MATRIX ELEMENTS, CORRESPONDENCE PRINCIPLES AND LINE BROADENING

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CHAPTER I

INTRODUCTION

During the early development of quantum mechanics much use was made of what Bohr referred to as "a formal analogy between the quantum theory and the classical theory". The conceptual foundation of this "formal analogy", which he later called the "correspondence principle", was based on the assumption that the quantum theory contains classical mechanics as a limiting case. With the advent of modern quantum mechanics, the applications of this correspondence have until recently been neglected, perhaps due to a feeling that they were not necessary or that their range of applicability was too limited.

There are unfortunately many cases where the methods of quantum mechanics are too cumbersome to be used without approximations. Recent astrophysical investigations have for instance involved transitions with principal quantum numbers of up to 250. If the approximations that have to be made become too restrictive a better policy could be to use an approximate method which can be used to solve the problem exactly. This theoretical investigation is in two parts. The first summarizes the correspondence principle methods and discusses their range of validity; by applying the correspondence principle to problems whose quantum mechanical solutions are known in special cases, we can compare the analytic expressions obtained by each method. We shall show that the two results agree over a far wider range of values than is generally realised, and that the agreement can be considerably improved by adjusting free parameters that arise naturally in the correspondence principle.

The second part considers the application of classical mechanics and the correspondence principle to the broadening of spectral lines. The observation of spectral lines involving very high principal quantum numbers has led to a resurgence of approximate methods because of the difficulty of applying quantum mechanics exactly. A survey of the existing literature showed either very formal solutions to the line broadening problem which were difficult to apply, or detailed results which had very limited validity. We shall show that our calculations agree with these accepted results in their region of validity whilst describing the line shape in the intermediate region.

In Chapter II we describe the correspondence principles we invoke. In Chapter III we obtain the solution of the motion of a particle in various potentials and calculate matrix elements and other quantities in these potentials. The potentials we consider are a harmonic potential, a Morse potential, and a Coulomb potential, and we compare the results of our calculation with the quantum mechanical expression where these are known. In Chapter IV we outline the main causes of spectral line broadening. We consider the limits in which various physical approximations can be made and examine in detail the work and conclusions of Lindholm, one of the foremost workers in the field of non-quantum mechanical line broadening. In Chapter V we present our theory and compare it with others in various limits, and in Chapters VI and VII we obtain line shapes which we compare with the Lindholm shapes.

CHAPTER II

CORRESPONDENCE PRINCIPLES

2.1 Action and Angles Variables

The classical theory of action and angle variables is well documented (Corben and Stehle , 1960 ; Goldstein , 1959) . We consider briefly perturbations of periodic systems for which the Hamilton-Jacobi equation is separable in some set of coordinates . For those systems ,.the Schröedinger equation is separable in the same coordinates .

In the case of only one degree of freedom , if q and p are conjugate position and momentum , new conjugate variables ϕ and α can be introduced in place of q and p such that α is a constant and ϕ is a linear function of time . These new variables are not determined uniquely : we can replace α by any function of itself and multiply ϕ by a corresponding function of α . For convenience we choose ϕ in such a way that it increases by 2π durinh any one period of the motion , in which case we denote it by w . Let the corresponding conjugate variable be I . We call w an angle variable and I an action variable .

We now consider in more detail the case of a system with N degrees of freedom . If now q_k and p_k , $k = 1,\ldots,N$, are the generalised coordinates of position and momentum , and $H(q_k,p_k)$ is the unperturbed Hamiltonian , then

$$p_k = \frac{\partial S}{\partial q_k} = \frac{\partial S_k}{\partial q_k}$$

where the action function S is the solution of the Hamilton-Jacobi equation

$$H\left(q_k, \frac{\partial S}{\partial q_k}\right) = E$$

and

$$S(q_1,\ldots,q_N) = \sum_{k=1}^{N} S_k(q_k; c_1,\ldots,c_N)$$

and $c_1,\ldots,c_N$ are the N constants of integration .

We now define a set of action variables I_k by

$$I_k = \frac{1}{2\pi} \oint p_k \, dq_k \qquad , \quad k = 1\ldots N \;\cdot$$

the integral being taken once round a complete cycle . This relation may be solved to give us the integration constants as functions of the action variables . Thus we can write

$$S(q_1,\ldots,q_N) = \sum_{k=1}^{N} S_k(q_k; I_1,\ldots,I_N)$$

and the corresponding angle variables w_k are defined by

$$w_k = \frac{\partial S}{\partial I_k} = \sum_{j=1}^{N} \frac{\partial S_j}{\partial I_k}$$

The equations of motion in these new coordinates become

$$\dot{w}_k = \frac{\partial H}{\partial I_k} = \text{constant} = \omega_k$$

$$w_k = \omega_k t + \delta_k$$

$$\dot{I}_k = -\frac{\partial H}{\partial w_k} = 0$$

$$I_k = \text{constant}$$

It can be shown (Born , 1927) that when q_j goes through a complete cycle the change in w_k is $2\pi\delta_{kj}$, where δ_{kj} is the Kroneckerdelta function which equals 1 if $k = j$ and equals 0 otherwise . The parameter ω_k is therefore the frequency of the motion , and the period is 2π . The constant δ_k will later be shown to be a phase factor .

In our definition of the action variables we have used a slightly different notation from that used by most authors , but one that is more consistent with present day quantum mechanics . We follow the notation of Landau and Lifshitz (1960) and replace the more usual action variables J_k by $I_k = J_k / 2\pi$. The angle variables now vary between 0 and 2π and are often actual angles instead of fractions of angles .

Although the notation might be recent , the theory and application of action and angle variables is not new . These techniques were first introduced by Delaunay in his " Théorie du Mouvement de la Lune " in 1860 , and were used extensively in the last century in investigations of planetary orbits by Poincaré (1905) , Charlier (1907) , and others . Their application to electron orbits however was ignored until the work of Schwarzschild (1916) and Epstein (1916) , which showed how quantum mechanical problems involving periodic systems have to be tied up with the Hamilton-Jacobi theory in classical mechanics . Sommerfeld then postulated definite values for the constant action variables

$$I = n\hbar$$

where n is a non-negative integer and $\hbar$ is Planck's constant divided by 2π ; this quantised the energy of the system and provided a set of discrete energy levels , or stationary states .

2.2 Bohr's Correspondence Principles , and others

A basic form of correspondence principle was first stated by Planck when he wrote , in 1906 . : " The classical theory can be simply characterised by the fact that the quantum of action becomes infinitesimally small " . It is easy to show for example that Planck's (quantum mechanical) radiation formula

$$u = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{\exp(h\nu/kT) - 1}$$

(in the usual notation) goes over to the (classical) Rayleigh-Jeans formula

$$u = \frac{8\pi\nu^2}{c^3} . kT$$

as $h \longrightarrow 0$

However , it was Bohr who first formulated a " Korrespondenprincip " which laid the conceptual foundation of the old quantum theory . It deals with the formal applicability of classical mechanics to quantum mechanics for those stationary states defined at the end of the previous section . Its basis is the well known relation , again due to Planck , between the observed frequency $\omega_{nn'}$ of the emitted radiation from an atom and the energy E_n of the nth state of that atom

$$\hbar\omega_{nn'} = \Delta E = (E_n - E_{n'})$$

Bohr's correspondence principle relates this observed frequecy with a corresponding classical frequency

Correspondence Principle 1

> In the limit where successive stationary states differ relatively little from each other , the observed (quantal) atomic frequencies tend to coincide with the classical ones .

That is

$$\omega_{nn'} \simeq s\omega$$

$$s = n - n'$$

$$\text{as} \quad |s| \ll n , n'$$

Bohr also predicted the approximate intensity of spontaneously emitted radiation . If $A_{nn'}$ is the spontaneous transition probability then

Correspondence Principle 2

> The mean power spontaneously emitted as radiation at any such frequency tends to coincide with the corresponding classical power emission

$$A_{nn'}\Delta E = W_s$$

The correspondence is thus between the frequency components of the power , W_s , and of the energy , and not the total energy . The principle was extended to absorption of radiation by Van Vleck (1924) by using the relation between Einstein's A and B coefficients , and was extended further to the effect of an electric field from any source , including a passing charged particle . A correspondence principle for collision processes can then be defined (e.g. Percival and Richards, 1970 - 1971).

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Before this , the correspondence principle had been incorrectly applied . The difficulty is that whereas the final quantum states are discrete , in classical mechanics all dynamical variables have a continuous range of values . A density of states method was originally developed to deal with this problem ; we define a differential cross section $\partial\sigma/\partial\Delta E$ with respect to energy transfer from the state n to another state n' , (figure 1) . If $\partial\sigma/\partial\Delta E$ is nearly constant over values of ΔE corresponding to several neighbouring final excited states n' it is possible to obtain an unambiguous excitation cross section

$$\sigma(n \rightarrow n') = \int d\Delta E \, \frac{\partial\sigma}{\partial\Delta E}$$

the limits of integration corresponding to $\Delta E = n' - 1 , n'$, or $\Delta E = n' , n' + 1$, or any other interval in the neighbourhood of n' . Thus

$$\sigma(n \rightarrow n') = \left|\frac{\partial\Delta E}{\partial n'}\right| \frac{\partial\sigma}{\partial\Delta E}$$

where ΔE is now the energy required to excite the atom from the state n to the state n' ,and

$$\left|\frac{\partial\Delta E}{\partial n'}\right| = \frac{2Ry}{n'^3}$$

is the mean energy between states about n' , or the inverse of the density of states per unit energy range .

Note that this concept requires that $\partial\sigma/\partial\Delta E$ varies little with ΔE .When ΔE (or Δn) is small , this is no longer true , and this "naive" correspondence principle , which will also be called the "density of states" correspondence principle , is thus

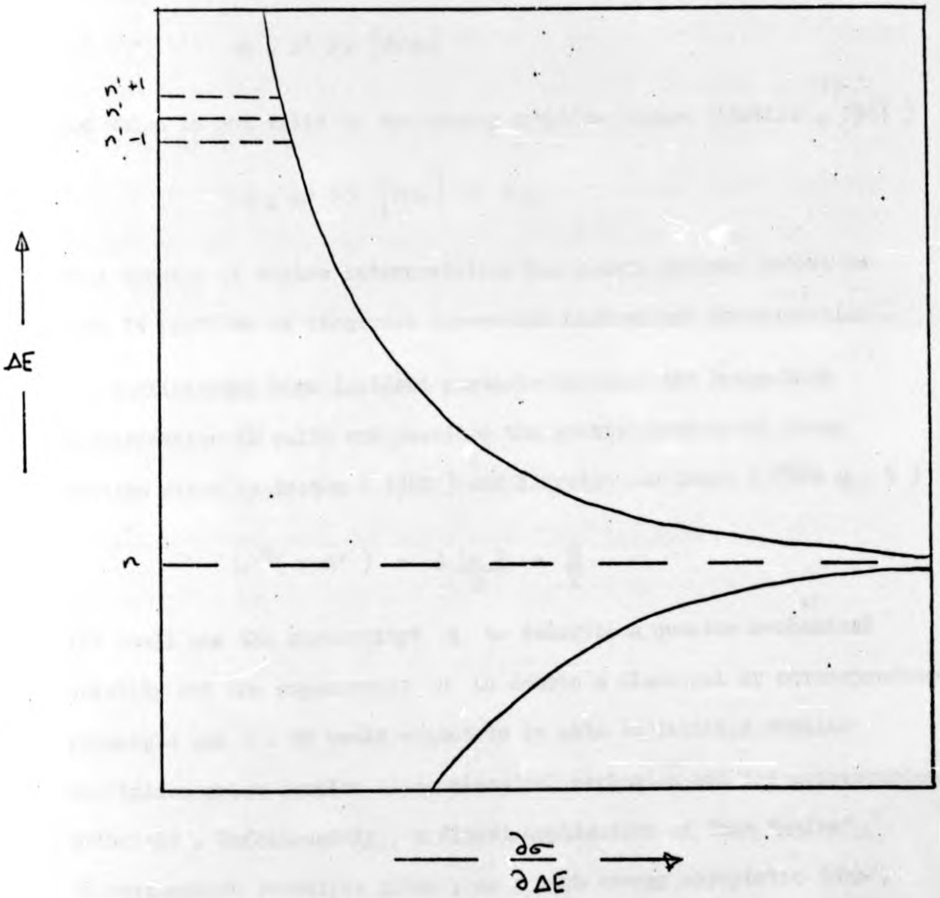

Fig 1

restricted to

$$n\ ,\ n'\ ,\left|\Delta n\right| \gg 1$$

which is not the same as Bohr's correspondence principle which requires that

$$n\ ,\ n' \gg \left|\Delta n\right|$$

and which is not valid in the strong coupling region (Stabler , 1964)

$$n\ ,\ n' \gg \left|\Delta n\right| \sim 1\ .$$

This density of states interpretation has a more serious defect in that it predicts an incorrect asymptotic high energy cross-section . For sufficiently high incident particle energies the Bethe-Born approximation is valid and provides the quantum mechanical cross section given by Seaton (1962) and Kingston and Lauer (1966 a , b)

$$\sigma^{q}(\ n\to n'\ )\ =\ A\,\frac{\ln E}{E}\ +\ \frac{B}{E}$$

(We shall use the superscript q to describe a quantum mechanical quantity and the superscript c to denote a classical or correspondence principle one) . We would expect to be able to derive a similar excitation cross section using classical mechanics and the correspondence principle . Unfortunately , a direct application of this "naive" correspondence principle gives , as a high energy asymptotic form ,

$$\sigma^{c}(\ n\to n'\ ) = \frac{B}{E}$$

The logarithmic term , which dominates at high enough energies , is absent .

This naive correspondence principle fails because the wrong correspondence is made between the quantum mechanical and the classical system . It supposes that if the final classical excitation energy ΔE lies between two energies $E_{n'}$ (corresponding to a state n') and $E_{n'+1}$ (corresponding to a state n'+1) then the classical excitation corresponds to a quantum mechanical excitation to a level n' (or n'+1 , since we require $n' \gg 1$) .But this is not the only way to derive quantal results from classical theory . Percival and Richards (1967) showed that the correct correspondence was between the frequency components of the energy and not the total energy .

Both the classical theory of emission/absorption of radiation (Landau and Lifshitz , 1962) and the classical perturbation theory of collisions (Fowler , 1925) depend on the Fourier expansion of the motion of the system . For instance , if r(t) is a position coordinate , it can be expanded in the form

$$r(t) = \sum_{s=-\infty}^{+\infty} r_s \exp(is\omega t)$$

where r_s and r_{-s} are the $\pm s$ th Fourier coefficients of r and give rise to emission and absorption at a frequency $s\omega$. Similarly , the energy ΔE^c transferred to the atom in a collision can be expressed as a sum over terms ΔE^c_s

$$\Delta E^c = \sum_{s=-\infty}^{+\infty} \Delta E^c_s$$

This leads to a new correspondence principle for collision induced transitions ,

Correspondence Principle 3

> The mean net energy transferred to an atom by a passing charged particle due to upward and downward transitions n - n' tends to coincide with the mean net energy transferred according to classical theory from independent Fourier components of order s and -s , provided the perturbation of the classical orbit is small and the probability of transition from the initial state is small

By the first requirement we mean that classical perturbation theory should be valid ; the second requires that quantum mechanical perturbation theory should be valid . The two are not the same . Their range of validity is different , and classical perturbation theory can be invoked in regions where quantum mechanical perturbation theory cannot , for instance in the case of small changes in the quantum numbers which do not significantly change the classical orbit .

Applying the above principle , and using detailed balance , Percival and Richards obtained a collision induced transition probability which , when integrated over impact parameter , produced a cross section which included a logarithmic term , in agreement with the quantum mechanical result . This shows why previous applications of classical mechanics to atomic scattering problems had given incorrect cross sections . In all of them the Fourier components had been treated as a single entity .E , whereas in fact each component contributes to a different process , and different components contribute to the same process .

2.3 Heisenberg's Correspondence Principle

The history of present day quantum mechanics is complicated (Jammer , 1966) , but its foundations were laid by Heisenberg . By applying the principle that only observables should appear in a dynamical system describing atomic phenomena , and since quantum mechanical matrix elements and classical Fourier components describe the same physical observables , he was able to deduce properties of quantum mechanical matrices through the correspondence principle .

Heisenberg's correspondence principle is most simply stated for one dimensional periodic motion of a particle with fundamental frequency ω and quantum number n . Any function of the classical position r , say $F^c(r)$, is also periodic and can be expressed as a Fourier series

$$F^c(r) = \sum_{s=-\infty}^{+\infty} F^c_s \exp(is\omega t)$$

Then Heisenberg's correspondence principle is that in the appropriate limit ,

$$\langle n' | F(r) | n \rangle = F^c_s \quad , \quad s = n' - n$$

where the Dirac notation for the quantal matrix elements has been used and where the state vectors are eigenfunctions of the unperturbed Hamiltonian H ,

$$H | n \rangle = E(n) | n \rangle$$

2.4 Ambiguities in the quantisation

The development of the old quantum theory was stimulated by research in spectroscopy . When Balmer found , in 1885 , that all the then known hydrogenic lines were predicted by the formula

$$\nu = Rgc(n_2^{-2} - n_1^{-2}) \quad ,$$

many attempts were made to derive this formula theoretically . In 1913 Bohr derived it by three different methods . In his second derivation he assumed a general relationship between the emitted energy E_n due to the formation of a stationary state and the frequency of revolution of the electron

$$E_n = f(n)\,\hbar\omega \quad ,$$

where $f(n)$ is an yet undetermined function of the integer n . On the basis of classical principles , Bohr obtained

$$E_n = \frac{\pi^2 me^4}{2h^3 f^2}$$

(in the usual notation) . Hence since

$$E_{n_2} - E_{n_1} = h\nu$$

then

$$\nu = \frac{\pi^2 me^4}{2h^3}\left\{ f^{-2}(n_2) - f^{-2}(n_1) \right\}$$

To obtain the functional dependence of f on n , Bohr had to rely on heuristic arguments and take recourse to the structure of the Balmer formula itself , in which the variable factor had the form

($n_2^{-2} - n_1^{-2}$) . To obtain such a factor , he concluded that $f(n)=cn$, c being a constant to be determined . To obtain the value of c , he considered a transition between two successive stationary states corresponding to $n_1 = n$ and $n_2 = n-1$, and obtained for the frequency of the radiation emitted

$$\nu = \frac{\pi^2 me^4}{2c^2h^3} \frac{2n-1}{n^2(n-1)^2} ,$$

and for the frequencies of revolution of the electron before and after the emission ,

$$\omega_n = \frac{\pi^2 me^4}{2c^3h^3n^3} , \quad \omega_{n-1} = \frac{\pi^2 mc^4}{2c^3h^3(n-1)^3} .$$

" If n is great , the ratio between the frequency before and after the emission will be very nearly equal to 1 ; and according to ordinary electrodynamics we should expect that the ratio between the frequency of radiation and the frequency of revolution also is very nearly equal to 1 . This condition will only be satisfied if $c = \frac{1}{2}$. " Thus

$$E_n = \tfrac{1}{2} n \hbar \omega .$$

The choice $f(n) = \frac{1}{2}n$ was therefore made not because of a priori theoretical considerations but because its asymptotic form produced results which agreed with observations at high values of n .

We now wish to quantize the action variable I in terms of Planck's constant . Sommerfeld assumed that

$$I = n\hbar$$

but while this choice is unambiguous for bound states , there is some logical difficulty in interpreting it for transitions between two states n_1 and n_2 . Presumably

$$I = f(n_1,n_2)\hbar \quad ,$$

but should one choose $I = n_1\hbar$, or $I = n_2\hbar$, or $I = \frac{1}{2}(n_1 + n_2)\hbar$? Of course in the limit where n_1 and n_2 are both large and differ little from each other the question is irrelevant since any form which had the correct asymptotic behaviour would be satisfactory . The question is extremely important if the correspondence principle is to be applied away from this limit , with for instance $n_1 = 1$ and $n_2 = 2$.

Although arguments may be put forward for using the initial or the final state parameters , the most reasonable suggestion would seem to be to use the arithmetic mean of these two quantities , whilst in no way assuming an "intermediate" state defined by that mean to exist during a transition . The limit necessarily does not distinguish between the two parameters n_1 and n_2 , and choosing their average gives them both equal weight . We shall show that letting

$$I = (n+\tfrac{1}{2}s)\hbar$$

with $n_1 = n$ and $n_2 = n+s$, good agreement is obtained for high values of n between results obtained using classical mechanics and the correspondence principle and results obtained using quantum mechanics .

A more ambitious and fruitful approach is to compare correspondence and quantal results for various low values of n and to choose

$$I = n_c \hbar$$

where $n_c = f(n_1, n_2)$ and is chosen so as to provide the best possible agreement between the two results at these low n values . Any such choice must tend asymptotically to n as $n \to \infty$ and $s/n \to 0$.

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CHAPTER III

MATRIX ELEMENTS

3.1 Simple Harmonic Potential

We consider in detail the application of the results quoted in the previous chapter to the case of a one dimensional harmonic potential . We recall that

$$I = \frac{1}{2\pi}\oint p \, dq \quad ,$$

and

$$w = \frac{\partial S}{\partial I} = \frac{\partial}{\partial I}\int p \, dq \quad .$$

For this potential , for a particle of mass m , the Hamiltonian

$$H = \frac{p^2}{2m} + \tfrac{1}{2} m\omega^2 q^2 \quad ,$$

and since the forces are conservative and the total energy must remain constant

$$p = \sqrt{2m\left(H - \tfrac{1}{2} m\omega^2 q^2 \right)} \quad ,$$

and

$$w = \sin^{-1}\left(\sqrt{\frac{m\omega}{2I}}\, q \right) + \text{constant} \quad .$$

Since

$$w = \omega t + \text{constant} \quad ,$$

the previous equation can be inverted to give

$$q = \sqrt{\frac{2I}{m\omega}} \sin(\omega t + \delta)$$

with δ a phase factor to be determined by the starting conditions . This trivial solution of the motion of a particle under the influence of a simple harmonic potential has been obtained using the methods of classical mechanics .

