. The eigenfunctions ψ_{jm} which diagonalize both J^2 and J_z transform as

$$R\psi_{jm} = e^{-i\theta(\mathbf{n}\cdot\mathbf{J})}\psi_{jm} \tag{13.15}$$

In the simplest case a rotation takes place around the transformation axis such that $\mathbf{n} \cdot \mathbf{J} = J_z$, hence

$$\langle jm' | e^{-\theta(\mathbf{n} \cdot J)} | jm \rangle = \delta_{m'm} e^{-im\theta} \tag{13.16}$$

hence there is a change of phase between one function and another:

$$R\psi_{jm} = e^{-im\theta}\psi_{jm} \tag{13.17}$$

In the quest for the matrix elements of the rotation matrix, one is inclined to consider the most general specification for a rotation, caste in terms of the Euler Angles., α, β, γ, specified as follows (after Rose):

1. A rotation is made about the z-axis through an angle α; the new coordinate axes are x', y', z'.

2. A rotation is made about the y'-axis through an angle β; the new coordinate axes are x'', y'', z''

3. A rotation is made about the z''-axis through an angle γ; the new coordinate axes are x'', y'', z''

Expressed in terms of the original coordinate system, this is:

$$R = e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z} \tag{13.18}$$

The matrix elements for R:

$$\begin{aligned} D^j_{m'm}(\alpha, \beta, \gamma) &= \langle jm'|e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z}|jm\rangle \\ &= e^{-im'\alpha}\langle jm'|e^{-i\beta J_y}|jm\rangle e^{-im\gamma} \end{aligned} \tag{13.19}$$

There remains one matrix to be determined, since $\exp(-i\beta J_y)$ is not diagonal in this representation; an expression due to Wigner:

$$\begin{aligned} d^j_{m'm}(\beta) &= \langle jm'|e^{-i\beta J_y}|jm\rangle \\ &[(j+m)!(j-m)!(j+m')!(j-m')!]^{\frac{1}{2}} \\ &\times \sum_\nu \frac{(-1)^\nu}{(j-m'-\nu)!(j+m-\nu)!(\nu+m'-m)!\nu!} \\ &\times \left(\cos\frac{\beta}{2}\right)^{2j+m-m'-2\nu} \left(-\sin\frac{\beta}{2}\right)^{m'-m+2\nu} \end{aligned} \tag{13.20}$$

The rotation matrices obey orthonormality;

$$\begin{aligned} \sum_m D^{j*}_{m'm}(\alpha\beta\gamma) D^j_{m''m}(\alpha\beta\gamma) &= \delta_{m'm''} \\ \sum_m D^{j*}_{mm'}(\alpha\beta\gamma) D^j_{mm''}(\alpha\beta\gamma) &= \delta_{m'm''} \end{aligned} \tag{13.21}$$

An irreducible tensor of rank L is defined as a set of $2L+1$ functions $T_{LM}(M + -L, -L+1, ..., L)$ which transform under the $2L+1$-dimensional representation of the rotation group:

$$RT^{-1}_{LM} = \sum_{M'} D^L_{M'M}(\alpha\beta\gamma) T_{LM'} \tag{13.22}$$