Suppose we now wish to investigate the behaviour of a quantum mechanical particle in a quantum mechanical harmonic potential , and require for instance transition amplitudes from a particular state . To find these we need matrix elements for those transitions . In the case of a simple harmonic potential these can easily be calculated quantum mechanically from first principles , but according to Heisenberg's form of the correspondence principle they can also be deduced by equating the matrix elements to an appropriate Fourier coefficient ,

$$\langle n | q | n+s \rangle \simeq q_s$$

$$q_s = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} e^{-is\omega t} \, q(t) \, dt$$

We now wish to fix the value of the phase factor δ . Since quantum mechanically we are generally only interested in the modulus squared of the complex quantities we calculate , we can only compare matrix elements and Fourier transforms to within a phase factor . For convenience , in order that they have the same phase , we set δ to $\pi/2$ so that

$$q(t) = \sqrt{\frac{2I}{m\omega}} \cos(\omega t)$$

and we find that the only non-zero q_s are those corresponding to a change in the quantum number of ±1 ,

$$q_s = \left(\frac{I}{2m\omega}\right)^{\frac{1}{2}} \qquad , \quad s = \pm 1$$

$$q_s = 0 \qquad , \quad s \neq \pm 1$$

To equate this with the quantum mechanical matrix elements it is necessary to quantise the action variable I . As indicated in the previous chapter , there is no unique way of doing this , so we let $I = n_c\hbar$, with n_c an as yet undetermined function of n and s which may initially be chosen to be $n_c = n+\frac{1}{2}s$. Substituting for I and letting q_s equal the matrix element for q ,

$$\langle n\,|\,q\,|\,n{+}s\rangle = \left(\frac{n_c\hbar}{2m\omega}\right)^{\frac{1}{2}} \quad , \quad s = \pm 1$$

$$\langle n\,|\,q\,|\,n{+}s\rangle = 0 \quad , \quad s \neq \pm 1$$

To check the validity of Heisenberg's correspondence principle , we can compare the matrix elements above with those calculated directly from quantum mechanics . We need first the harmonic oscillator wavefunctions u_n obtained by solving Schroedinger's equation

$$-\frac{\hbar^2}{2m}\frac{d^2u_n}{dq^2} + \tfrac{1}{2}m\omega^2q^2u_n = E_n u_n$$

The wavefunction u_n has the well known form

$$u_n = b^{\frac{1}{2}}\left(\pi^{\frac{1}{2}}2^n n\right)^{-\frac{1}{2}} \exp(-\tfrac{1}{2}b^2q^2)\;H_n(bq)$$

where $H_n(bq)$ is the nth Hermitian polynomial and $b = \sqrt{m\omega/\hbar}$. The matrix element of the position q is proportional to the integral

$$\int dq\; q\; H_n^{*}(bq)\; H_{n+s}(bq)\; \exp(-b^2q^2)$$

which can be evaluated to give

$$\langle n \,|\, q \,|\, n+1 \rangle \;=\; \left(\frac{(n+1)\hbar}{2m\omega}\right)^{\frac{1}{2}} \quad ,$$

$$\langle n \,|\, q \,|\, n-1 \rangle \;=\; \left(\frac{n\hbar}{2m\omega}\right)^{\frac{1}{2}} \quad ,$$

$$\langle n \,|\, q \,|\, n+s \rangle \;=\; 0 \qquad , \quad s \neq \pm 1$$

Thus the quantal result and the correspondence result are essentially the same ; if we choose $n_c = n+\frac{1}{2}s$ their ratio is $1 + s/2n$, which is small for large $n \gg 1$ and small s of order unity . However this choice of n_c does not distinguish between upward and downward transitions and implies that the transitions $n \rightarrow n+1$ and $n+1 \rightarrow n$ produce identical results , in agreement with the quantal results . A better choice for n_c in this case is $n_c = \max(n,n+s)$, which provides correspondence results identical to the quantum mechanical ones .

One of the advantages of using the correspondence principle to evaluate matrix elements is that , having solved the equation of motion of the particle in the potential under consideration , it is relatively simple to calculate the matrix element of any function of that position . This involves integrals of the form

$$\int dt\; e^{-is\omega t}\; f(q(t))$$

The equivalent quantum mechanical method involves solving Schroedinger's equation for the wavefunction u_n and evaluating integrals of the form

$$\int dq \, u_n^*(q) \, u_{n+s}(q) \, f(q)$$

which are in general more difficult to evaluate . We can for instance evaluate the matrix elements of higher powers of q and obtain a general equation for the Fourier transform of q^k , k being some positive integer ,

$$\langle n \,|\, q^k \,|\, n+s \rangle = \left(\frac{\hbar n_c}{2m\omega} \right)^{k/2} \frac{k\,!}{\left(\frac{k-s}{2}\right)!\left(\frac{k+s}{2}\right)!}$$

with the following selection rule

$$s = k - 2l \quad , \quad l = 0,1,2,\ldots,k$$

One consequence of this selection rule is that the mean value of q^k is zero if k is odd . This was first noticed quantum mechanically by Bell and Guggenheim in 1936 in their calculations of mean values of dipole moments . We see here that it is but a special case of a more general selection rule .

There is no known equivalent quantum mechanical formula for the matrix element of q^k , but given a value of k the appropriate integral can be calculated using for example generating functions for the Hermitian polynomials . Table 1 shows results for the first few values of k . Comparing the matrix elements obtained using the correspondence principle with those obtained using quantum mechanics we find that the two are very similar for high values of n and low values of s , as predicted by the correspondence principle . However we also find that using the substitution

$$(n_c)^s = \frac{(n+s)!}{n!}$$

Matrix element	Correspondence value	Quantum mechanical value
$\langle n\vert p\vert n+1\rangle$	$An_c^{1/2}$	$A(n+1)^{1/2}$
$\langle n\vert p\vert n-1\rangle$	$-An_c^{1/2}$	$-A(n)^{1/2}$
$\langle n\vert p^2\vert n+2\rangle$	A^2n_c	$A^2\{(n+1)(n+2)\}^{1/2}$
$\langle n\vert p^2\vert n\rangle$	$-2A^2n_c$	$-2A^2(n+\frac{1}{2})$
$\langle n\vert p^2\vert n-2\rangle$	A^2n_c	$A^2\{n(n-1)\}^{1/2}$
$\langle n\vert p^3\vert n+3\rangle$	$A^3n_c^{3/2}$	$A^3\{(n+1)(n+2)(n+3)\}^{1/2}$
$\langle n\vert p^3\vert n+1\rangle$	$-3A^3n_c^{3/2}$	$-3A^3(n+1)^{3/2}$
$\langle n\vert p^3\vert n-1\rangle$	$3A^3n_c^{3/2}$	$3A^2n^{3/2}$
$\langle n\vert p^3\vert n-3\rangle$	$-A^3n_c^{3/2}$	$-A^3\{n(n-1)(n-2)\}^{1/2}$
$\langle n\vert p^4\vert n+4\rangle$	$A^4n_c^2$	$A^4\{(n+1)(n+2)(n+3)(n+4)\}^{1/2}$
$*\langle n\vert p^4\vert n+2\rangle$	$-4A^4n_c^2$	$-4A^4(n+\frac{3}{2})\{(n+1)(n+2)\}^{1/2}$
$*\langle n\vert p^4\vert n\rangle$	$6A^4n_c^2$	$6A^4(n^2+n+\frac{1}{2})$
$*\langle n\vert p^4\vert n-2\rangle$	$-4A^4n_c^2$	$-4A^4(n-\frac{1}{2})\{n(n-1)\}^{1/2}$
$\langle n\vert p^4\vert n-4\rangle$	$A^4n_c^2$	$A^4\{n(n-1)(n-2)(n-3)\}^{1/2}$

Table 1

Comparison of correspondence and quantum mechanical (Wilson et al) matrix elements of p^k, $k = 1,2,3,4$. ($A = i(\frac{1}{2}m\hbar\omega)^{\frac{1}{2}}$) A similar table is obtained for q^k.

the two sets of results are identical for $k = 1,2,3$ and for all matrix elements of the form $\langle n | q^k | n \pm k \rangle$. We shall make use of this substitution later and shall refer to it as the "factorial" substitution. For small values of s and large values of n compared to unity, a careful expansion leads to

$$n_c = n + \tfrac{1}{2}s + \tfrac{1}{2}$$

so that for $s = 0$

$$n_c = n + \tfrac{1}{2}$$

This substitution leads to a mean value of q^2 which is identical with the quantum mechanical one. The mean value of q^4 obtained is proportional to $(n^2 + n + \tfrac{1}{4})$ whereas the quantum mechanically calculated mean value is proportional to $(n^2 + n + \tfrac{1}{2})$. For $n = 1$, well outside the region of validity of the correspondence principle, these two mean values agree to 10 %; for $n = 10$ they agree to 0.2 %. It is not understood why some correspondence matrix elements and their quantum mechanical counterparts are identical while the rest are only very similar and nearly equal. An explanation may lie in the work of Norcliffe and Percival on correspondence identities, (1968, 1969).

A similar procedure yields matrix elements of the conjugate momentum

$$p = m\frac{dq}{dt} = m^{\frac{1}{2}}(2I\omega)^{\frac{1}{2}} \sin(\omega t)$$

from which

$$\langle n | p^k | n+s \rangle = i^{2k-s}\, m^{\frac{1}{2}k} \left(\tfrac{1}{2} n_c \hbar\omega\right)^{\frac{1}{2}k} \frac{k!}{\left(\frac{k-s}{2}\right)!\left(\frac{k+s}{2}\right)!}$$

with the restriction on s that

$$s = k - 2l \quad , \quad l = 0,1,2,\ldots,k$$

The agreement with the quantum mechanically calculated matrix elements is identical with the agreement of matrix elements of q^k described above .

More interesting perhaps is the calculation of matrix elements of products of position and momentum . All equations now have to be written in terms of Poisson brackets since quantum mechanically we are dealing with non-commuting operators . In going from classical mechanics to quantum mechanics and vice versa we replace p by $-i\hbar\,\partial/\partial q$, write the classical Hamiltonian equations in terms of Poisson brackets , and replace the Poisson brackets by commutator brackets ,

$$\left\{A,B\right\} \leftrightarrow \frac{1}{i\hbar}\left[A,B\right]$$

(Note that the algebraic properties of Poisson brackets and commutator brackets are identical .) For all contact transformations involving canonical variables Q_i and P_i the following relations hold for the Poisson brackets ,

$$\left\{Q_i,P_j\right\} = \delta_{ij}$$

$$\left\{Q_i,Q_j\right\} = 0$$

$$\left\{P_i,P_j\right\} = 0$$

Thus if we are looking at the mean value of pq we have the special case that quantum mechanically

$$\langle n \,|\, [p,q] \,|\, n \rangle = -i\hbar$$

which should be compared with $i\hbar$ times the Fourier coefficient of p,q

$$\langle n \,|\, \{p,q\} \,|\, n \rangle = -1$$

This applies especially to the calculation of the mean value of pq . For $s \neq 0$, we find that classically

$$\langle n \,|\, pq \,|\, n+s \rangle = \pm i\hbar n_c \qquad , \qquad s = \pm 2$$

$$\langle n \,|\, pq \,|\, n+s \rangle = 0 \qquad , \qquad s \neq \pm 2$$

Using the substitution $n_c = n + \tfrac{1}{2}s + \tfrac{1}{2}$, this is in exact agreement with the quantum mechanical result .

The analysis described in this section can be extended indefinitely to matrix elements of any function of p or q , which may be difficult to evaluate using quantum mechanics ; for example the matrix elements of q^a or $\exp(iap)$, where a is not necessarily a positive integer

$$\langle n \,|\, q^a \,|\, n+s \rangle = \left(\frac{\hbar n_c}{2m}\right)^{\frac{1}{2}a} \frac{\Gamma(a+1)}{\Gamma\left(\frac{a+s}{2}+1\right)\Gamma\left(\frac{a-s}{2}+1\right)}$$

$$\langle n \,|\, e^{iap} \,|\, n+s \rangle = J_s\left(a\sqrt{\frac{2\hbar}{m}n_c}\right)$$

with $J_s(x)$ the Bessel function of order s .

The results presented in this section have been used by Clark and Dickinson (1971) who used the correspondence principle for strongly coupled states (Percival and Richards, 1970) to obtain approximate transition probabilities for a forced harmonic oscillator. They formally and numerically showed that the correspondence principle results have a much larger range of validity than those obtained using first order quantum mechanical perturbation theory, even for 0 → 1 transitions.

3.2 Morse Potential

The Morse potential is one of the best approximations for all values of the radial coordinate q of a diatomic molecule . It is a one-dimensional potential which may be transformedwith the radial part of the Coulomb potential for a particular angular momentum by the transform $q-q_e \rightarrow \log(r)$, where q_e is the equilibrium value of q . The Morse potential is defined by

$$V(q) \;=\; D\,(\,1 - e^{-a(q-q_e)}\,)^2$$

The values of D , a , and q_e are assumed known . The parameter D indicates the depth of the potential and the parameter a indicates its range (Fig. 2) .

We apply a contact transformation S to the system such that I , the new conjugate momentum,is a constant of the motion and the new coordinate , v , is given by $\partial S/\partial I$. The new conjugate momentum is defined by

$$I \;=\; \frac{1}{2\pi}\oint p\,dq$$

For convenience , we define the following quantities :

$$Q \;=\; q-q_e \;\;;\;\; b^2 \;=\; \frac{E}{D} \;\;;\;\; x \;=\; 1 - e^{-aQ}$$

Substituting for p and q in the above equation ,

$$I \;=\; \frac{(2mD)^{\frac{1}{2}}}{2\pi}\oint (\,b^2 - x^2\,)^{\frac{1}{2}}\,dQ$$

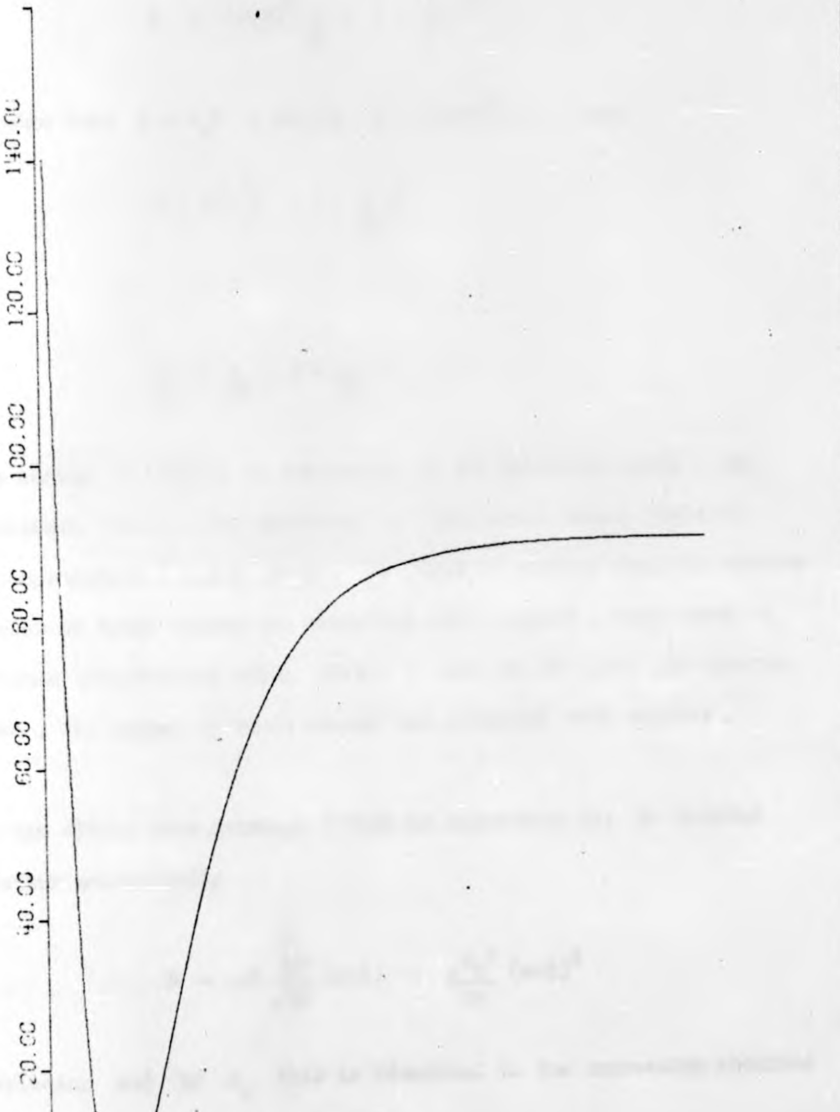
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
← V(q) →
0.00
q_e
2.00
4.00
6.00
8.00
10.00
→ q →

Fig. 2

from which -

$$I = (2mD)^{\frac{1}{2}} \frac{1}{a} \left(1 - \sqrt{1-b^2} \right)$$

We know that $I = n_c \hbar$; define $t = (2mD)^{\frac{1}{2}}/a\hbar$, then

$$1 - b^2 = \left(1 - \frac{n_c}{t} \right)^2$$

or

$$\frac{E}{D} = \frac{n_c}{t} \left(2 - \frac{n_c}{t} \right)$$

The energy E refers to the energy of the nth bound state , and therefore $E < D$. The parameter t then has a simple physical interpretation ; since $E < D$, t must be greater than the maximum number of bound states the potential will support . Since when n_c reaches this maximum value $E \simeq D$, t must be of order ,but greater than , the number of bound states the potential will support .

We can obtain from Herzberg (1950) an expression for E derived quantum mechanically

$$E = a\hbar \sqrt{\frac{D}{2m}} (n+\tfrac{1}{2}) - \frac{a^2\hbar^2}{2m} (n+\tfrac{1}{2})^2$$

Replacing $n+\frac{1}{2}$ by n_c this is identical to the expression obtained using the correspondence principle .

It is now possible to obtain values for the frequency ω and for w .

$$\omega = \frac{\partial E}{\partial I} = \frac{a^2\hbar}{m} (t - n_c)$$

Since

$$S = \int p(I)\, dq$$

then

$$w = \frac{\partial S}{\partial I} = (1 - b^2)^{\frac{1}{2}} \int (-y^2 + y^2 b^2 + 2y - 1)^{-\frac{1}{2}}\, dy$$

where we have substituted $y = \exp(-aQ)$. Thus

$$\sin(w) = b^{-1} \left\{ (1 - b^2) \exp(aQ) - 1 \right\}$$

and finally the position coordinate Q is given by

$$aQ = \log(1 + b \sin(w)) - \log(1-b)$$

(We use the symbol log rather than ln to prevent any confusion with the quantum numbers used later in the text.) . The position coordinate is a periodic function of w and can therefore be expanded in a Fourier series

$$aQ = \sum_s B_s \exp(isw)$$

whose coefficients are given by

$$\begin{aligned} B_s &= \int_0^{2\pi} \frac{aQ}{2\pi} \exp(-isw)\, dw \\ &= \frac{1}{2\pi} \int_0^{2\pi} \exp(-isw) \log(1 + b \sin(w))\, dw \end{aligned}$$

To evaluate the integral , we use complex variables and let $z = -ie^{-iw}$.

Then

$$B_s = \frac{-i^{s-1}}{2\pi} \int_C z^{s-1} \log\left\{\frac{b}{2z}\left(z^2 + \frac{2z}{b} + 1\right)\right\} dz$$

The log term splits into three parts , leading to

$$B_s = -\frac{i^{s-1}}{2\pi}\int_c z^{s-1}\log\left(\frac{b}{2}\right) dz$$

$$+\frac{i^{s-1}}{2\pi}\int_c z^{s-1}\log(z)\, dz$$

$$-\frac{i^{s-1}}{2\pi}\int_c z^{s-1}\log\left(z^2 + \frac{2z}{b} + 1\right)$$

$$= I_1 + I_2 + I_3$$

The first term , I_1 , is zero . To calculate I_2 , cut along the positive real axis from 0 to 1 . Above the cut , $z = x + i$ and $\log(z) = \log(x)$, whilst below the cut $z = x - i$ and $\log(z) = \log(x)+2i\pi$ Since there are no singularities in the contour indicated (Fig 2a) we find that

$$I_2 = \frac{i^s}{s}$$

To calculate I_3 we note that only one of the roots of the quadratic lies inside the unit circle (Fig. 2b) so that I_3 can be simplified to

$$I_3 = -\frac{i^{s-1}}{2\pi}\int z^{s-1}\log(z-c)\, dz$$

where c is the root of the quadratic that lies within the unit circle . The form of I_3 is similar to that of I_2 and we find

$$I_3 = \frac{i^s}{s}(c^s - 1)$$

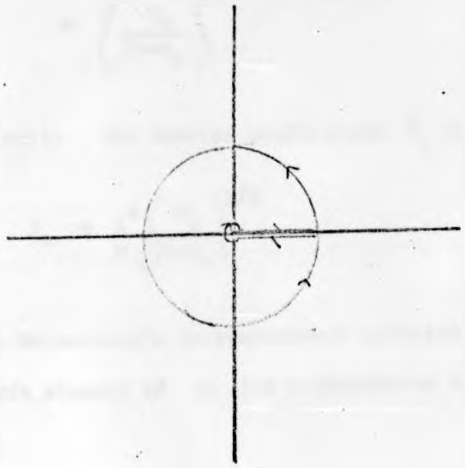

Fig 2a

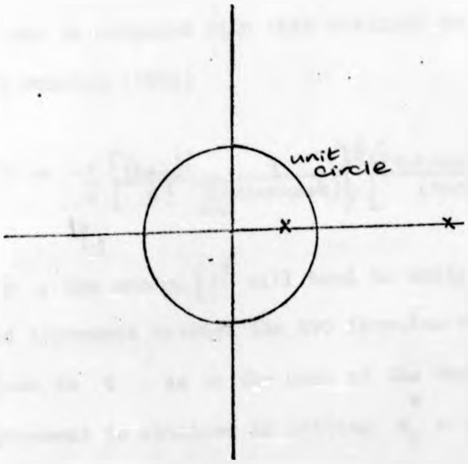

Fig 2b

contours for I_2 and I_3

with

$$c = -b^{-1} + (b^{-2} - 1)^{\frac{1}{2}}$$

$$= \left(\frac{n_c}{2t-n_c}\right)^{\frac{1}{2}}$$

Collecting results , the Fourier coefficient B_s is given by

$$B_s = \frac{i^s}{s}\left\{\frac{n_c}{2t-n_c}\right\}^{s/2}$$

We now invoke Heisenberg's correspondence principle and equate B_s with the matrix element of aQ for a transition between states n and $n+s$,

$$\langle n\,|aQ\,|n+s\rangle = \frac{i^s}{s}\left\{n_c^s\,\frac{1}{(2t-n_c)^s}\right\}^{\frac{1}{2}}$$

This formula can be compared with that obtained quantum mechanically by Herman and Schuler (1953)

$$\langle n\,|\,aQ\,|n+s\rangle = -\frac{1}{s}\left\{\frac{(n+s)!}{n!}\,\frac{1}{\prod_{k=0}^{s}(2t-n-s+k)}\right\}^{\frac{1}{2}}\left\{\frac{(t-n-s-\frac{1}{2})(t-n-\frac{1}{2})}{(t-n-\frac{1}{2}s-\frac{1}{2})^2}\right\}^{\frac{1}{2}}$$

For $s \ll t-n-\frac{1}{2}$, the second $\{\}^{\frac{1}{2}}$ will tend to unity , and in general there is good agreement between the two formulae except when n_c or n_c+s is close to t . As in the case of the Harmonic potential , very good agreement is obtained by letting $n_c^s = (n+s)!/n!$ in which case the two formulae become identical as $s, n \ll t$, since in this limit the particle executes simple harmonic motion .

For $s = 0$, the mean value of aQ is

$$\langle n | aQ | n \rangle = \log\left(1 + \frac{n_c}{2t}\right)$$

with $$n_c = n + \tfrac{1}{2}$$

Momentum in the Morse potential

The equation for the momentum can be obtained by differentiating that for the position and multiplying by a mass factor , m .

$$p = \frac{mb\omega}{a} \frac{\cos(w)}{1 + b\sin(w)}$$

This can be expanded in a Fourier series whose coefficients can be calculated by contour integration . Equating these coefficients with the matrix elements of p ,

$$\langle n | p | n+s \rangle = -i^{s-1} \frac{mb\omega}{2a\pi} \int_{c} \frac{(z^2-1)\, z^{s-1}}{(z-c)(z-1/c)}\, dz$$

There is a pole of order 1 at $z = c$, and when $s = 0$ there is a further pole of order 1 at $z = 0$, so that

$$\langle n | p | n+s \rangle = -i^{s-1} \frac{m\omega}{a} \left\{\frac{n_c}{2t-n_c}\right\}^{\frac{1}{2}s} (1-\delta_{0,s})$$

with $\delta_{0,s} = 1$ if $s = 0$ and 0 otherwise . The matrix elements of p and Q are in fact related by

$$\langle n | p | n+s \rangle = ims\omega \langle n | Q | n+s \rangle$$

and this relation is often used in quantum mechanics to obtain the matrix element of the momentum .

Of more interest in quantum mechanics are the matrix elements of momentum squared . An application of the correspondence principle leads to

$$\langle n \,|\, p^2 \,|\, n+s \rangle = \frac{-i}{2\pi}^{s-1} \frac{m^2\omega^2}{a^2} \int_C \frac{(z^2-1)^2 \, z^{s-1}}{(z-c)^2(z-1/c)^2} \, dz$$

from which , substituting for ω ,

$$\langle n \,|\, p^2 \,|\, n+s \rangle = -i^{s-1} a^2 \hbar^2 \left\{ \frac{n_c}{2t-n_c} \right\}^{\frac{1}{2}s} (t-n_c) \left\{ t(s-1) - n_c s + \delta_{0,s}(t-n_c) \right\}$$

Quantum mechanically , the eigenfunctions of the Morse potential are conveniently expressed as

$$u_n = N_n^{-\frac{1}{2}} \, y^{-\frac{1}{2}} \, M_{t,t-n-\frac{1}{2}}(y)$$

where

$$y = 2t \, e^{-aQ}$$

$$N_n = \frac{\Gamma(n+1)\Gamma(2t-2n)\Gamma(2t-2n-1)}{a\Gamma(2t-n)}$$

and the $M_{t,u}(y)$ is a Whittaker function (Slater,1960) . Using the integrals given by Slater , Greenawalt and Dickinson derived (1969) an expression for the matrix element of d^2/dq^2 , which , inserting a factor of $\frac{1}{2}$ which was erroneously omitted from their published formula , can be written as

$$\langle n | \frac{d^2}{dq^2} | n+s \rangle = (-1)^s \tfrac{1}{2}a \frac{\Gamma(2t-2n)\Gamma(2t-2n-2s)\Gamma(n+s+1)}{(N_n N_{n+s})^{\frac{1}{2}}\,\Gamma(2t-n)}$$

$$* \left\{ t(s-1+\delta_{0,s}) - \tfrac{1}{2}s(2n+s+1) + \tfrac{1}{2}(2n+1)\delta_{0,s} \right\}$$

When $s = 0$, and $n_c = n + \frac{1}{2}$, the correspondence principle and quantum mechanics provide identical expressions for the mean value

$$\langle n | p^2 | n \rangle = -a^2\hbar^2 \, (t-n-\tfrac{1}{2})(n+\tfrac{1}{2})$$

For non-diagonal elements , the quantum mechanical formula can be simplified and compared with the correspondence principle one , each being denoted by the superscripts q and c respectively

$$\langle n | p^2 | n+s \rangle^q = (-1)^{s-1} a^2\hbar^2 \left\{ \frac{(n+s)!}{n!} \, (t-n-\tfrac{1}{2})(t-n-s-\tfrac{1}{2}) \frac{\Gamma(2t-n-s)}{\Gamma(2t-n)} \right]^{\frac{1}{2}}$$

$$* \left\{ t(s-1) - s(n+\tfrac{1}{2}s+\tfrac{1}{2}) \right\}$$

$$\langle n | p^2 | n+s \rangle^c = -i^{s-1} \, a^2\hbar^2 \left\{ n_c^s \qquad (t-n_c)^2 \qquad \frac{1}{(2t-n_c)^s} \right\}^{\frac{1}{2}}$$

$$* \left\{ t(s-1) - sn_c \right\}$$

A term by term comparison of the two formulae shows that they both have the same functional dependence on n,s,t ; for $s<n$, the factorial substitution for n_c , or its low s expansion $n_c = n+\frac{1}{2}s+\frac{1}{2}$, both give agreement to at least $s/(t-n)$, and better for $n<\frac{1}{2}t$. Figure 3 shows the excellent agreement for $s = 1$ and various values of n,t and illustrates how the correspondence principle result starts to disagree with the quantum mechanical one when $n+s$ is of order t .

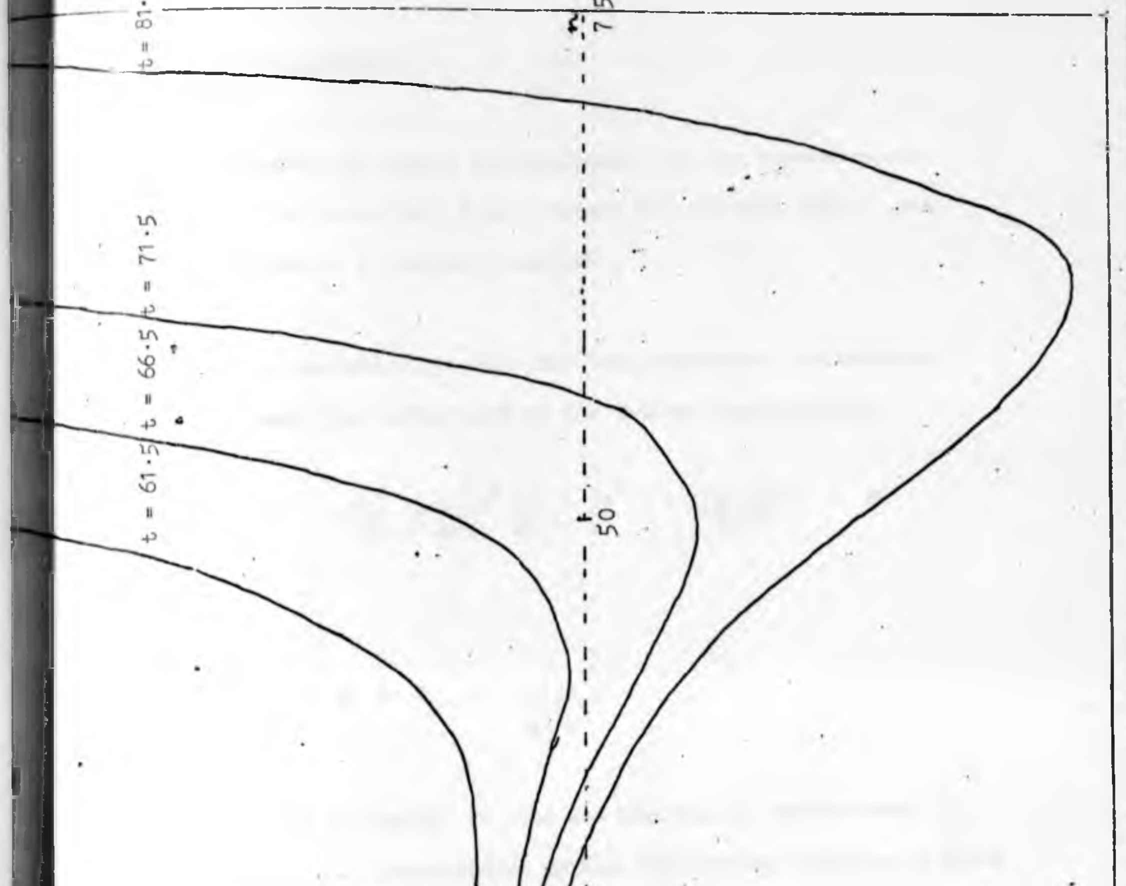

Figure 3
Percentage difference between quantum and correspondence
$\langle n|p^2|n-1\rangle$ v.s. n

3.3 Coulomb potential

We now consider in detail the application of the correspondence principle to the motion of an electron in a central field , and in particular in a Coulomb potential .

The quantum mechanical problem has been exaustively investigated ; consider only the radial part of the Coulomb wave equation

$$-\frac{h^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left\{r^2\frac{dR}{dt}\right\} - \frac{Ze^2}{r}R + \frac{l(l+1)h^2R}{2\mu r^2} = ER$$

and

$$E = E_n = -\frac{\mu(Ze^2)^2}{2h^2n^2}$$

for a nucleus of charge Ze and and electron of reduced mass μ and charge $-e$. The solution to the Schroedinger equation is given in terms of Laguerre polynomials

$$R_{n,l}(r) \propto e^{-\frac{1}{2}r_1} r_1^{l} L_{n+l}^{2l+1}(r_1) \quad , \quad r_1 = \left\{-\frac{8\mu E}{\hbar^2}\right\}^{1/2} r$$

and we are interested in matrix elements of the form

$$< n \mid F(r) \mid n+s > = \int_0^\infty r^2 R_{n,l}(r)\, F(r)\, R_{n+s,l}(r)\, dr$$

with $F(r)$ some general function of r .

The equivalent classical problem consists of first solving the equation of motion of the electron . This was done by Born in 1927 . Using polar coordinates r, θ, ϕ, the kinetic energy T is

$$T = \tfrac{1}{2}\mu(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2(\theta)\dot{\phi}^2)$$

or alternatively using conjugate momenta

$$p_r = \mu\dot{r}$$

$$p_\theta = \mu r^2\dot{\theta}$$

$$p_\phi = \mu r^2\sin^2(\theta)\ \dot{\phi}$$

we can write

$$T = \tfrac{1}{2}\mu^{-1}(p_r^2 + r^{-2}p_\theta^2 + r^{-2}\sin^{-2}(\theta)p_\phi^2)$$

Since the Hamiltonian H is time independent ,

$$H = E = T + V(r)$$

and writing

$$S = S_r(r) + S_\theta(\theta) + S_\phi(\phi)$$

the Hamilton Jacobi equation

$$\left\{\frac{\partial S}{\partial r}\right\}^2 + r^{-2}\left\{\frac{\partial S}{\partial \theta}\right\}^2 + r^{-2}\sin^{-2}(\theta)\left\{\frac{\partial S}{\partial \phi}\right\}^2 + 2\mu\left\{V(r) - E\right\} = 0$$

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the Hamilton Jacobi equation

$$\left\{\frac{\partial S}{\partial r}\right\}^2 + r^{-2}\left\{\frac{\partial S}{\partial \theta}\right\}^2 + r^{-2}\sin^{-2}(\theta)\left\{\frac{\partial S}{\partial \phi}\right\}^2 + 2\mu\left\{V(r) - E\right\} = 0$$

splits into three differential equations, with solutions

$$\frac{dS_\phi}{d\phi} = P_\phi = M$$

$$\frac{dS_\theta}{d\theta} = P_\theta = \left\{L^2 - M^2\sin^{-2}\theta\right\}^{\frac{1}{2}}$$

$$\frac{dSr}{dr} = Pr = \left\{2\mu(E-V) - L^2r^{-2}\right\}^{\frac{1}{2}}$$

with L and M integration constants. In fact

$$M = \mu r^2\sin^2\theta\,\dot{\phi}$$

is the angular momentum about the polar axis (the line $\theta = o$) and

$$L = \mu r\left\{(r\dot{\theta})^2 + (r\sin\theta\,\dot{\phi})^2\right\}^{\frac{1}{2}}$$

$$= \mu|\underline{r}\times\dot{\underline{r}}|$$

is the magnitude of the resultant angular momentum. Since the system is not subject to external forces, the orbit of the electron lies in a plane; this plane is inclined at an angle α to the (r,ϕ) plane, with

$$M = L\cos(\alpha)$$

Note that the requirement that pr, p_θ, p_ϕ are real places constraints on θ and (E-V). There are no restrictions on ϕ, which is a periodic function of time. The condition that

$$\left\{L^2 - M^2\sin^{-2}\theta\right\}^{\frac{1}{2}}$$

be real requires that

$$|\sin\theta| \geq M/L$$

so θ performs a libration about $\theta = \pi/2$ with limits $\pm\alpha$, so that $\theta_{min} = \pi/2 - \alpha$, $\theta_{max} = \pi/2 + \alpha$.

The requirement that

$$2\,\Gamma(E-V) - L^2 r^{-2}$$

be real, and the characteristics of that function, determine the motion in the potential. Since we are interested in the Coulomb potential, we shall only consider attractive fields. $V(r)$ is then negative, and E may be positive or negative. The detailed behaviour of the radicant, and the location of its zeros, will depend on the sign of E, the behaviour of $V(r)$ as $r \rightarrow 0$ and $r \rightarrow \infty$, and the value of L. Thus if $E = 0$, and $V(r) \propto -r^{-k}$, the orbits will get infinitely close to the centre of force if $k > 2$. If $k \leq 2$, there exist bound orbits corresponding to solutions of the Hamilton-Jacobi equation, in which case we can apply the methods developed for periodic systems.

We calculate the actions I_r, I_θ, I_ϕ corresponding to p_r, p_θ, p_ϕ.

$$I_\phi = (2\pi)^{-1} \oint p_\phi \, d\phi .$$

$$\therefore \quad I_\phi = M$$

Since p_θ is only real for $\theta_{\min} < \theta < \theta_{\max}$,

$$I_\theta = 1/\pi \int_{\theta_{\min}}^{\theta_{\max}} p_\theta \, d\theta$$

$$= 2/\pi \int_{\theta_{\min}}^{\pi} \left\{ L^2 - M^2 \sin^{-2}\theta \right\}^{\frac{1}{2}} d\theta$$

Substituting $u = \sin^2\theta$,

$$I_\theta = 1/\pi \int \left\{ \frac{L^2 u - M^2}{1 - u} \right\}^{\frac{1}{2}} \frac{du}{u}$$

the limits being $(M/L)^2$ and 1. To perform this integral we notice that replacing u by u^{-1} changes the sign and interchanges L and M, which shows that I_θ is a function of (L - M). Furthermore, when M = 0,

$$I_\theta = L,$$

$$\therefore \quad I_\theta = L - M.$$

To work out I_r,

$$I_r = 1/2\pi \oint \left\{ 2\mu(E-V) - (I_\theta + I_\phi)^2 r^{-2} \right\}^{\frac{1}{2}} dr$$

we need detailed knowledge of V(r), to calculate the behaviour of the energy E as a function of the I's, which we will later quantize. We therefore look at the simplest attractive potential which is proportional to r^{-k}, $k \leq 2$:

$$V(r) = - \frac{\text{constant}}{r}$$

If the constant is set to Ze^2, the potential defines the mutual attraction between a nucleus of charge Ze and an electron of charge e.

Substituting for V and using complex integration,

$$I_r = \frac{\mu^{\frac{1}{2}} Z e^2}{(-2E)^{\frac{1}{2}}} - I_\theta - I_\phi$$

so that

$$E = - \frac{\mu Z^2 e^4}{2(I_r + I_\theta + I_\phi)^2}$$

We see that the motion is degenerate, since the energy is independent of both L and M, the total angular momentum and its resultant magnitude. Following Born, we define new variables I_1, I_2, I_3, and w_1, w_2, w_3, such that

$$I_1 = I_r + I_\theta + I_\phi \quad , \quad w_1 = w_r$$

$$I_2 = I_\theta + I_\phi \quad , \quad w_2 = w_\theta - w_r$$

$$I_3 = I_\phi \quad , \quad w_3 = w_\phi - w_\theta$$

Then, for a given atom, I_1 uniquely defines the energy, I_2 uniquely defines the angular momentum, and I_3 the component of angular momentum along the polar axis;

$$E = -\frac{\mu Z^2 e^4}{2 I_1^2}$$

$$L = I_2$$

$$M = I_3$$

we now quantize all three of these actions,

$$I_1 = n\hbar$$

$$I_2 = l\hbar$$

$$I_3 = m\hbar$$

To obtain an equation of motion for the bound particle, we use

$$w_r = w_1 = \frac{\partial S}{\partial I_1}$$

$$\text{i.e.} \quad w_1 = \int \frac{\partial p_r}{\partial I_1} \, dr$$

$$= \int \frac{\mu \omega_1}{\left\{ 2\mu (V-E) - \frac{I_2^2}{r^2} \right\}^{\frac{1}{2}}} \, dr$$

with $\omega_1 = \partial E / \partial I_1$, so that

$$dt = \frac{dw}{\omega_1} = \frac{\mu}{\left\{ 2\mu (V-E) - \frac{I_2^2}{r^2} \right\}^{\frac{1}{2}}} \, dr$$

which would give us r as a function of time. However, it is more convenient to first consider the motion as a function of the radial distance r and an angle ψ in the plane of the motion. Since the angular momentum is I_2,

$$\mu r^2 d\psi = I_2 \; dt$$

using which we can eliminate dt from the equation of motion,

$$\frac{d\psi}{dr} = \frac{I_2}{r^2 \left\{ -2\mu E + \frac{2\mu Ze^2}{r} - \frac{I_2^2}{r^2} \right\}^{\frac{1}{2}}}$$

Integration gives

$$\psi - \psi_0 = \cos^{-1} \left\{ \frac{I_2^2 - \mu Ze^2 r}{r \left(\mu^2 Z^2 e^4 - 2\mu E I_2^2 \right)^{1/2}} \right\}$$

If we write

$$d = \frac{I_2^2}{\mu Ze^2} \quad ; \quad \epsilon^2 = 1 + \frac{2EI_2^2}{\mu Z^2 e^4}$$

then

$$r = \frac{d}{1 + \epsilon \cos(\psi - \psi_0)}$$

which is the equation of an ellipse, with eccentricity ϵ and semi-latus rectum d, and a focal point at the origin of the coordinates.

The eccentricity can be more conveniently expressed in terms of the quantum numbers l and n.

$$\epsilon^2 = 1 - \frac{l^2}{n^2}$$

and can be used to evaluate another useful property of the ellipse, the semi-major axis a given by

$$a = \frac{d}{1-\epsilon^2} = \frac{I_1^2}{\mu Z e^2}$$

Before finally proceeding to the calculation of matrix elements we return to the calculation of the motion as a function of time. We find that

$$w_1 = \frac{1}{2\pi} \int \frac{\mu r \, w_1 \, dr}{\left[-2\mu E \left\{ a(1+\epsilon) - r \right\} \left\{ r - a(1-\epsilon) \right\} \right]^{\frac{1}{2}}}$$

Letting $r = a(1 - \epsilon \cos u)$, gives

$$w_1 = u - \epsilon \sin u = \omega_1 t$$

which defines $r(t)$, (with $r(0)$ = perihelion)

To summarize the results obtained, the energy of the motion is

$$E = - \frac{\mu Z^2 e^4}{2 I_1^2} ,$$

the motion is confined to an ellipse of eccentricity

$$\epsilon^2 = 1 - \frac{l^2}{n^2} ,$$

and semi-major axis

$$a = \frac{I_1^2}{\mu Z e^2}$$

and the normal to the plane of the ellipse is inclined at an angle α to the polar axis of the $r\,\theta\,\phi$ plane, with

$$\cos(\alpha) = \frac{m}{l}$$

The motion evolves through time as

$$r = a \quad (1 - \epsilon \cos u)$$

with $\omega_1 t = u - \epsilon \sin u$

$$\omega_1 = \mu \frac{Z^2 e^4}{I_1^{\,3}}$$

(the last being Kepler's 3rd law),

$$I_1 = n\hbar .$$

Furthermore, defining a new set of rectangular coordinates ξ and η such that ξ is along the major axis of the ellipse and the origin is at the centre of force,

$$\xi = a(\cos u - \epsilon)$$

$$\eta = a\left(1 - \epsilon^2\right)^{1/2} \sin u.$$

We are now in a position to use the results obtained above via the correspondence principle to obtain results of physical interest which can be compared with the results obtained from quantum mechanics. As indicated before, there are few quantum mechanical results which can be calculated for high values of n, say for n $\sim$ 100. We therefore compare the correspondence principle results with quantum mechanical ones for the lowest values of n, well away from the region of validity of the correspondence principle.

We start by evaluating the mean values of various powers of r. These are easily calculated from

$$\overline{r^{+k}} = \frac{1}{2\pi} \int_0^{2\pi/\omega} r^k \omega \; dt$$

$$= \frac{a^k}{2\pi} \int_0^{2\pi} (1 - \epsilon \cos u)^{k+1} \, du$$

Henceforth, for convenience, we change to units in which

$$\hbar = 1 = e = \mu$$

and consider hydrogen, for which Z = 1. Then

$$\overline{r^k} = \frac{n^{2k}}{2\pi} \int_0^{2\pi} (1 - \epsilon \cos u)^{k+1} \, du.$$

For k = -1, $\overline{r^{-1}} = n^{-2}$

which can be used to verify the virial theorem that the mean value of the potential energy is equal to twice the total energy:

$$\overline{V} = \overline{-r^{-1}} = -n^{-2} = 2E$$

This proof of the virial theorem using the correspondence is identical to the quantum mechanical proof since quantum mechanically $\overline{r^{-1}} = n^{-2}$ also. For higher values of $|k|$ this identity of results breaks down, although as expected the results are similar for high values of n and l. Thus

$$\overline{r}_c = \tfrac{1}{2}(3n^2 - l^2)$$

$$\overline{r}_Q = \tfrac{1}{2}(3n^2 - l(l+1))$$

and

$$\overline{r^{-2}}_c = \frac{1}{n^3 l}$$

$$\overline{r^{-2}}_Q = \frac{1}{n^3(l + \frac{1}{2})}$$

Table 2 shows that this agreement holds for increasing values of $|k|$. In general, for $k \geq -1$,

$$\overline{r^{k}} = n^{2k} \sum_{m=0} \frac{(k+1)!\ \epsilon^{2m}}{(k+1-2m)!} \frac{1}{4^{m}\ m!\ m!}$$

the upper limit of the sum being the integer part of $(k+1)/2$. For $k \leq -2$, it is more convenient to rewrite

$$r^{-1} = l^{-2} (1 + \epsilon \cos \psi)$$

and integrate with respect to ψ

$$\overline{r^{-k}} = n^{-3}\, l^{3-2k} \quad \frac{1}{2\pi} \int_{0}^{2\pi} (1 + \epsilon \cos \psi)^{k-2} \quad d\psi$$

(Alternatively, we can substitute $\tan \psi = (1+\epsilon)^{\frac{1}{2}} \tan (\tfrac{1}{2}u)\ (1-\epsilon)^{-\frac{1}{2}}$)

Since odd powers of the cosine integrate to zero over one cycle, the result is essentially similar to that for $\overline{r^{k-3}}$,

$$\overline{r^{-k}} = n^{-3}\, l^{3-2k} \sum_{m=0} \frac{(k-2)!\ \epsilon^{2m}}{(k-2-2m)!} \frac{1}{4^{m} m!\ m!}$$

We thus have the unexpected result that for high n and l

$$\overline{r^{k}} = (nl)^{3+2k} \quad \overline{r^{-k-3}}$$

Quantum mechanically, (Bethe and Salpeter, 1957)

$$\overline{r^{k}} = \left(\frac{n}{2}\right)^{k} \frac{J^{k+1}_{n+l,\ 2l+1}}{J^{1}_{n+l,\ 2l+1}}$$

	C	Q
$\overline{r}$	$\frac{1}{2}(3n^2 - l^2)$	$\frac{1}{2}(3n^2 - l(l + 1))$
$\overline{r^2}$	$\frac{n^2}{2}(5n^2 - 3l^2)$	$\frac{n^2}{2}(5n^2 - 3l(l + 1) + 1)$
$\overline{r^3}$	$\frac{n^2}{8}(35n^4 - 30n^2l^2 + 3l^4)$	$\frac{n^2}{8}(35n^2(n^2 - 1) - 30n^2(l + 2)(l - 1) + 3(l + 2)(l + 1)l(l - 1))$
$\overline{r^4}$	$\frac{n^4}{8}(63n^4 - 70n^2l^2 + 15l^4)$	$\frac{n^4}{8}(63n^4 - 35n^2(2l^2 + 2l - 3) + 5l(l + 1)(3l^2 + 3l + 10) + 12)$
$\overline{r^{-1}}$	$\frac{1}{n^2}$	$\frac{1}{n^2}$
$\overline{r^{-2}}$	$\frac{1}{n^3 l}$	$\frac{1}{n^3(l + \frac{1}{2})}$
$\overline{r^{-3}}$	$\frac{1}{n^3 l^3}$	$\frac{1}{n^3(l + 1)(l + \frac{1}{2})l}$
$\overline{r^{-4}}$	$\frac{(3n^2 - l^2)}{2n^5 l^5}$	$\frac{(3n^2 - l(l + 1))}{2n^5(l + \frac{3}{2})(l + 1)(l + \frac{1}{2})l(l - \frac{1}{2})}$

Table 2

where $J^{z}_{x,y}$ is a function whose value depends on whether z is greater than or less then zero. For $z \geqslant 0$,

$$J^{z}_{x,y} = (-1)^{z} \frac{x!}{(x-y)!} z! \sum_{i=0}^{z} (-1)^{i} \binom{z}{i}\binom{x+i}{z}\binom{x+i-y}{z}$$

and

$$J^{1}_{n+1,\ 2l+1} = \frac{(n+1)!}{(n-l-1)!} \quad 2n$$

and for $z < 0$, letting $s = -z-1$,

$$J^{z}_{x,y} = \frac{x!}{(x-y)(s+1)!} \sum_{j=0}^{s} (-1)^{s-j} \frac{\binom{s}{j}\binom{x+j-y}{s}}{\binom{y+s-j}{s+1}}$$

The quantum mechanical expression implies no direct relation between positive and negative powers of r, yet table 2 demonstrates that such a relationship does in fact exist for high values of l, at least for low powers of r. (Note that the mean value of r^{0} is 1).

However, Blanchard (1974) has recently shown that quantum mechanically the mean values of powers of r are related by

$$\overline{r^{-k-2}} = (\tfrac{1}{2}n)^{-2k-1} \frac{(2l-k)!}{(2l+1+k)!} \overline{r^{k-1}}$$

for

$$0 \leqslant k \leqslant 2l \ .$$

For any value of k, as l becomes large, the factorials can be expanded and provide the correspondence principle relation. In fact both these formulae can be generalised to non-integer values of k. The correspondence principle leads to the same form,

$$\overline{r^{\beta}} = (nl)^{3+2\beta} \overline{r^{-\beta-3}}$$

and quantum mechanically

$$\overline{r^{\beta}} = (\tfrac{1}{2}n)^{3+2\beta} \frac{\Gamma(2l+3+\beta)}{\Gamma(2l-\beta)} \overline{r^{-\beta-3}}$$

for any ρ . These are again essentially the same for high values of l.

Classically, we can also find the mean values of the orthogonal coordinates ξ and η . These will define the electrical centre of gravity of the bound electron. We find that

$$\bar{\xi} = -\frac{3}{2} \epsilon a$$

and

$$\bar{\eta} = 0$$

Since the electron is moving in an ellipse with the proton at one focus at (o,o) and the other focus at ($-2\epsilon a$, o), the electrical centre of gravity is therefore on the major axis halfway between the midpoint and that focus not occupied by the proton.

Having solved the equation of motion, we can just as easily evaluate matrix elements in which the principal quantum number changes from n to n+s. It is convenient to work in dimensionless units (r/a), (ξ/a), (η/a). We expand these in Fourier series

$$r/a = 1 - \epsilon \cos u = \sum_s A_s e^{is\omega t}$$

$$\xi/a = \cos u - \epsilon = \sum_s B_s e^{is\omega t}$$

$$\eta/a = (1 - e^2)^{\frac{1}{2}} \sin u = \sum_s C_s e^{is\omega t}$$

with

$$A_s = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} (1 - \epsilon \cos u)^2 e^{-is\omega t} \, dt$$

$$B_s = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} (1-\epsilon\cos u)(\cos u - \epsilon) e^{-is\omega t} \, dt$$

$$C_s = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} (1-\epsilon\cos u)(1 - e^2)^{\frac{1}{2}} \sin u \, e^{-is\omega t} \, dt.$$

Substituting

$$\omega t = u - \epsilon \sin u$$

and using the integral definition of a Bessel Function $J_s(x)$

$$J_s(x) = \frac{1}{2\pi}\int_0^{2\pi} du \quad \exp(-isu + ix \sin u)$$

we find that

$$A_s = \frac{-\epsilon}{s} \quad J_s{}'(s\epsilon)$$

$$B_s = \frac{1}{s} \; J_s{}'(s\epsilon)$$

$$C_s = i\,\frac{(1-\epsilon^2)^{\frac{1}{2}}}{s\epsilon}\; J_s\,(s\epsilon)$$

where the primes denote differentiation with respect to $s\epsilon$.

Applying Heisenberg's correspondence principle,

$$\langle n|r|n+s\rangle = \frac{-a\epsilon}{s} \; J_s{}'\,(s\epsilon)$$

$$\langle n|\xi|n+s\rangle = \frac{a}{s} \quad J_s{}'\,(s\epsilon)$$

$$\langle n|\eta|n+s\rangle = ia\,\frac{(1-\epsilon^2)^{\frac{1}{2}}}{s\epsilon}\; J_s\,(s\epsilon)$$

Matrix elements of higher orders of r, ξ, η, have been evaluated. For any positive integer k,

$$\langle n|r^{k-1}|n+s\rangle = a^{k-1}\sum_{p=0}^{k}\;\sum_{l=0}^{p}\binom{k}{p}\binom{p}{l}\left(\frac{-\epsilon}{2}\right)^{p} J_{s-p+2l}^{(p)}(s\epsilon)$$

with $J_s^{(p)}(x)$ the pth derivative of the Bessel function with respect to x. For negative values of k, the upper limit in the first sum becomes infinite.

This solution for a general power of r provides a way of obtaining matrix elements of any function of r which can be expanded in a power series, thus

$$\langle n | e^{\alpha r} | n + s \rangle = \langle n \Big| \sum_{k=2}^{\infty} \frac{(\alpha r)^{k-1}}{(k-1)!} \Big| n+s \rangle$$

$$= \sum_{k=2}^{\infty} \frac{(a\alpha)^{k-1}}{(k-1)!} \sum_{p=0}^{k} \binom{k}{p} \left(-\frac{\epsilon}{2}\right)^{p} \sum_{l=0}^{p} \binom{p}{l} J_{s-p+2\ell}^{(p)} (s\epsilon)$$

In this case the integration can also be carried out directly and a result obtained in a closed form , if $s > \alpha a$. Let $\alpha a = t$.

$$\langle n | e^{\alpha r} | n+s \rangle = \frac{1}{2\pi} \int_{0}^{2\pi} du \, (1 - \epsilon \cos u) \, e^{t(1-\epsilon \cos u)} \, e^{-isu + is\epsilon \sin u}$$

$$= \frac{e^{t}}{2\pi} \int_{0}^{2\pi} du \, (1 - \epsilon \cos u) \, e^{-isu} \, e^{ix \sin (u + \delta)}$$

with $x^2 = \epsilon^2 (s^2 - a^2)$; $\exp(2i\delta) = \dfrac{s-t}{s+t}$

Redefining a new variable equal to $(u + \delta)$ and integrating,

$$\langle n | e^{\alpha r} | n + s \rangle = \frac{\epsilon^2 t}{x} \, e^{t} \left(\frac{s-t}{s+t}\right)^{s/2} \left\{ J_s^{1}(x) - \frac{t}{x} J_s(x) \right\}$$

For $s = o$, the mean value of $e^{\alpha r}$ is obtained in terms of the modified Bessel functions $I_o(x)$ and $I_1(x)$ by

$$\langle n | e^{\alpha r} | n \rangle = e^{t} \left\{ I_o(\epsilon t) + I_1(\epsilon t) \right\}$$

We have thus shown that in the case of the Coulomb potential, as with the simple harmonic potential and the Morse potential, the correspondence principle can be used to obtain matrix elements which are in good agreement with available quantum mechanically calculated matrix elements, although much simpler in form. In the cases where no quantum mechanical results are available, it would therefore be expected that the correspondence principle results are good approximations to the exact solutions.

Transitions between n,l,m states

The previous section concerned transitions only between the principal quantum numbers n. To consider transitions between n,l,m states it is convenient to define a new orthogonal coordinate system. The previous equations defined the motion of the bound electron in the plane of its ellipse. The orientation of the ellipse and its coordinates ξ and η can be in turn described by three cartesian coordinates x,y,z by means of Euler angles. We use the Euler angles and transformation matrices defined by Goldstein, the ξ and η coordinates being Goldstein's x' and y' coordinates. The z axis forms an angle θ with the angular momentum vector, (and $\cos\theta = m/l$), the x axis forms an angle of ϕ with the line of nodes which in turn forms an angle ψ with the perihelion. Applying the transformation matrix to ξ and η,

$$x/a = D(\cos u - \epsilon) + E\sqrt{1-\epsilon^2}\,\sin u$$

$$y/a = F(\cos u - \epsilon) + G\sqrt{1-\epsilon^2}\,\sin u$$

$$z/a = H(\cos u - \epsilon) + K\sqrt{1-\epsilon^2}\,\sin u$$

with

$$D = \cos\psi\cos\phi - \cos\theta\sin\phi\sin\psi$$

$$F = \cos\psi\sin\phi + \cos\theta\cos\phi\sin\psi$$

$$H = \sin\theta\sin\psi$$

$$E = -\sin\psi\cos\phi - \cos\theta\sin\phi\cos\psi$$

$$G = -\sin\psi\sin\phi + \cos\theta\cos\phi\cos\psi$$

$$K = \sin\theta\cos\psi\ .$$

To obtain the matrix elements of these coordinates, we expand them in a triple Fourier series involving Δn ($= S$), Δl, Δm and their associated angle variables w, ψ, ϕ. The Fourier coefficients are obtained by integrating over the three angles, although the triple integral does not always have to be explicitly performed. Consider the equation for the z coordinate. Since $\cos\theta = m/l$, then

$$z = a\left\{1 - \frac{m^2}{l^2}\right\}^{\frac{1}{2}} \left\{\sin\psi\,(\cos u - \epsilon) + \frac{1}{n}\cos\psi\,\sin u\right\}.$$

Writing this as an expansion in w, ψ, ϕ,

$$z = \sum_{\Delta n}\sum_{\Delta l}\sum_{\Delta m} z_{n,l,m}^{n+\Delta n,\ l+\Delta l,\ m+\Delta m}\, e^{i\Delta n w}\, e^{i\Delta l\psi}\, e^{i\Delta m\phi}$$

We see first that since z is not a function of ϕ the only non-zero coefficients are those for which

$$\Delta m = 0$$

Similarly, we require

$$\Delta l = \pm 1$$

and we have selection rules for the matrix elements. Since there is no simple relation between w and u ($w = u - \epsilon\sin u$) we still have to evaluate the integral over w. Finally, applying Heisenberg's correspondence principle,

$$\langle n,l,m|z|n+s,\ l+\Delta l,\ m\rangle = -\Delta l\,\frac{ia}{2s}\left\{1 - \frac{m^2}{l^2}\right\}^{\frac{1}{2}} \left\{J_s{}'(s\epsilon) + \Delta l.\frac{1}{n\epsilon}\,J_s(s\epsilon)\right\}$$

for $\Delta l = \pm 1$.

Following the same procedure for the x and y coordinates, the following selection rules apply

$$\Delta m = \pm 1$$

$$\Delta l = \pm 1$$

Collecting results,

$$\langle n,l,m|x|n+s,\ l+\Delta l,\ m+\Delta m\rangle = \frac{\Delta l}{4}\left\{1 + \frac{\Delta m.m}{\Delta l.l}\right\} R_{n,l}^{n+s,\ l+\Delta l}$$

$$\langle n,l,m|y|n+s,\ l+\Delta l,\ m+\Delta m\rangle = -i\,\frac{\Delta m\ \Delta l}{4}\left\{1 + \frac{\Delta m.m}{\Delta l.l}\right\} R_{n,l}^{n+s,\ l+\Delta l}$$

$$\langle n,l,m|z|n+s,\ l+\Delta l,\ m\rangle = -\frac{i}{2}\left\{1 - \frac{m^2}{l^2}\right\}^{\frac{1}{2}} R_{n,l}^{n+s,\ l+\Delta l}$$

where

$$R^{n+s,\, l+\Delta l}_{n,l} = \Delta l \, \frac{a}{s} \left\{ J_s{}'(s\epsilon) + \Delta l \, \frac{\sqrt{1-\epsilon^2}}{\epsilon} \, J_s(s\epsilon) \right\}$$

will be shown to be the dipole moment, for $s \neq o$, and

$$R^{n,\, l+\Delta l}_{n,l} = \frac{3}{2} \epsilon a$$

for $s = o$.

Since we are dealing with transitions between different states, the meaning and the value of the eccentricity ϵ have both become ambiguous. The eccentricity for a state (n,l) is $(1 - l^2/n^2)^{\frac{1}{2}}$ and that for a state $(n+s,\, l+\Delta l)$ is $(1 - (l+\Delta l)^2/(n+s)^2)^{\frac{1}{2}}$. The value of the eccentricity that is to be used in dealing with transitions between these two states can be thought of as some sort of average between these two eccentricities, or as the eccentricity of some average state. This second course is more convenient and is consistent with the work already carried out. We define the eccentricity to be

$$\epsilon^2 = 1 - \frac{l_c{}^2}{n_c{}^2}$$

and choose l_c and n_c by comparing correspondence principle results for simple cases with equivalent quantum mechanical results. The value of n_c might be expected to arise from some average of the two states n and n+s. We could with equal justification choose $n_c = n+s/2$ which would lead to an average angular momentum, or

$$n_c = \left\{ \frac{n^2 (n+s)^2}{n + s/2} \right\}^{\frac{1}{3}}$$

which would lead to an average frequency, or

$$n_c = \frac{n(n+s)}{n+s/2}$$

which would lead to an average velocity (since the velocity is inversely proportional to n), or any other value of n_c. The correspondence principle is valid for a high enough value of n whatever choice is made, but as will be shown later it can also be applied to surprisingly low values of n if the choice

$$n_c = \frac{n(n+s)}{n+s/2}$$

is made. For l_c, the best choice is more difficult to find as it is in some sense a second order effect, and depends on the correct choice having been made for n_c. We can, however, look at the case $s = 0$, when we know from the mean values of powers of r that $n_c = n$. For $s = o$, the dipole moment

$$R_{n,l}^{n,l+\Delta l} = \frac{3}{2}\epsilon a$$

$$= \frac{3}{2} n \left(n^2 - l_c^2\right)^{\frac{1}{2}}$$

The quantum mechanical value (Bethe and Salpeter)

$$R_{n,l}^{n,l+\Delta l} = \frac{3}{2} n \left(n^2 - lq^2\right)^{\frac{1}{2}}$$

with $lq = \max(l, l + \Delta l)$,

which implies that $l_c = \max(l, l + \Delta l)$, at least for $s = 0$.

For off-diagonal elements comparison between quantal and correspondence principle results is more difficult. The general formula is obtained as an integral over Associated Laguerre functions, and we shall just quote the closed form formula obtained by Gordon (1929), in atomic units.

$$R_{n,l}^{n+s,l-1} \doteq \frac{(-1)^{n-l}}{4(2l-1)!} \left\{\frac{(n+l)!\,(n+s+l-1)!}{(n-l-1)!\,(n+s-l)!}\right\}^{\frac{1}{2}} \frac{(4n(n+s))^{l+1}\, s^{2n+s-2l-2}}{(2n+s)^{2n+s}}$$

$$X \left\{ F\left(-n+l+1, -n-s+l, 2l; -\frac{4n(n+s)}{s^2}\right) \quad \ldots \right.$$

$$- \frac{s^2}{(2n+s)^2} \quad F\left(-n+l-1,\ -n-s+1,\ 2l;\ -\frac{4n(n+s)}{s^2}\right) \Bigg\}$$

with F the hypergeometric function defined by

$$F(i,j,k;x) = \sum_m \frac{i(i+1)(i+2)\ldots.(i+m-1)j(j+1)\ldots.(j+m-1)}{k(k+1)\ldots.(k+m-1)} \cdot \frac{x^m}{m!}$$

We recall that the result obtained using the correspondence principle is

$$R_{n,l}^{n+s,l-1} = \frac{-1}{s} \left\{ J_s'(s\epsilon) - \frac{\sqrt{1-\epsilon^2}}{\epsilon} J_s(s\epsilon) \right\}$$

with $\epsilon^2 = 1 - \frac{l_c^2}{n_c^2}$.

Detailed comparison with quantum mechanical result

We compare the matrix elements obtained using the correspondence principles with those obtained using quantum mechanics in two stages. We first examine their dependence on the dipole moment, then compare the two expressions for the dipole moment. Bethe and Salpeter quote values for the matrix elements of x + iy, x - iy, and z, in terms of the dipole moment. The selection rules are identical to those obtained using the correspondence principle, and they are all equal to some coefficient times the dipole moment. Table 3 compares the values of these coefficients (squared) for all the allowed transitions. We see that for higher values of l the two sets are essentially the same, and that in general the ratio of the quantal coefficient to the correspondence coefficient is of the form

$$\frac{l^2}{(l^2-\frac{1}{4})}\;\frac{(l-m+\frac{3}{2})^2-\frac{1}{4}}{(l-m+1)^2}$$

In table 3 we have used the substitution $l_c = \max(l, l+\Delta l)$ indicated from the previous section, and simply set $m_c = m$. Careful consideration of the coefficients may lead to other rules giving better agreement, but these have the advantage of simplicity.

The best available numerical values of the squares of the quantum mechanical radial integral $R_{n,l}^{n'l'}$ appear to be those calculated by Green et al (1957). They tabulate results for the allowed transitions from any lower state n,l to any upper state n', l' for all values of n and n' less than 21. Previous calculations had either been inaccurate or too restricted, and the value of a wide ranging accurate calculation was suggested to the authors by M.J. Seaton. Their quoted numerical values are to six significant figures.

	Coefficient of $R_{nl}^{n'l'}$	
Matrix Element	Quantum	Corresp.
$\langle n,l,m \mid x+iy \mid n',l+1,m+1 \rangle$	$\left\{\frac{(l+m+2)(l+m+1)}{(2l+3)(2l+1)}\right\}^{\frac{1}{2}}$	$\frac{(l+m+1)}{2l+2}$
$\langle n,l,m \mid x-iy \mid n',l+1,m-1 \rangle$	$-\left\{\frac{(l-m+2)(l-m+1)}{(2l+3)(2l+1)}\right\}^{\frac{1}{2}}$	$-\frac{(l-m+1)}{2l+2}$
$\langle n,l,m \mid x-iy \mid n',l-1,m+1 \rangle$	$-\left\{\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}\right\}^{\frac{1}{2}}$	$-\frac{(l-m)}{2l}$
$\langle n,l,m \mid x+iy \mid n',l-1,m-1 \rangle$	$\left\{\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}\right\}^{\frac{1}{2}}$	$\frac{(l+m)}{2l}$
$\langle n,l,m \mid z \mid n',l+1,m \rangle$	$\left\{\frac{(l+1)^2 - m^2}{(2l+3)(2l+1)}\right\}^{\frac{1}{2}}$	$\left\{\frac{(l+1)^2 - m^2}{(2l+2)^2}\right\}^{\frac{1}{2}}$
$\langle n,l,m \mid z \mid n',l-1,m \rangle$	$\left\{\frac{l^2 - m^2}{(2l+1)(2l-1)}\right\}^{\frac{1}{2}}$	$\left\{\frac{l^2 - m^2}{4l^2}\right\}^{\frac{1}{2}}$

Table 3

For numerical calculations of the correspondence principle result it is convenient to use the property of Bessel functions that

$$2J_s'(s\epsilon) = J_{s-1}(s\epsilon) - J_{s+1}(s\epsilon)$$

$$\frac{2}{s\epsilon}J_s(s\epsilon) = J_{s-1}(s\epsilon) + J_{s+1}(s\epsilon)$$

and rewrite

$$R_{nl}^{n'l'} = \frac{n_c^2}{2s}\,\Delta l\left\{\left(1 + \Delta l\,\frac{l_c}{n_c}\right) J_{s-1}(s\epsilon) - \left(1 - \Delta l\,\frac{l_c}{n_c}\right) J_{s+1}(s\epsilon)\right\}$$

Table 4 compares values of $(R_{nl}^{n'l'})^2$ calculated using $n_c = n+\frac{1}{2}s$ and $n_c = n(n+s) / (n+\frac{1}{2}s)$ with the quantum mechanical result. The following points emerge:

(1) For fixed l, l', the difference between the two sets of values decreases as n increases. This is just Bohr's correspondence principle. The percentage difference decreases roughly as n^2. The difference is considerably smaller for $n_c = n(n+s) / (n+\frac{1}{2}s)$ than for $n_c = n+\frac{1}{2}s$, as would be expected since that choice of n_c was originally made to obtain good agreement with quantum mechanics.

(2) For fixed n, n', the percentage difference decreased with decreasing l, the worst errors occuring when $l = n-1$. This is because the classical perturbation of the orbit of the electron is greatest when l changes from n-1 to n-2, since the eccentricity of the orbit is $\epsilon^2 = 1 - l^2/n^2$. (Green et al also admit that their checking procedure for high values of l was not as valid as that for low values of l).

Transition	Quantum value	Corres. value $n+\frac{1}{2}s$	$\left(\frac{Q}{C}-1\right)$ %	Corres. value $n(n+s)/(n+\frac{1}{2}s)$	%
2s-3p	9.3931	11.022	17.3	9.7203	3.48
3s-4p	29.914	32.527	8.74	30.374	1.54
4s-5p	72.553	76.395	5.30	73.181	0.865
5s-6p	149.18	154.49	3.56	150.00	0.552
6s-7p	274.19	281.22	2.56	275.25	0.385
7s-8p	464.53	473.51	1.93	465.85	0.284
8s-9p	739.69	750.86	1.51	741.29	0.217
9s-10p	1121.7	1135.3	1.21	1123.6	0.171
10s-11p	1635.0	1651.3	0.996	1637.3	0.139
11s-12p	2306.8	2326.0	0.834	2309.5	0.116
12s-13p	3166.7	3189.1	0.707	3169.8	0.0969
13s-14p	4246.9	4272.7	0.702	4250.4	0.0832
14s-15p	5582.0	5611.4	0.527	5586.0	0.0710
15s-16p	7209.3	7242.6	0.462	7213.8	0.0625
16s-17p	9168.7	9206.1	0.414	9173.6	0.0539
17s-18p	11502	11544	0.363	11508	0.0476
18s-19p	14255	14301	0.325	14261	0.0428
19s-20p	17474	17525	0.293	17481	0.0389
4s-5p	72.553	76.395	5.30	73.181	0.865
4p-5d	121.86	127.86	4.92	123.18	1.083
4d-5f	197.83	207.00	4.64	200.46	1.33
(13,7)-(20,8)	39.51	47.18	19.4	37.96	-3.93

Table 4

(3) Restricting $s/n < 1$ and $(l+1)/n < 1$, the worst disagreements found were of order 10% . Applying the stricter condition that $s(l+1)/n < 1$ all differences were less than 3·5%. Since a strict interpretation of the correspondence principle would imply that the two sets of results should only agree for $s/n \ll 1$, the agreement for these (relatively) low values of n is excellent.

We can also compare sums of intensities obtained from the correspondence principle and from quantum mechanics:

(1) Adding the intensities of a transition from a state nlm to all substates m^1 of a state $n^1 l^1 m^1$ for all directions of polarization of the emitted radiation

$$\sum_{m^1} \left| r_{nlm}^{n^1 l^1 m^1} \right|^2 = \left| x_{nlm}^{n^1 l^1 m+1} \right|^2 + \left| x_{nlm}^{n^1 l^1 m-1} \right|^2 + \left| y_{nlm}^{n^1 l^1 m+1} \right|^2$$

$$+ \left| y_{nlm}^{n^1 l^1 m-1} \right|^2 + \left| z_{nlm}^{n^1 l^1 m} \right|^2$$

$$= \tfrac{1}{2} \left| R_{nl}^{n^1 l^1} \right|^2$$

from the correspondence principle, and

$$\sum_{m^1} \left| r_{nlm}^{n^1 l+1 m^1} \right|^2 = \frac{l+1}{2l+1} \left| R_{nl}^{n^1 l+1} \right|^2$$

$$\sum_{m^1} \left| r_{nlm}^{n^1 l-1\, m^1} \right|^2 = \frac{l}{2l+1} \left| R_{nl}^{n^1 l-1} \right|^2$$

from quantum mechanics. In all cases the sum over m^1 is independent of m, and all formulae agree with each other in the limit of large l. Since the lifetime of a state depends on the intensity of transitions out of it, this implies that the lifetime is independent of a state's magnetic quantum number and depends only on the values of n and l. This was known in quantum mechanics but we have shown that it can be deduced by applying classical mechanics and the correspondence principle.

(2) For a fixed direction of polarization, the sum of the intensities over all values of m (i.e. over all the Zeeman components of a spectral line),

$$\sum_{m} \left| z^{n'l-1m}_{nlm} \right|^2 = \frac{1}{4} \left| R^{n'l-1}_{nl} \right|^2 \sum_{m} \left(1 - \frac{m^2}{l^2}\right)$$

$$= \frac{1}{12l} (2l+1)(2l-1) \left| R^{n'l-1}_{nl} \right|^2$$

$$\sum_{m,m'} \left| x^{n'l'm'}_{nlm} \right|^2 = \sum_{m,m'} \left| y^{n'l'm'}_{nlm} \right|^2$$

$$= \frac{1}{24l} (2l+1)(4l+1) \left| R^{n'l'}_{nl} \right|^2$$

from the correspondence principle results, and

$$\sum_{m} \left| z^{n'l-1\,m}_{nlm} \right|^2 = \sum_{mm'} \left| x^{n'l-1\,m'}_{nlm} \right|^2$$

$$= \sum_{mm'} \left| y^{n'l-1\,m'}_{nlm} \right|^2$$

$$= \frac{1}{3} \left| R^{n'l-1}_{nl} \right|^2$$

from quantum mechanics. Again the asymptotic values for large l are equal.

(3) The correspondence principle gives a similar result to quantum mechanics for the sum over all m, m^1 and all directions of polarization:

$$\sum_{mm^1} \left| r_{nlm}^{n^1 l^1 m^1} \right|^2 = (l+\tfrac{1}{2}) \left| R_{nl}^{n^1 l^1} \right|^2$$

as opposed to

$$\sum_{mm^1} \left| r_{nlm}^{n^1 l-1\ m^1} \right|^2 = l \left| R_{nl}^{n^1 l-1} \right|^2 \quad .$$

Oscillator Strengths

An immediate use of the matrix elements evaluated above can be found in the calculation of oscillator strengths between highly excited states. Besides being useful quantities in themselves they provide further checks on the accuracy of the correspondence principle.

The definition of the oscillator strength for a transition between a state n,l and a state $n^1 l^1$ is (Bethe and Saltpeter)

$$f_{nl}^{n^1 l^1} = \frac{2}{3}\, \omega_{n^1 n} \sum_{m^1} \left| r_{nlm}^{n^1 l^1 m^1} \right|^2$$

with

$$\omega_{n^1 n} = E_{n^1} - E_n$$

or alternatively

$$\omega_{n^1 n} \simeq s\omega \quad .$$

Substituting for the matrix elements of x,y,z, and summing over the final m^1 states we obtain

$$f_{nl}^{n+s,l+\Delta l} = \frac{1}{3s} \, n_c \left\{ J_s^{1}(s\epsilon) + \Delta l \frac{\sqrt{1-\epsilon^2}}{\epsilon} \, J_s(s\epsilon) \right\}^2 .$$

Averaging over initial l states and summing over final l^1 states, we find the average oscillator strength for a transition between two states defined by n and n^1:

$$f_{nn^1} = \frac{4}{3} \frac{n_c}{s^2} \, J_s(s) \, J_s^{1}(s)$$

To compare this with other calculations it is convenient to define

$$M(s) = \frac{4}{3} \, \frac{J_s(s) \, J_s^{1}(s)}{s^2}$$

Thus

$$f_{nn^1} = n_c \, M(s)$$

and we have chosen

$$n_c = n\,(n+s)/(n+\tfrac{1}{2}s) \quad .$$

Alternative calculations have led to

$$f_{nn^1} = n \quad M(s) \qquad \text{(Mezger)}$$

$$f_{nn^1} = (n+\tfrac{3}{2}\,s)\,M(s) \qquad \text{(Menzel)}$$

$$f_{n,n-1} = n \, \frac{1}{6} \qquad \text{(Kardashev)}$$

$$f_{nn^1} = \frac{(n+s)^2}{n+\frac{s}{2}} \, M(s) \qquad \text{(Percival and Richards)}$$

The Percival and Richards result was obtained by requiring that the correspondence principle result should obey detailed balance.

For large values of s, we can use the asymptotic form of the Bessel functions to obtain

$$f_{nn}^{1} = \frac{4}{3\sqrt{3}\pi} \frac{n_c}{s^3} .$$

which is the same as the asymptotic form obtained by Unsöld.

3.4 Resumé

We have shown that for the three potentials considered in detail classical mechanics and the correspondence principle can provide results which are valid not only in the limit of high quantum numbers, as is generally known, but also for low quantum numbers. We have concentrated on calculating quantities whose quantum mechanical values are known so that comparisons between the two could be made, and we have shown that although any reasonable choice of n_c would produce results which have the same form as the quantum mechanical ones a more careful choice of n_c can produce agreement for low quantum numbers, even for $n = 1$.

Having shown the ability of classical methods to cope with problems which are usually solved using quantum mechanics we next consider a case which has yet to be solved exactly quantum mechanically, the observed broadening of spectral lines of high quantum number emitted from laboratory or astrophysical plasma.

CHAPTER IV

CAUSES OF LINE BROADENING

Fundamental factors governing the width of spectral lines are natural broadening, Doppler broadening, and pressure broadening. We shall consider these in that order, but first we briefly mention factors which may contribute to the observed breadth of a spectral line.

a) All spectrometers will produce lines of finite width, even for monochromatic radiation. This is the only mention we shall make of the detection of spectral lines, and in what follows we implicitly assume that the resolving power of any apparatus used is such that the "instrumental width" is negligible compared with widths arising from other causes.

b) Radiation emitted in the body of a gas may suffer partial absorption on its passage through the gas. In consequence of Kirchoff's laws, the more intense portions of the line will be more strongly absorbed so that the centre of the line will be weakened compared with the wings of the line. This is known as "self absorption" and to ignore it we assume that the light has come through an optically thin layer of gas.

c) For absorption lines, the intensity distribution $I(w)$ depends on the thickness of the layer of gas (d) according to

$$I(w,d) = I_o \exp(-a(w)d)$$

with I_o a constant, and $a(w)$ the absorption coefficient. For small values of d, the line profile is proportional to the absorption coefficient, and the following will apply to absorption lines from optically thin layers.

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4.1 Natural Broadening

This is present in all spectral lines and can be explained either in terms of classical theory or in terms of quantum mechanics. Classically, it is due to the damping of the oscillator because of loss of energy by radiation, and is thus alternatively called radiation broadening. The rate of decay of energy of a classical electron oscillator is

$$E(t) = E_0 \exp(-bt)$$

with the decay constant b given by

$$b = 2e^2 w_0^2 / 3mc^3$$

for charge e, frequency w_0, and mass m. A Fourier expansion of the damped wave train leads to

$$I(w) = I(w_0) \frac{b}{(w-w_0)^2 + (b)^2}$$

A useful quantity in line broadening is the width of the spectral line at half the maximum intensity. For brevity we call this the half-width, which for natural broadening is equal to b, measured in radians per second. In terms of w, it is numerically equal to $1{\cdot}17 \times 10^{-12}$ cm, or 0·000117 Å.

Quantum mechanically, the broadening is explained by the uncertainty principle. Since exited states only have a finite lifetime their energy levels will be diffuse, and thus radiation from those levels will be broadened. The same line shape is obtained but the constant b is now the sum of the decay constants of the initial and final states, $b_i + b_f$. These are inversely proportional to the lifetimes of atoms in the two states, and are therefore proportional to the uncertainty in the energy levels. The half width is thus equal to the sum of the widths of the energy levels associated with the line.

For the special case of strong resonance lines, those associated with the ground state with a decay constant of zero, when the oscillator strength is 1, the half width obtained quantum mechanically is equal to that obtained classically.

Radiation broadening is usually negligible, though its effects on the wings of spectral lines are sometimes noticeable.

4.2 Doppler Broadening

Translational motion of the radiating atom leads to a line broadening which Rayleigh first demonstrated as due to the Doppler effect.

Consider an atom emitting radiation of wavelength λ, and moving with velocity v in the line of sight of an observer. The Doppler effect means that the observer will receive radiation of wavelength λ', with

$$\lambda' = \lambda\,(1 - v/c)$$

assuming that $v \ll c$, so that

$$v^2 = \lambda^2(\Delta\nu)^2$$

The distribution of velocities in the line of sight is given by the Maxwellian distribution $\exp(-mv^2/2kT)$, with k the Boltzmann constant, and T the temperature in degrees Kelvin. We can consider λ to be the wavelength corresponding to the line centre, and $\Delta\nu$ as the frequency difference between the centre and the frequency whose displacement corresponds to the velocity v. Then

$$I(w) = I_0 \exp\left(-m\lambda^2(\Delta\nu)^2/2kT\right)$$

Lord Rayleigh (F.W. Strutt) proved the above and showed that the half width is given by

$$\frac{2}{\lambda}\left\{\frac{2kT\ln 2}{m}\right\}^{\frac{1}{2}}$$

Doppler half-widths will therefore be more important at higher temperatures, and we shall show that they can also be expected to dominate at low pressures.

4.3 Collision broadening

We now consider the broadening of spectral lines emitted by high temperature laboratory and astrophysical plasmas, mediums which are strongly ionized but have no net charge. We examine the development of the theory in chronological order.

Michelson, 1895

Michelson began his consideration of line broadening by reviewing the hypotheses which had been put forward to account for line broadening:

1. As a consequence of Kirchhoff's law "the ratio of brightness of two immediately contiguous portions of a discontinuous, bright-line spectrum constantly decreases, if the number of luminous strata is multiplied or if the coefficient of absorption of the single stratum is increased, until the value is reached which, for the same wave-length and the same temperature, corresponds to the ratio in the continuous spectrum of a body completely opaque for the given thickness.
2. The direct modification of the period of the vibrating atoms in consequence of presence of neighbouring molecules.
3. The exponential diminution in amplitude of the vibrations due to communication of energy to the surrounding medium, or to other causes.
4. The change in wave-length due to the Doppler effect of the component of the velocity of the vibrating atom in the line of sight.

To these the following causes may be added:

5. The limitation of the number of regular vibrations by more or less abrupt changes of phase amplitude or place of vibration, caused by collisions.
6. The possible variations in the properties of the atoms within such narrow limits as to escape detection by other than spectroscopic observations.

Although conceding that cause 4 (Doppler broadening) was "the chief if not the only effective cause in operation when the density of the radiating body is low", he concluded that causes 1,3,4, and 6 together are insufficient to account for the observed effects of line broadening. Cause 2 we shall call statistical broadening and will consider later. Cause 5 has been called velocity broadening, impact broadening, interruption broadening and, the term we shall use, collision broadening, and is Michelson's major contribution to the theory.

Consider Fig. 4. The circles represent perturbing (broadening) atoms whilst the arrow represents the trajectory at the centre of the emitter through the perturbers. Michelson used billiard ball atoms so that a collision is deemed to have taken place when the separation of the emitter and broadener centres is less than the sum of their atomic radii. Michelson assumed collisions had the following effect:

A collision has just occurred between points "a" and "b". The radiating atom emits coherent radiation from "b" to "c", when another collision occurs. No more coherent radiation is emitted until "d". However, the radiation emitted after "d" is completely incoherent with that emitted between "b" and "c". This is the crux of the argument. If t is now the time taken between "b" and "c", we have a wave train of finite length t x velocity of light. We recall that the Fourier analysis used in the previous section is a way of expressing finite wave trains in terms of an infinite number of wave trains of

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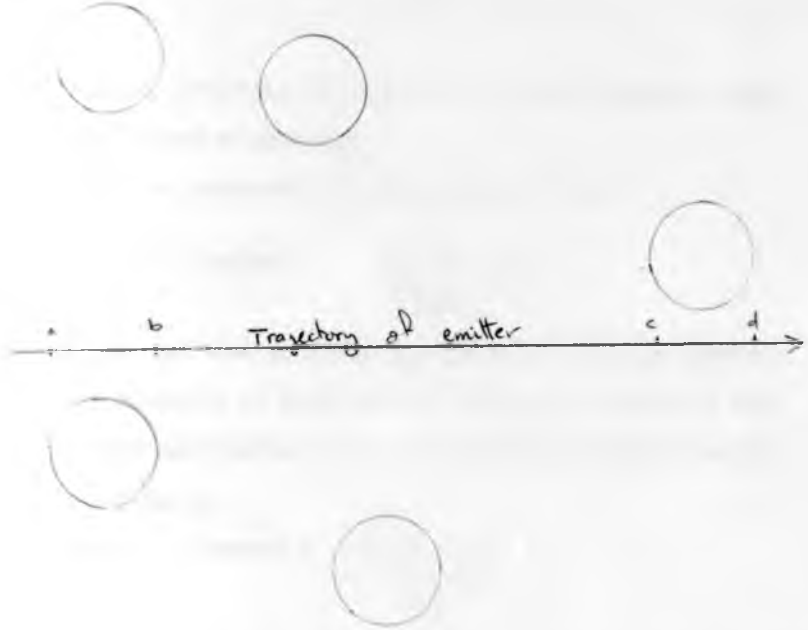

Fig 4
Illustration of Michelson's model

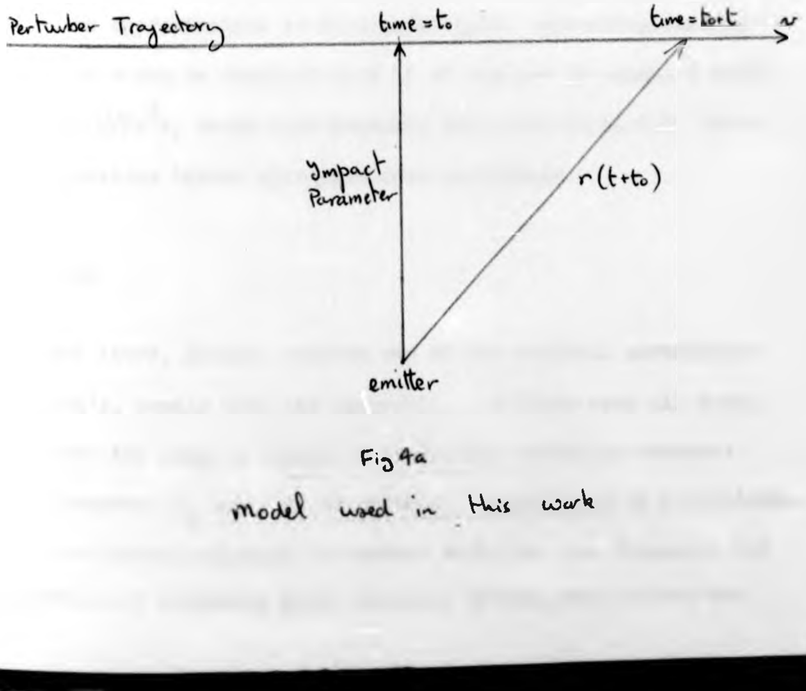

Fig 4a
model used in this work

infinite length. To obtain the relative magnitude of each of these infinite wave trains we calculate

$$J(w) = \text{constant} \times \text{Real} \int_0^t \exp\left(i(w-w_0)t'\right)\, dt'$$

$$= \text{constant} \times \frac{\sin\left((w-w_0)t\right)}{(w-w_0)}$$

We now suppose that this amplitude function represents the spectral line. Since intensity is always associated with the square of the amplitude, Michelson assumed that the intensity distribution within the line was given by

$$I(w) = \text{constant} \times \frac{\sin^2\left((w-w_0)t\right)}{(w-w_0)^2}$$

If all the velocities and all the free paths were equal, this expression should provide the widths of the spectral line. Taking this to be the separation of the minima to either side of the maximum, Michelson obtained a width of $\lambda^2 v/c^2 t$. For a particular line of hydrogen, he calculated a numerical value of 0·057 tenth-meter (sic) compared with his experimental value of 0·16 tenth-meter, an agreement to within an order of magnitude, which is excellent considering the simplicity of the theory. Not fully satisfied with this result, he calculated an approximation to Rayleigh's Doppler broadening formula and added the width he obtained from it to his own to obtain a width of $\lambda(3ct+\lambda)v/c^2 t$, which overestimates the width to be 0·22 tenth-meter but provides better agreement with experiment.

Lorentz, 1906

Eleven years later, Lorentz removed one of the critical assumptions of Michelson's, namely that the intercollision times were all equal. His model was the same, a classical oscillator radiating undamped waves of frequency w_0 until it is suddenly interrupted by a collision. After the collision radiation is resumed with the same frequency but with a completely arbitrary phase relative to the phase before the collision. For an intercollision time of t, this leads to the expression for J(w). Lorentz then reasoned that the probability of collision in time t obeys an exponential law, $(1/\tau)\exp(-t/\tau)$ for a mean intercollision time τ. The radiation therefore consists of a set of wave trains whose finite lengths have an exponential distribution. The intensity is given by integrating over this distribution,

$$I(w) = \text{constant} \int_0^\infty |J(\omega,t)|^2 \exp(-t/\tau)\, dt$$

$$= \text{constant} \; \frac{1}{(w-w_0)^2 + (1/\tau)^2}$$

This is the Lorentz line shape. Its half-width is equal to the collision frequency, which is generally found to be experimentally true. Since the collision frequency can be equated to Nqv, with N the number density of perturbers, q the collision cross-section and v their velocity (mean or r.m.s.), this width is thus proportional to the pressure at a constant temperature.

Lenz, 1924; Weisskopf, 1932

Contemporarily with the development of the correspondence principle and with the rise of quantum mechanics, a feeling arose that the Lorentz and Michelson theories could not be expected to survive quantum mechanics. However, beginning with Lenz' appeal to correspondences in 1924, a large number of authors have devoted themselves to showing the incorrectness of this viewpoint.

The first development concerns the definition of the cross-section q. In the Michelson model the atom was considered to be a hard billiard ball with a fixed diameter defining the cross-section. A collision between two "billiard balls" would only occur if the separation of their centres was less than the sum of their radii. Now we would expect that short range forces, say van der Waals, between the broadener and the emitter would exert some influence on the broadening of a spectral line before a collision in the above sense occurs. This influence can be expected to manifest itself by a phase change in the emitted radiation as the two bodies approach one another. Weisskopf suggested an "optical collision diameter" within which a collision could be considered to have taken place, and which we now define. Consider the angular frequency w_o, which in the Michelson theory was a constant, unchanged until a collision destroyed it. However if we now assume some sort of action at a distance, this frequency will no longer be constant but will change with time as the radiator and the perturber approach each other and enter the range of this force. If this force is some function of the emitter/perturber separation, say V(r), then , setting $\hbar = 1$,

$$w_o(t)t = w_o t + \int_0^t V(r)\, dt'$$

$$= w_o t + \eta(t)$$

where w_o is the original frequency in the absence of any force and $\eta(t)$ is the change in the phase of the vibration due to the perturbation. The latter quantity was used by Weisskopf to define a collision: A collision has been undergone by the emitter when the phase of the emitted radiation has changed by 1, i.e. when $\eta \geqslant 1$.

We are assuming binary collisions and straight line trajectories, so that at any time only two bodies are "colliding" in the sense above, and that the path of the perturber relative to the emitter is a straight line. Then

$$\eta(t) = \int_0^t V(r)\, dt'$$

$$= \int_{t_0}^{t_0+t} V\left(\sqrt{b^2+v^2t'^2}\right) dt'$$

where b is the impact parameter, v is the velocity of the perturber relative to the emitter, and t_o is the time from some arbitrary origin (Fig. 4a). The criterion $\eta \gg 1$ then defines for a fixed velocity a critical impact parameter, b_c. Since in general a smaller impact parameter leads to a greater value of η (since V is usually inversely proportional to r) then the relation $\eta \gg 1$ defines a b_c below which all impacts broaden the line. The quantity πb_c^2 then replaces the Lorentz cross-section and is called the "optical" cross section. Of course the choice of the value 1 was completely arbitrary, but having chosen a critical phase this leads to a critical impact parameter and an optical cross-section, which need not be related to the Lorentz cross-section.

We have now described the Lenz-Weisskopf modifications to the Michelson-Lorentz theory. The results obtained from these are valid within a limited region, at low pressures and at frequencies near the line center. The reasons for these restrictions are two of the approximations we have made:

(1) Binary Collisions. By considering each collision to involve only two bodies, we are neglecting the influence of other perturbers on the collision. We are not only completely ignoring all perturbers which do not approach closer than the critical collision radius but also assuming that there is never more than one perturber within the collision "sphere". This approximation will break down at higher pressures.

(2) Zero collision time. The effects of very close collisions are also ignored in the sense that as soon as a perturber approaches within b_c of the emitter a collision is deemed to have occurred. No consideration is given to the magnitude of the change in phase -, η, and all η's are considered to be 1. This will restrict the theory to the line centers if

> we assume that the large frequency shifts associated with the line wings are due to large changes in the phase.

We next consider attempts to widen this range of applicability. Lenz first attempted to remove approximation (2), but only with partial success. The next major improvement was due to Lindholm.

Lindholm, 1938

We shall return to the Lindholm theory in the next chapter, but we first present the concepts behind his method. The idea seems to have been originally put forward by Lenz but was developed by Lindholm.

We recall that we can write

$$J(w) \quad \propto \int_{-\infty}^{+\infty} \exp -i \left\{ (\omega-\omega_0)t + \eta(t) \right\} dt$$

Since $$I(w) \quad \propto \quad | J(\omega) |^2$$

then $$I(w) \quad \propto \iint_{-\infty}^{+\infty} \exp -i \left\{ (\omega-\omega_0)(t''-t') + \eta(t'') - \eta(t') \right\} dt' dt''$$

$$= \int_{-\infty}^{+\infty} \exp -i \left\{ (\omega-\omega_0) t \right\} dt \int_{-\infty}^{+\infty} \exp -i \left\{ \eta(t+t') - \eta(t') \right\} dt'$$

The integral over t' is a time average over t' and according to Boltzmann's ergodic hypothesis can be replaced by a mean over a statistical distribution $\langle \exp -i \left\{ \eta(t+t') - \eta(t') \right\} \rangle$. To calculate this mean we suppose that in a collision only a finite number of phase changes can occur, and for convenience we arbitrarily set this number to 2, ηa and ηb. Suppose we have A collisions of type "a" and B collisions of type "b". Then

$$\eta(t+t') - \eta(t') = A\eta_a + B\eta_b$$

The collision cross-section q is made up of two differential cross-sections,

$$q = q_a + q_b$$

and the probability that A collisions of type "a" and B collisions of type "b" occur in a time interval t is

$$\left(\frac{q_a}{q}\right)^A \left(\frac{q_b}{q}\right)^B \frac{1}{A!B!} \left(\frac{t}{\tau}\right)^{A+B} \exp\left(-t/\tau\right)$$

Then

$$\langle \exp -i \left\{ \eta(t+t') - \eta(t') \right\} \rangle = \sum_A \sum_B \left(\frac{q_a}{q}\right)^A \left(\frac{q_b}{q}\right)^B \frac{1}{A!B!} \left(\frac{t}{\tau}\right)^{A+B} \exp(-t/\tau) \exp i\left(A\eta_a + B\eta_b\right)$$

and since

$$\sum_{A=0}^{\infty} \left\{ \frac{q_a}{q} \frac{t}{\tau} \exp i\eta_a \right\}^A \cdot \frac{1}{A!} = \exp\left\{ \frac{q_a}{q} \frac{t}{\tau} \exp i\eta_a \right\}$$

we obtain

$$\langle \exp -i \left\{ \eta(t+t') - \eta(t') \right\} \rangle = \exp\left\{ \frac{t}{q\tau} \left(q_a \exp -i\eta_a + q_b \exp -i\eta_b \right) - \frac{t}{\tau} \right\}$$

A more general expression for any number of phase changes can be obtained by the same method

$$\langle \exp -i \left\{ \eta(t+t') - \eta(t') \right\} \rangle = \exp\left\{ \frac{t}{\tau} \sum_i \frac{q_i}{q} \left(\exp -i\eta_i - 1 \right) \right\}$$

If we define

$$\alpha = \frac{1}{\tau} \sum_i \frac{q_i}{q} \left(\cos\eta_i - 1 \right)$$

$$\beta = \frac{1}{\tau} \sum_i \frac{q_i}{q} \sin\eta_i$$

the line intensity is

$$I(w) = \int_{-\infty}^{+\infty} \exp -i \left\{ (w-w_0)t \right\} \exp \left\{ (\alpha - i\beta)\, t \right\} dt$$

$$= \frac{\text{constant}}{(w-w_0 + \beta)^2 + \alpha^2}$$

This is the fundamental result due to Lindholm. It has a Lorentzian shape but exhibits a feature not found in Lorentz's profile, a shift of the whole spectral line by an amount β, a shift which is experimentally observable. This shift was obtained by considering "weak" collisions, that is collisions which individually do not cause a phase change greater than 1, but which have a cumulative effect on the emitter. For a fixed velocity these are caused by collisions with large impact parameter, $b > b_c$.

Lindholm and Unsold both showed why ignoring distant collisions led to no line shift for the case of short range forces, $V(r) \propto r^{-6}$. The explanation also holds for long range potential, and at this stage can best be explained by reference to Fig. 5. The area under the upper curve is a measure of the broadening, the area under the lower curve is a measure of the shift. By only considering the area to the left of $\eta = 1$ the simple theory obtains most of the broadening, but the shift is due to values of η much less than 1.

Lindholm, 1946

Lindholm next considered the effect of including effects arising from the duration of the collision. Whereas the change in phase as a function of time had previously been considered a step function being zero up to a time t when it immediately rose to a fixed quantity, Lindholm investigated the way in which the function rose from zero to this constant. As he had previously considered "incomplete" phase changes, i.e. phase changes with $\eta < 1$, he now considered "incomplete"

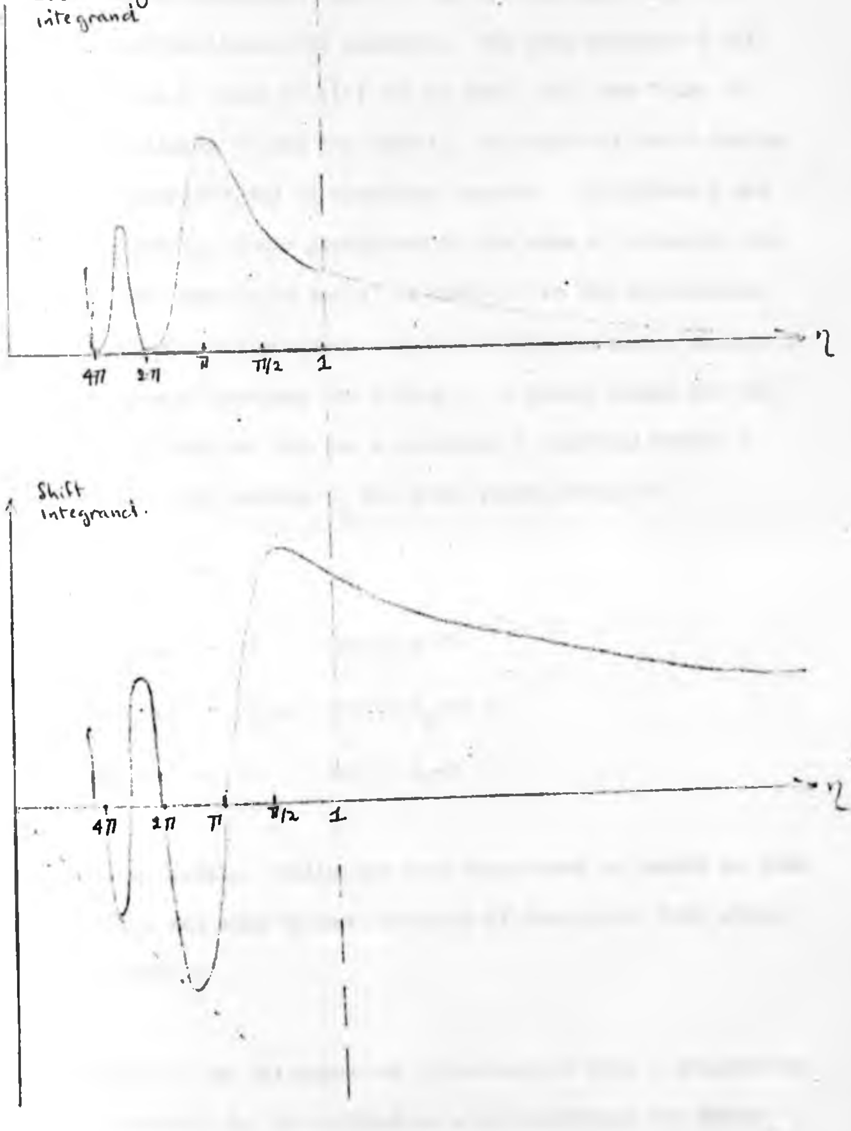
broadening integrand
4π
2π
π
π/2
1
η
Shift integrand.
4π
2π
π
π/2
1
η

Fig. 5

collision times.

Figure 6 is due to Lindholm. The five arrows represent the five general types of collisions he examined. The time interval t will be used to define a value of $\eta(t)$ and we shall call the "time of interest". Collision 1 last for time t_1, but does not occur during the "time of interest" and is therefore ignored. Collisions 2 and 5, lasting t_2 and t_5, occur partly within the time of interest, and that part of the time (t_2-x and y) is included in the calculation. Collision 4 occurs wholly within t and is wholly included, whereas collision 3 is only included for a time t. A phase change per unit time, k_i, is defined so that for a collision i starting within a time interval dx and lasting t_i the total phase change is

$$k_i \quad Q(t_i-x)$$

where

$$Q(t_i-x) = 0 \qquad \text{for } t_i-x < 0$$

$$Q(t_i-x) = t_i-x \qquad \text{for } 0 < t_i-x < t$$

$$Q(t_i-x) = t \qquad \text{for } t < t_i-x$$

On the previous models, collisions were considered as points in time and a collision was said to have occurred if that point fell within the time interval t.

Defining N(x,i) to be the number of collisions of type i originating during the interval dx, the collisions will contribute the factor

$$\exp{-i}(N(x,i)\ k_i\ Q(t_i-x))$$

to the mean of $\exp i(\eta(t'+t) - \eta(t'))$. Generalizing this expression and by analogy to his treatment of "partial" phases, he obtained

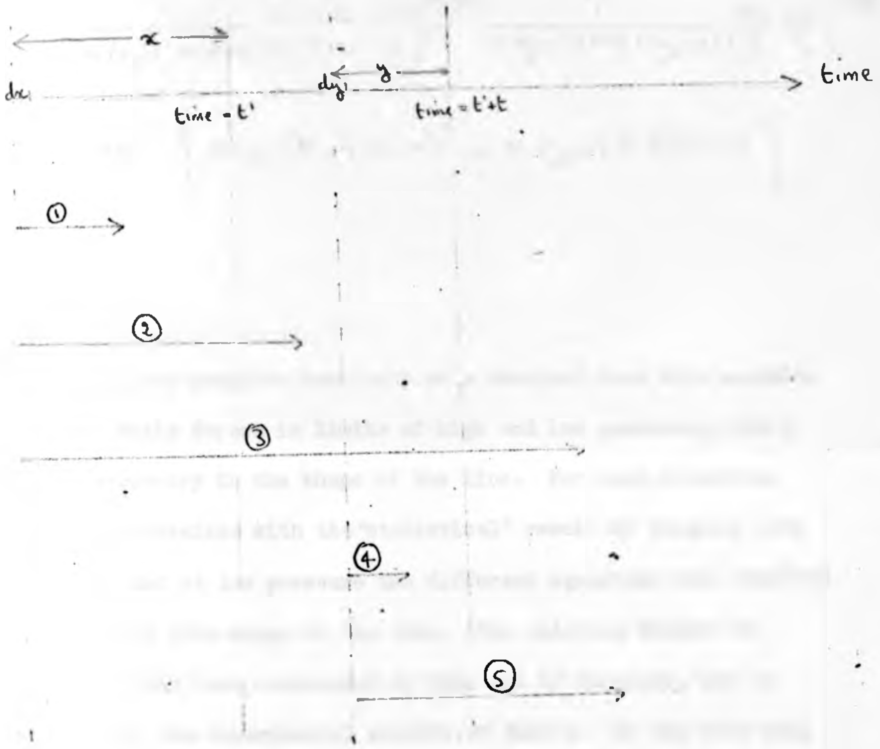

Figure 6

Classification of Collisions according to Lindholm

$$\langle \exp[\eta(t'-t)-\eta(t')] \rangle = \sum_{N(x_1,1)} \cdots \sum_{N(x_1,i)} \cdots \sum_{N(x_2,i)} \cdots \sum_{N(x_j,i)} \cdots \sum_{N(y_l,i)} \cdots \prod_{i} \prod_{dx_j} \prod_{dy_l}$$

$$\times \frac{1}{N(x_j,i)!\,\exp(dx_j/\tau)} \left(\frac{q_i}{q}\,\frac{dx_j}{\tau}\right)^{N(x_j,i)} \frac{1}{N(y_l,i)!\,\exp(dy_l/\tau)} \left(\frac{q_i}{q}\,\frac{dy_l}{\tau}\right)^{N(y_l,i)}$$

$$\times \exp -i \left\{ N(x_j,i)\,k_i\,Q(t_i-x) + N(y_l,i)\,k_i\,Q(t_i-y) \right\}$$

Formulae for line profiles have only been obtained from this equation for van der Waals forces in limits of high and low pressures, where they show asymmetry in the shape of the line. For high pressures, agreement was obtained with the "statistical" result of Margenau (see Appendix 1), and at low pressure two different equations were obtained for the red and blue wings of the line. The red wing decayed as $(w-w_o)^{-3/2}$ as had been calculated by Kuhn and by Margenau, and in agreement with the experimental results of Kuhn's. In the blue wing a dependence of $(w-w_o)^{-7/2}$ was obtained, in agreement with measurements by Minkowski.

CHAPTER V

GENERALIZATION OF THE CLASSICAL METHODS

5.1 The Autocorrelation function treatment

We recall that

$$I(w) = \text{constant} \times \int_{-\infty}^{+\infty} \exp -i \left\{ (\omega - \omega_0) t \right\} dt$$

$$\times \int_{-\infty}^{+\infty} \exp -i \left\{ \eta(t+t') - \eta(t') \right\} dt'$$

A convenient way of writing this is

$$I(w) = \text{constant} \times \int_{-\infty}^{+\infty} \exp -i \left\{ (w-w_0)s \right\} \phi(s)\, ds$$

$$\phi(s) = \int_{-\infty}^{+\infty} \exp -i \left\{ \eta(s+t') - \eta(t') \right\} dt'$$

The function $\phi(s)$ was first called the "correlation function" by Foley and is now much used in quantum mechanical treatments, where it is called the "autocorrelation function". It is large when $s = 0$ and decreases with increasing s. Speaking unscientifically, it is a measure of how much the atom "remembers" its previous state and of how quickly it "forgets".

According to the Ergodic theorem the integral over t' can be replaced by an average over a statistical distribution, so that Lindholm's method in fact involved calculating the autocorrelation function. We note that if we can write $\ln \phi(s) = -As + iBs$ (with A and B both real) then the line profile will be Lorentzian with a width of A and a shift of B. If $\ln \phi(s)$ has a more complicated dependence on s, an asymmetric profile is obtained.

5.2 The Classical model

We consider the interaction between a hydrogenic atom and a passing charged particle. We neglect "back reaction" from the atom to the particle, so that the particle trajectory is described by a straight line. We define the distance of closest approach to be the impact parameter, b, and assign a constant velocity v to the particle. To define the collision uniquely in time we also define a time of closest approach, t_o, that is the time at which the particle was at a distance b from the atom.

The set of parameters (b, v, t_o) define a unique collision. In a plasma the atoms undergo many such collisions. Since the number of radiators is usually a small fraction of the total number of particles, the average distance between radiators will be large enough so that any interaction between them can be ignored. In the manner of Smith et al we can regard the system as a large number of non-interacting cells, each cell containing one radiator and a large number of perturbers undergoing collisions with it, each collision defined by a set of parameters (b, v, t_o).

The theory presented here suffers from one major restriction in that we only consider collisions which do not significantly change the state of the atom. We restrict ourselves to cases which involve no change in the principal quantum number n, but allow small proportional changes in the angular quantum number l since these do not greatly affect the phase of the motion and only cause slight distortion in the electron orbit. We do not consider the case of n = 2 and l changing from 0 to 1, which completely changes the shape of the orbit. We are thus dealing with classical perturbation theory as opposed to quantum mechanical perturbation theory which does not allow any change in any of the quantum numbers.

It is known that in certain cases, for instance for small impact parameters, the atomic states are completely disrupted by strong collisions. However it is as yet impossible to provide a general theory which would include the effect of impact parameters of the same order of magnitude as the Bohr radius of the atom, especially for the weakly bound electrons in highly excited states. This would involve a classical three-body problem (or a quantum mechanical interweaving of wavefunctions) which might be solved by Monte-Carlo simulations of the collisions, as investigated by Banks et al(1969). These strong collisions cause a total disruption of the phase of the emitter and can be treated individually by the theory of Lorentz.

Since we do not claim that this theory is valid for b $\rightarrow 0$, we can make the following assumptions:

(1) The orientation of the classical atom with respect to the trajectory of the perturber does not need to be considered.

(2) The interaction between the emitter and the perturber can be represented by the first term in a multipole expansion, i.e. the dipole approximation is made.

(3) The electric field due to the perturber is uniform over the atom.

We shall show in the following sections that although the value of b does determine what physical approximations can be made, more critical parameters are the product and the ratio of the impact parameter and velocity.

THEORY

We now define two new variables, and let

$$\Delta\eta(s) = \eta(t+s) - \eta(t)$$

so that $\Delta\eta(s)$ is the change in $\eta(t)$ after a time s (we recall that $\eta(t)$ is the change in the phase after a time t) and we choose $\rho(\Delta\eta)$ to be the probability of that phase change $\Delta\eta$ occuring in the time interval s. Then the autocorellation function can be written

$$\phi(s) = \int_{-\infty}^{+\infty} d\Delta\eta \; \rho(\Delta\eta) \exp -i\,\Delta\eta$$

Let X be a variable or a set of variables which define a unique collision, and let $\alpha_x = P(X)dX$ be the probability that a collision defined by X occurs in the interval dX and nowhere else. Since X defines a unique collision it also defines a unique $\Delta\eta_x(s)$ so that the probability of that collision causing a phase change is

$$\rho_x(\Delta\eta) = (1-\alpha_x)\,\delta(\Delta\eta) + \alpha_x \,\delta(\Delta\eta - \Delta\eta_x(s))$$

The autocorellation function for that X collision is then given by

$$\phi_x(s) = (1-\alpha_x) + \alpha_x \exp -\left\{i\,\Delta\eta_x(s)\right\}$$

We now wish to consider the cumulative effect of different collisions. We make the simplest assumption, that collisions are "additive" in that the total phase shift caused by a series of collisions is given by the sum of the phase shifts which would have been caused by each of the collisions occurring singly. We do not require the collisions to be sudden and not to overlap in time, but only assume that the perturbers do not interact with each other and that consecutive collisions permute. The resultant probability $\rho(\Delta\eta)$ of a final phase shift $\Delta\eta$ occurring due to different X collisions is the convolution of the individual probabilities $\rho_x(\Delta\eta)$, and since the Fourier transform of a convolution is the product of each of the Fourier transforms

$$\phi(s) = \prod_x \phi_x(s)$$

or

$$\ln \phi(s) = \sum_x \ln \phi_x(s)$$

$$= \sum_x \ln \left\{ 1 - \alpha_x + \alpha_x \exp - \left[i \Delta\eta_x(s) \right] \right\}$$

This can be rewritten in a more convenient form. By adjusting the interval dX, α_x can be made as small as necessary, and we can write

$$\ln\phi(s) = \sum_x \alpha_x \left\{ \exp - \left[i \Delta\eta_x(s) \right] - 1 \right\}$$

so that, replacing the sum over X by an integral,

$$\ln \phi(s) = \int dx \;\; \rho(X) \left\{ \exp - \left[i \Delta\eta_x(s) \right] - 1 \right\}$$

with the line intensity related to $\phi(s)$ by

$$I(w) = \text{constant} \int_0^\infty ds \exp - \left[i \Delta w s \right] \;\; \phi(s)$$

we now calculate $\Delta\eta$.

Without loss of generality, using the definition of η, we recall that $\hbar = 1$ and redefine

$$\Delta\eta(s) = \eta(t+s) - \eta(t)$$

to be $\eta(s)$

and define

$$\eta_x(s) = \int_0^s dt \; \Delta w_x(t')$$

In general, the form of $\Delta w_x(t)$ may not be simple. However we are making a dipole approximation and therefore set it proportional to the local electric field at the emitting atom. (We are implicitly assuming that the field is uniform over the atom, in keeping with our requirement of large impact parameter.) Then where c is the force constant and we have set $X = (b, v, t_o)$, this leads to a value for the phase shift of

$$\eta(s) = \frac{c}{bv}\left\{\arctan\left[\frac{v}{b}(t_o+s)\right] - \arctan\left[\frac{vt_o}{b}\right]\right\}$$

Similar expressions for $\eta(s)$ can be obtained using the same assumptions for shorter range potentials.

Since t_o is only defined to an arbitrary additive constant, we can define a new t_o to be $t_o + \frac{1}{2}s$. We also introduce a parameter, a, whose significance will become apparent later:

$$a = \frac{c}{2bv}$$

Then

$$\eta(s) = 2a\left\{\arctan\left[\frac{v}{b}(t_o+\tfrac{1}{2}s)\right] - \arctan\left[\frac{v}{b}(t_o-\tfrac{1}{2}s)\right]\right\}$$

This expression for $\eta(s)$ can be further simplified by combining the two arctans. Care has to be taken since there is a cut in the arctan plane, and depending on the relative values of t_o, s, and v/b it is possible to move from one sheet to another. To allow for this we write

$$\eta(s) = 2a\arctan\left\{\frac{S}{1+T^2-\frac{1}{4}S^2}\right\} + 2a\pi\,.\,H$$

$$S = \frac{vs}{b}\ ,\quad T = \frac{vt_o}{b}$$

and H is a step function with values

$$\begin{aligned} H &= 0\ , \quad 1 + T^2 - \tfrac{1}{4}S^2 \geqslant 0 \\ &= 1\ , \quad 1 + T^2 - \tfrac{1}{4}S^2 < 0 \end{aligned}$$

The presence of the step function is a major source of difficulty in computing actual line profiles from the analysis presented above and it is sometimes more useful to consider the form of η which involves the two arctans.

Summarizing, the line profile is given by the following set of equations:

$$I(w) = \text{constant} \int_0^\infty ds\, \phi(s) \exp(-i\, \Delta ws)$$

$$\ln \phi(s) = 4\pi N v \int_0^\infty b\,db \int_0^\infty dt_o \left\{ \exp(-i\eta) - 1 \right\}$$

$$\eta = 2a \left\{ \arctan\left(T+\tfrac{1}{2}S\right) - \arctan\left(T-\tfrac{1}{2}S\right) \right\}$$

$$a = \frac{c}{2bv}, \quad T = \frac{vt_o}{b}, \quad S = \frac{vs}{b}$$

In addition to the previously mentioned assumptions, we have replaced what should have been an average over a Maxwellian distribution over velocities by a mean (or root mean square) velocity v. Although this assumption is not necessary for the model, it is in keeping with the feelings and the experience of most workers in the field (private communications). The probability $P(X)$ has thus been replaced by $P(b)\ P(t_o)$, and

$$P(t_o)dt_o = \frac{dt_o}{\tau}$$

$$P(b)db = \frac{2\pi\, b\,db}{q}$$

for a mean intercollision time τ and a total collision cross-section q. Since the collision frequency $1/\tau = Nvq$ for a density N, the two probabilities can be combined to give the quoted result.

CHAPTER VI

CALCULATION OF LINE PROFILE

We first show that the result obtained reduces to the well known expressions of the impact and the statistical theory in the appropriate limits.

For small values of v, we would expect to obtain the statistical shape which arises from assuming fixed perturbers. Setting $r^2 = b^2 + v^2 t_o^2$, so that r is the perturber/emitter separation at $t = 0$, then letting $v \rightarrow 0$,

$$\ln \phi(s) = 4\pi N \int_0^\infty r^2 dr \left\{ \exp -i\eta - 1 \right\}$$

and in this case

$$\eta = \frac{cs}{r^2}$$

This is the statistical result obtained by Margenau, and which is valid in the line wings. We note that although it is obtained by setting $v = 0$, a sufficient requirement is that $v^2 s^2 \ll 4(v^2 t_o^2 + b^2)$, i.e. $S^2 \ll 4(T^2 + 1)$ and that $vsb \ll b^2 + v^2 t^2$, i.e. $S \ll (T^2 + 1)$, which will occur when v is small, s is small, or b is large. A sufficient requirement for the validity of the statistical approximation is thus that the distance travelled during the time of interest (s) should be small compared with the impact parameter.

For $v \rightarrow \infty$, the Lindholm result is obtained. Again the limit is strictly defined in terms of S and T. If

$$|S| \ll \left| 1 + T^2 - \tfrac{1}{4} S^2 \right|$$

then

$$\ln\phi(s) = 4\pi N v \int_0^\infty b\,db \int_0^\infty dt_0 \left\{ \exp(-i\eta) - 1 \right\}$$

$$\eta = 2a\pi \quad , t_0 \leq \tfrac{1}{2}s$$

$$= 0 \quad , t_0 > \tfrac{1}{2}s$$

so that

$$\ln\phi(s) = 2\pi N v s \int_0^\infty b\,db \left\{ \exp(-2ia\pi) - 1 \right\}$$

which is the Lindholm result.

It is instructive to examine a plot of η as a function of t_0 for various values of s (Fig 5.7). The Lindholm approximation is a step function of height $2a\pi$ terminating at $t_0 = \frac{1}{2}s$ (curve a). The Lenz result replaces the sudden chop to zero by a steep slope (curve b), and the Lindholm variation of the Lenz result (curve c) is an adjustment of the slope until agreement is obtained with the statistical limit. All three seem atfirst to be reasonable approximations to the exact result (curve d) although the only exact agreement is at $t_0 = 0$ and $t_0 = \pm\frac{1}{2}s$ (since the function is symmetric about $t_0 = 0$). As s increases, the exact curve approximates more and more to a step function, and agreement with the approximation improves. We shall show, however, that as the parameter a increases, the increase in the height of the function shows fundamental failings in these approximations.

We start by attempting to evaluate $\ln\phi(s)$ by non-numerical "analytical" techniques. We define

$$\ln\phi(s,b) = \int_0^\infty dt_0 \left\{ \exp(-i\eta) - 1 \right\}$$

and try to evaluate $\ln\phi(s,b)$ followed by

$$\ln\phi(s) = \int_0^\infty b\,db\,\ln\phi(s,b) \cdot 4\pi N v$$

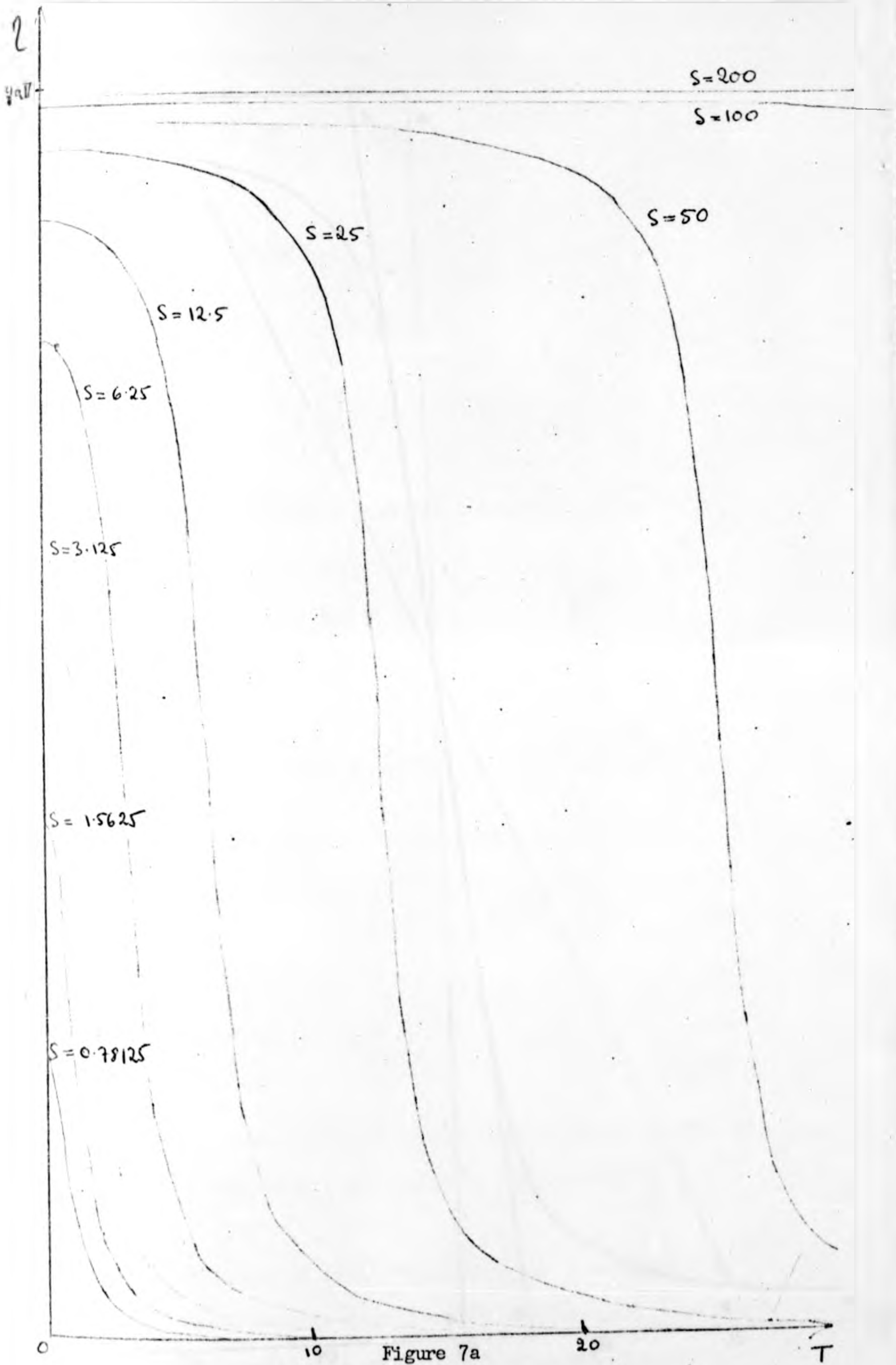

Figure 7a

Plot of η v.s. T for different values of S

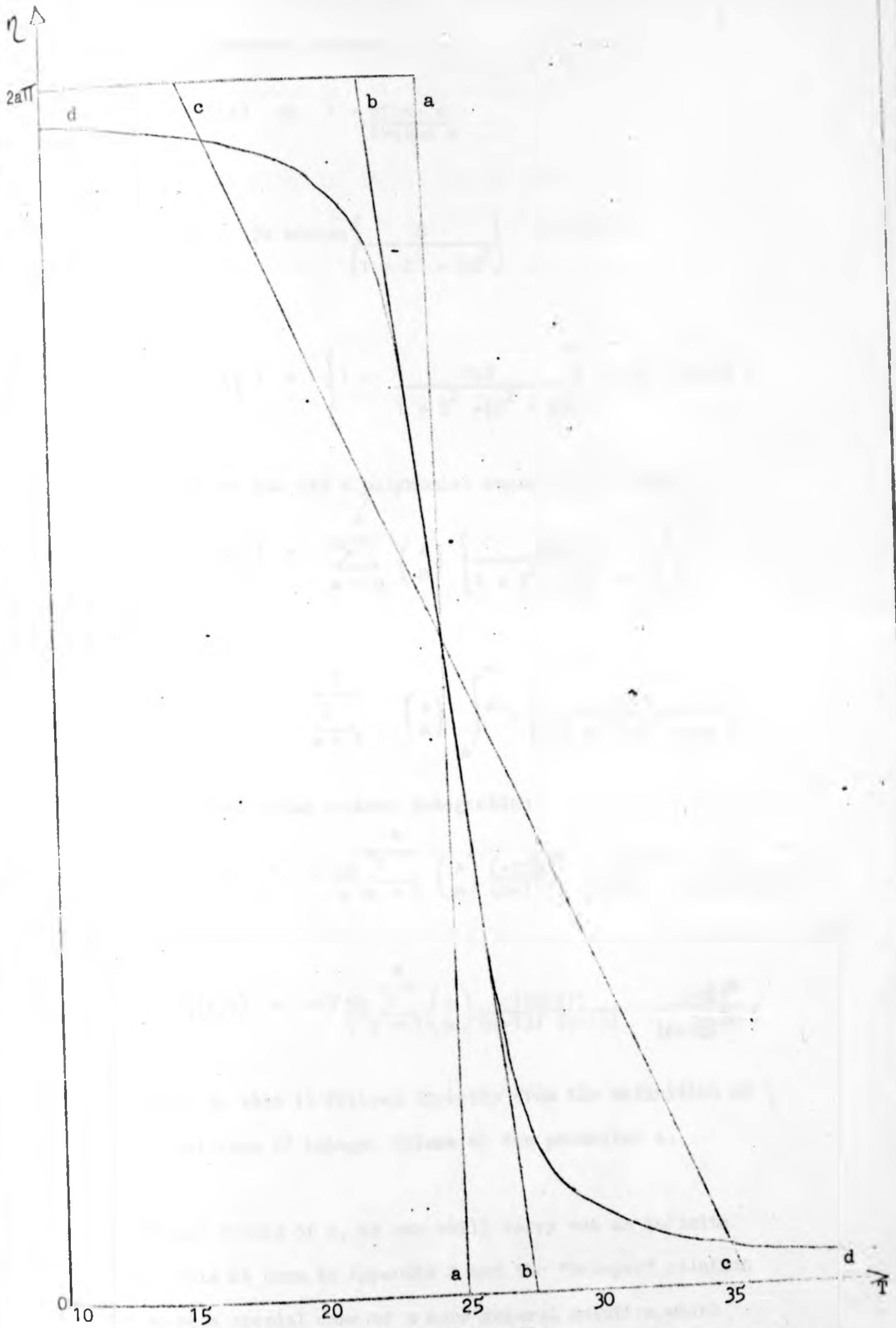

Figure 7b

Plot of η v.s. T for S = 50, showing the various approximations

We use the trigonometric property

$$\exp(-2ix) \equiv 1 - \frac{2i\tan x}{1+i\tan x}$$

so that since

$$\eta(s) = 2a \arctan\left\{\frac{S}{1 + T^2 - \frac{1}{4}S^2}\right\} + 2a\pi H$$

then

$$\exp(-i\eta) = \left\{1 - \frac{2iS}{1 + T^2 - \frac{1}{4}S^2 + iS}\right\}^a \exp(-2ai\pi H)$$

If a is integer, we can use a polynomial expansion to obtain

$$\exp(-i\eta) = \sum_{m=o}^{a} \binom{a}{m} \left\{\frac{-2iS}{1 + T^2 - \frac{1}{4}S^2 + iS}\right\}^m$$

and

$$\ln \phi(s,b) = \sum_{m=1}^{a} \binom{a}{m} \int_o^{\infty} dt_o \left\{\frac{-2iS}{1 + T^2 - \frac{1}{4}S^2 + iS}\right\}^m$$

which can be solved using contour integration

$$\ln \phi(s,b) = \pi \frac{ib}{v} \sum_{m=1}^{a} \binom{a}{m} \frac{(-2iS)^m}{(m-1)!} \left[\left(\frac{d}{dT}\right)^{m-1} \frac{1}{(T+i-\frac{1}{2}S)^m}\right]$$

$$\text{at } T = i-\tfrac{1}{2}S$$

i.e. $$\ln \phi(s,b) = -\pi \frac{ib}{v} \sum_{m=1}^{a} \binom{a}{m} \frac{(2m-2)!}{(m-1)!\,(m-1)!} \frac{(2iS)^m}{(2i-S)^{2m-1}}$$

This is <u>exact</u>, in that it follows directly from the definition of η for the special case of integer values of the parameter a.

For non integer values of a, we can still carry out an infinite expansion. This is done in Appendix 2 and the "integer" solution is shown to be a special case of a more general solution which unfortunately is of little practical use, due partly to very slow convergence. The exact "integer" solution however is of use as a test of any other expression which may be obtained for ln $\phi(s,b)$.

After numerous vain attempts, it was decided that there was no general closed form exact solution for ln $\phi(s,b)$. As ln $\phi(s,b)$ was proportional to a function of only a and S, the limiting behaviour as a and S tended to 0 or ∞ were examined.

For small values of a, and for small $S/1 + T^2 - \frac{1}{4}S^2$,

$$a \arctan \left\{ \frac{S}{1 + T^2 - \frac{1}{4}S^2} \right\} \simeq \arctan \left\{ \frac{aS}{1 + T^2 - \frac{1}{4}S^2} \right\}$$

Then

$$\ln \phi(s,b) \simeq -\int_0^\infty dt_o \quad \frac{2aiS}{1 + T^2 - \frac{1}{4}S^2 + 2aiS}$$

$$= \frac{b}{v} \quad \frac{2\pi\ aS}{2i - aS}$$

The factor $\frac{b}{v}$ arises since we are integrating a function of T with respect to t_o. Alternative expansions for small a reduce to the above expression. We could for instance consider an expansion for small η. Starting from

$$\ln \phi(s,b) = \int_0^\infty dt_o \left\{ \exp \left[-ic \int_0^s \frac{dt}{b^2 + v^2\ (t_o + t)^2} \right] - 1 \right\}$$

We expand the exponential and reverse the order of integration

$$\ln \phi(s,b) = -ic \int_0^s dt \int_0^\infty dt_o \frac{1}{b^2 + v^2(t + t_o)^2}$$

$$-c^2 \iint_0^s dt_1 dt_2 \int_0^\infty dt_o \frac{1}{b^2 + v^2(t_1 + t_o)^2} \quad \frac{1}{b^2 + v^2\ (t_2 + t_o)^2}$$

After some analysis this leads to

$$\ln \phi(s,b) = -ia\pi S \quad - 2\pi a^2 \frac{b}{v} \left\{ S \arctan \left(\tfrac{1}{2}S\right) - \ln \left(1 + \tfrac{1}{4}S^2\right) \right\}$$

For small values of S and aS both these approximations reduce to

$$\ln \phi(s,b) = -ia\pi \dot{s} - \frac{\pi}{2} a^2 S^2 \frac{b}{v}$$

We can show that for small s the "integer a" solution reduces to this expression. Let

$$X = \frac{2iS}{(2i-S)^2} = \frac{-8S^2 - 8iS + 2iS^3}{(4 + S^2)^2}$$

then

$$\ln \phi(s,b) = \pi \frac{ib}{v}(S-2i) \left\{ aX + a(a-1)X^2 + a(a-1)(a-2)X^3 \cdots \right\}$$

for integer a, where the ratio of the mth term to the (m-1) is

$$2 \frac{(a-m+1)(2m-3)X}{m(m-1)} \quad , m \neq 1 .$$

This is exact for integer values of a. This expression also holds true for small value of a, although the number of terms become infinite. For small S, $X \simeq -\frac{1}{2}(iS + S^2)$, and

$$X^m \simeq \left(\tfrac{1}{2}\right)^m (-1)^m \left\{ (iS)^m + mS^2 (iS)^{m-1} \right\}$$

so that

$$\ln \phi(s,b) = \pi \frac{ib}{v}(S-2i) \left\{ \frac{a}{2}(iS-S^2) + \frac{a}{4}(a-1)(+2iS^3 - S^2) + \frac{a}{8}(a-1)(a-2)(+iS^3 + 3S^4) \cdot\cdot \right\}$$

noting that each term has some cancellation with its successor. Having checked for convergence, the required result is obtained.

For large values of S, the Lindholm approximation is obtained. If $S \geqslant 2\sqrt{1+T^2}$, and $S \gg 1$, (which Lindholm effectively replaced by $S \geqslant 2T$)

$$\eta(S) \simeq 2a\pi \quad , \quad s \geqslant 2\sqrt{1+T^2}$$

$$\eta(S) \simeq 0 \quad \text{otherwise}$$

so that

$$\ln \phi(s,b) = \frac{b}{v}\left\{\exp(-2ia\pi) - 1\right\} \sqrt{\frac{S^2}{4} - 1}$$

or, since S is large

$$\ln \phi(s,b) = \left\{\exp(-2ia\pi) - 1\right\} \tfrac{1}{2}S$$

This unfortunately does not agree with the exact "integer a" solution, since it is zero for all integer values of a. The reason is that a complete expansion of η for large values of S is

$$\eta(s) \simeq 2a\pi - \frac{4a}{S}\left\{1 + T^2 - \tfrac{1}{4}S^2\right\} , \quad T^2 \leqslant \tfrac{1}{4}S^2 - 1$$

$$\simeq \frac{4aS}{1 + T^2 - \tfrac{1}{4}S^2} , \quad T^2 > \tfrac{1}{4}S^2 - 1 .$$

Since we then consider an integrand of $\exp(-i\eta) - 1$, it is insufficient to only take the dominant term in the first expansion whenever the value of a is close to an integer. In those regions, the Lindholm approximation breaks down. Further, since we are considering trigonometric functions, there is no guarantee that that contribution to the integral arising from large values of T will not contribute significantly. By taking these extra terms into account, better approximations can be obtained for high values of S.

By combining the various limiting cases for high and low S and a, and by other approximations, integrable forms of $\ln \phi(s,b)$ can be obtained which lead to analytic expressions for $\ln \phi(s)$ which were numerically integrated to give line profiles. These profiles were unacceptable since they exhibited spurious "satellite" lines between the line centre and the line wings. The "satellites" were due to the crude way in which the asymptotic expansions for $a,S \rightarrow \infty$ (say η_∞) and $a,S \rightarrow 0$ (say η_0) were extrapolated back to intermediate regions. This was checked by examining the totally different line shapes which were obtained using different extrapolation techniques one in which η was chosen to be η_0 until $\eta_0 = \eta_\infty$ when η was set to η_∞, the other in which

$$\eta = \frac{\eta_0 . \eta_\infty}{\eta_0 + \eta_\infty}$$

It was therefore decided that any method which did not produce satisfactory results for intermediate values of a and S would produce spectral lines which although satisfactory in the wings and in the centre, were wrong in the intermediate region. Since the behaviour of a line over the whole profile was the purpose of this investigation, and since it was felt that no way could be found to produce a general analytical expression for ln $\phi(s)$, the problem had to be solved on a computer.

CHAPTER VII

NUMERICAL COMPUTATION OF LINE PROFILE

Most of the computing was carried out on a CDC 7600, after attempts on an Elliot 4100. Various programs were written to calculate the triple integral

$$I = \int_0^\infty \exp(-i\Delta ws)\ \phi(s)\ ds$$

$$\ln \phi(s) = 4\pi Nv \int_0^\infty bdb\ \ln \Phi(s,b)$$

$$\ln \phi(s,b) = \int_0^\infty \left\{\exp(-i\eta) - 1\right\} dt,$$

$$\eta = 2a\left\{\arctan(T + \tfrac{1}{2}S) - \arctan(T - \tfrac{1}{2}S)\right\}$$

$$a = \frac{c}{2bv}, \quad T = \frac{vt}{b}, \quad S = \frac{vs}{b}$$

In practice it was found that the imaginary part of the integral over the impact parameter could diverge as $b \rightarrow \infty$, and in those cases the upper limit of b was replaced by b_{max}, whose value will be discussed later.

The integral was evaluated by defining a new variable

$$x = \frac{u}{u + t}$$

The parameter u was varied to check the sensitivity of the integrating method, since the value of $\ln \phi(s,b)$ should be independent of the value of u. The limits of integration became (0,1), and an n-point Gaussian quadrature method was used. For selected values of a and S, n was varied from 4 to 20, and an optimum value of 12 was chosen as using more points changed the value of the integral by less than about 5%. Varying the value of u from 0·1 to 1 to 10 caused negligible change. The alternative form of η combining the two arctangents was found to be computationally 20% faster and was therefore used.

The numerical values obtained provided an integrand for the b integral which was non-oscillatory and which was easily integrated and checked to an accuracy of better than a few percent. A trapezoidal rule technique was used to calculate the Fourier transform, and obtain a line profile. Unfortunately the resulting line profiles did not agree with the known and accepted shapes in the centre and in the wings. The three integrals were then checked simultaneous, inter alia by varying u and n, and it was belatedly realised that since we are dealing in the Fourier transform with terms which involve the sine and cosine of $\ln\phi(s)$, it is essential to calculate $\ln\phi(s)$ extremely accurately when the imaginary part of $\ln\phi(s)$ is much greater than 1. To obtain an accuracy of 10% in the line shape we need to calculate $\{\ln\phi(s) \text{ modulus } 2\pi\}$ to better than 10% and not $\ln\phi(s)$ itself. This was found to be impossible for large values of a, even using hundreds of points in the Gaussian quadrature. The program was therefore abandoned and was only used as a check in the relevant regions for the next suite of programs. The new programs were written with the aim of obtaining a value of $\ln\phi(s)$ accurate to the limit of the single length precision of the computer, i.e. to about 13 significant figures.

7.1 t integral

We first discuss the physical significance of the dimensionless parameters a, S, and T. Since t is the time of closestapproach, vt is the distance between the perturber's position at $t = 0$ and its point of closest approach. T is then the ratio of this distance to the impact parameter and is the tangent of the angle subtended at the atom by the distance covered between times 0 and t. (Fig. 4a). The distance travelled during the time of interest (the autocorrelation time s) is vs, and S is the ratio of that distance to the impact parameter. The value of the parameter a indicates the strength of the collision and its effect on the atom. As the impact parameter and the velocity decrease, so a increases, and the collisions become more violent.

In calculating ln $\phi(s,b)$ we use as a check the various approximations derived above for small and large value of a and S. We are also helped by the fact that given a and S the phase shift η_l is bounded

$$0 \leqslant \eta_l \leqslant 2a\pi$$

and

$$0 \leqslant \eta_l \leqslant 2a \arctan(S) \quad , \text{ if } T^2 > \tfrac{1}{4}S^2 - 1$$

or

$$0 \leqslant \eta_l \leqslant 2aS \quad , \text{ if } S < 1$$

Difficulties arise when a is large since we are then trying to evaluate a highly oscillatory function, the number of oscillations being approximately equal to a (Fig. 8). For fixed v and c, these arise from small b, and on physical grounds we are not interested in the behaviour of ln $\phi(s,b)$ as $b \rightarrow 0$ since all the assumptions on which the model is based become invalid. Since we are claiming that the small b region does not contribute significantly to the broadening, all that we require is that as $b \rightarrow 0$, ln $\phi(s,b)$ should be smooth and continuous.

If the impact parameter is such that $a \gg 1$, we cannot approximate the arctangent, since any small approximation we make will be multiplied by a, and may become significant. If, for example, we expand the arctangent to an accuracy of 1 part in 10^3, and if $a \sim 10^3$, the value obtained for $\sin(\eta_l)$ will be meaningless. In

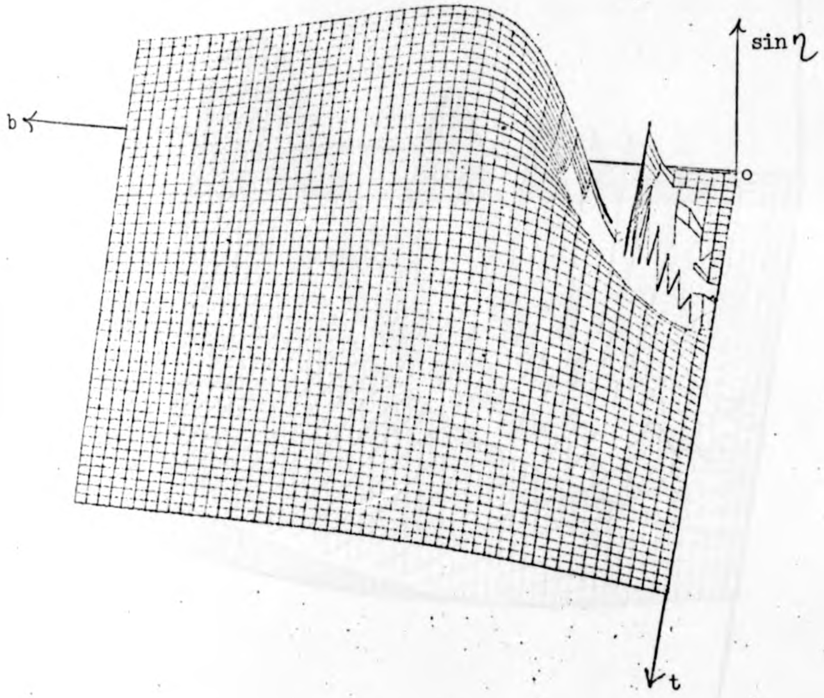

Fig8 a

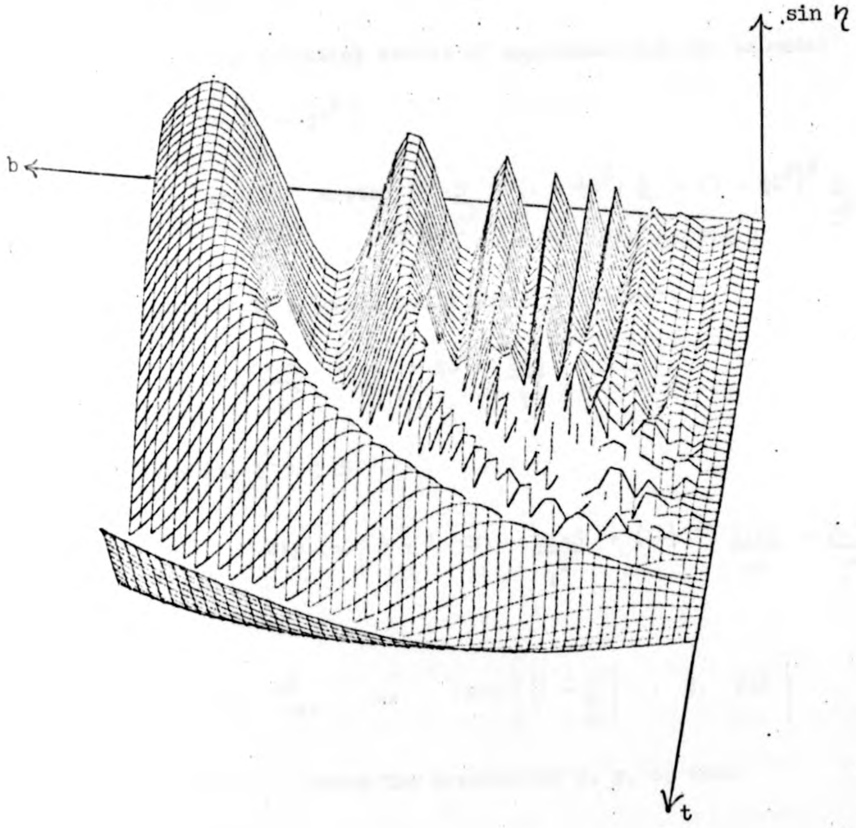

Fig 8b

Detail near $t = b = 0$

fact we must continue integrating at least until $t > t_{max}$, where $\eta < 1$ for all $t > t_{max}$. For $S > 2$ this immediately requires

$$T^2 > \tfrac{1}{4}S^2 - 1$$

If we define t_{max} by requiring that $\eta \ll 1$ for all $t > t_{max}$, we can expand $\exp(-i\eta)$ and evaluate

$$\int_{t_{max}}^{\infty} \left\{ -i\eta - \tfrac{1}{2}\eta^2 \right\} dt$$

Alternatively the following series of approximations can be made:

i) If $T^2 \gg \left| 1 - \tfrac{1}{4}S^2 \right|$

$$\eta \simeq 2a \arctan \left\{ \frac{S}{T^2} - (1 - \tfrac{1}{4}S^2)\frac{S}{T^4} + (1 - \tfrac{1}{4}S^2)^2 \frac{S}{T^6} \cdots \right\}$$

ii) If also $T^2 \gg S$ (which would normally follow)

$$\eta \simeq \frac{2aS}{T^2} - (1 - \tfrac{1}{4}S^2)\frac{2aS}{T^4} + \cdots$$

iii) If further $T^2 \gg 2aS$

$$\exp(-i\eta) - 1 \simeq -\frac{2iaS}{T^2} + (1 - \tfrac{1}{4}S^2)\frac{2iaS}{T^4} - \frac{2a^2S^2}{T^4} \cdots$$

so that if

$$\frac{v^2t^2_{max}}{b^2} \equiv T^2_{max} \gg \max\left\{ \left|1 - \frac{S^2}{4}\right| , S, 2aS \right\}$$

where $\max\{x,y,z\}$ means the greatest of x, y, z, then

$$\int_{t_{max}}^{\infty} (e^{-i\eta} - 1)\, dt = \frac{-2ias}{T_{max}} - \frac{2ba^2S^2}{3vT^3_{max}}$$

The integral was evaluated numerically and the results compared with the expression above. They were found to agree exactly if a high enough value of t_{max} was used. A sufficiently high and a useful value of t_{max} was obtained from

$$T^2_{max} = \left|1 - \tfrac{1}{2}S^2\right| + S + 2aS$$

Obtaining the value of the integral from t_{max} to infinity does not remove the difficulty associated with large values of a, but means we can concentrate on the region about $t = \frac{1}{2}s$, where the difficulties arise. It also means that we have a bound on the integral over t, since

$$(-2-i)t_{max} \leq \int_0^{t_{max}} dt \left\{\exp(-i\eta) - 1\right\} \leq it_{max}$$

against which we can check the numerical integration. This bound is of no use in calcultating line shapes, since it is only a bound on ln $\phi(s)$ and not on sin $\phi(s)$.

We can also obtain a cut-off for large b. We recall that one of the low a and S approximations consisted of expanding exp $(-i\eta)$ as $1 - i\eta - \eta^2$. Although it wasn't explicitly stated at the time this requires $\eta \ll 1$. Since $\eta \leq 2aS$, a sufficient condition for the expansion to be valid is that

$$2aS \ll 1 .$$

Alternatively, since $\eta \leq 2a\pi$, a sufficient condition also is

$$2a\pi \ll 1 .$$

Neither of these criteria depend on t, and rewriting them in terms of b and s, $cs \ll b^2$ and $c\pi \ll bv$, we see that there exists a b beyond which the approximations will be valid. Thus for some b > some b_{max}, the integral over t need not be evaluated numerically. Since we already have an analytic approximation for $t > t_{max}$, we need only evaluate the t integral over a finite range, (Fig 9)

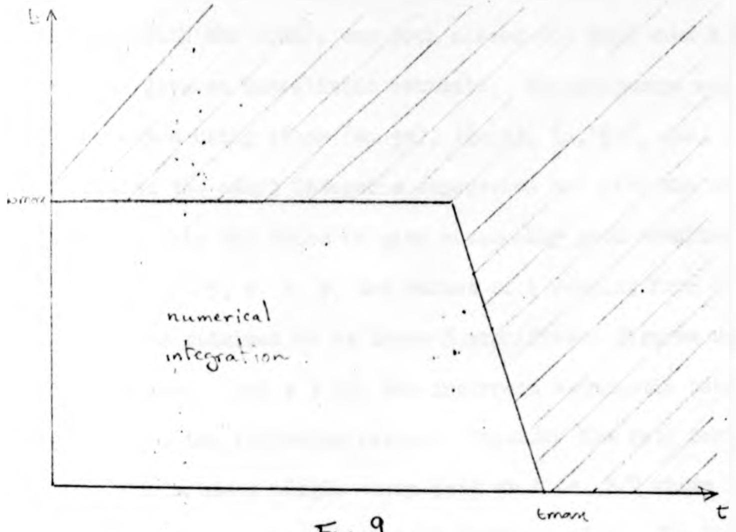

Fig. 9

To carry out the numerical integration, it was decided as a matter of policy to use a simple numerical integration technique whose behaviour could easily be checked at each stage, rather than a sophisticated package whose behaviour when faced with an unusual function could be unpredictable. A combination of Simpson's rule and Newton's rule was used. If n equidistant points were used to estimate the value of the integral, one method used all the even points, the other used all the odd ones, and the two estimates were checked for consistency. Since the oscillations generally occurred in the range (o,s), this range was split into N parts and integrated as described above. This was repeated for the intervals (s,2s), (2s,3s), etc., until $t > t_{max}$, or until further steps ceased to contribute significantly to the sum of the previous steps.

This method was checked for the special case a = 1, since if it could not cope with a single peak or oscillation it would be unable to cope with more. For a = 1 it was found unsatisfactory since one of the two methods missed the peak at t = s/2 when N was odd, and thus disagreed with the other, and both missed the peak when N was even, and thus gave an unrealistic estimate. The procedure was therefore repeated using steps $(o, \frac{1}{2}s)$, $(\frac{1}{2}s, s)$, $(s, 1\frac{1}{2}s)$, etc. By checking with the exact integer a expression and with the small s approximation this was found to give reasonably good results: for $a = 1$, $b = 0{\cdot}5$, $v = 9$, and values of s ranging from 0 to 10, agreement was obtained to at least 5 significant figures using 500 points per step. For $s > 10$, the incorrect asymptotic behaviour was obtained, for the following reason. Consider the real part of the integral; this has a single sharp peak at $t = s/2$ whose half-width is inversely proportional to some function of s. The "peak" value is -2, the function being of order $8/s$ or less elsewhere. Any Simpson-type integration technique using a step size of $-s/2(N-1)$ would therefore provide an estimate of order $-s/(N-1)$ for the value of the integral for large s instead of the asymptotic value of $\pi/9$.

The third procedure was to take a greater number of steps in the intervals $(0, \frac{1}{2}s)$ and $(\frac{1}{2}s\ 0)$ than in the remaining intervals. Using 4,000 steps in each of the first two intervals and 600 in each of the subsequent intervals, agreement was obtained to 4 figures for values of s up to $s = 100$. The difficulty arose from the presence in the imaginary part of the integrand of two close peaks, one of height +1 and the other of height -1, both peaks having similar shapes. Although the accuracy obtained was more than sufficient for $a = 1$, in view of the earlier arguments a more accurate method was felt to be needed for the imaginary part.

Procedure number 4 tried to overcome the cancellation problems by getting as short a step size as possible close to $t = \frac{1}{2}s$, where the sharpest oscillations occurred. As in number 3, two different step sizes N1 and N2 were used for $t \leqslant s$ and $t > s$, but now the intervals $(\frac{1}{2}s - s/2(N-1), \frac{1}{2}s)$ and $(\frac{1}{2}s, \frac{1}{2}s + s/2(N-1))$ were combined and split into N3 steps, and N1 was varied until most of the severe oscillations occurred in this region. A further refinement was to use N4 steps when t became large (in practice $t > 4s$) to save computing time.

The final program used the following number of steps in each interval:

from $t = 0$ to $t = \frac{1}{2}s(1 - 1/300)$: 299 steps
from $t = \frac{1}{2}s(1 - 1/300)$ to $t = \frac{1}{2}s(1 + 1/300)$: 7000 steps
from $t = \frac{1}{2}s(1 + 1/300)$ to $t = s$: 299 steps
from $t = s$ to to $t = 3s/2$: 200 steps
from $t = 3s/2$ to $t = 2s$: 200 steps
" " "
" " "
" " "
from $t = 4s$ to $t = 9s/2$: 50 steps
" " "
" " "
" " "

This proceeded until either $t > t_{max}$ or until the series converged, which usually occurred within the first 30 steps. This gave results which agreed with the integer a result to better than 1 % for $s = 10^5$, by which time cancellation was occurring to four figures (by which we mean that if we summed the positive and negative parts of the integral separately, the leading 4 figures were identical). The number of steps chosen only proved insufficient when s reached 10^9 when rounding and cancellation effects dominated. As will be shown later, we are not very interested in these high values of s, and for s of the order of 100, or less, agreement was obtained to at least 11 significant figures. Again, as the value of the parameter a increased, the number of oscillations increased proportionally, and since at least about 4 quadrature points were required per oscillation a limit was reached with the above number of steps when $a > 10^3$, $s \gg 1$. Above these values, progressive loss of accuracy was observed.

To verify that the errors encountered when accuracy was finally lost were only due to computational limitations, a limited number of trial runs were initiated using 20,000 steps. This improved the agreement for high s and high a, but proved expensive in C.P.U. time. For small values of a, no problems arose and considerably fewer steps were used.

7.2 b integral

The integration over t produces a smoothly varying function of b which is non-oscillatory and well behaved. We now require

$$\ln \phi(s) = 4\pi N v \int_c^\infty \ln \phi(s,b) b\,db$$

We can consider the behaviour in both limits, as $b \to 0$ and as $b \to \infty$. For large b, we can approximate the imaginary part of $\ln \phi(s,b)$ whenever one of two conditions is satisfied. For small S and small aS,

$$\text{Imag} \left\{ \ln \phi(s,b) \right\} = -\pi a s$$

The same expression is obtained for small values of $2a\pi$, which is a sufficient condition to expand $\exp(-i\eta)$. Rewriting this in terms of c,b,v,s

$$\text{Imag} \left\{ \ln \phi(s,b) \right\} = \frac{-\pi c s}{2bv}$$

either if $b \gg sv$

and $b^2 \gg \frac{1}{2}sc$

or if $b \gg \pi c/v$

It was checked numerically that whenever the value of the impact parameter was greater than 10 times the least of either c/v or $s(v + c)$, the imaginary part was accurately represented by the approximation (even though $s(v + c)$ is dimensionally incorrect).

The imaginary part of the integral thus diverges as $b \rightarrow \infty$, and we need to introduce a cut-off, B. The value of the cut-off follows from the way we set up the model by splitting up the gas or plasma into separate cells each containing one emitter and a large number of perturbers. The potential therefore has a mean maximum range of $n^{-1/3}$. We could also choose a value of $\left(\frac{4\pi n}{3}\right)^{-1/3}$, this being the radius of a sphere with a volume equal to the mean volume per emitter (Margenau and Lewis). Ideally, the final line shape should not depend critically on the choice of this cut-off.

At this stage of the problem, we have two impact parameter of interest: one (b_{max}) beyond which $\ln \phi(s,b)$ can be represented by a simple analytic function, another (B) beyond which the impact parameter integral need not be carried out. After evaluating $\ln \phi(s)$ we will integrate trigonometric functions of

$$\text{Imag} \left\{ \ln \phi(s) \right\} + \Delta w s \quad .$$

Large values of B will give rise to severe oscillations. To remove these we evaluate

$$\text{Imag} \int_{b_{max}}^{B} \ln \phi(s,b)\, b\,db = -\frac{\pi cs}{2v} (B - b_{max})$$

and redefine without change of notation

$$\Delta w = w - w_0 + 2\pi^2 N c B$$

so that the functions we need to evaluate are trigonometric functions of

$$4\pi N v \ \mathrm{Imag}\left\{\int_0^{b_{max}} \ln \phi(s,b)\, b\,db\right\} + 2\pi^2 N c b_{max} s - \Delta w s$$

which hopefully will be well behaved.

The real part of $\ln \phi(s)$ is obtained in a similar manner. If $b > 10c/v$,

$$\mathrm{Real}\ \ln \phi(s,b) = -\frac{\pi c^2}{2bv^3}\left\{\frac{sv}{b} \arctan\left(\frac{sv}{2b}\right) - \ln\left(1 + \frac{s^2v^2}{4b^2}\right)\right\}.$$

If $b > 10s(v + c)$ this can be further simplified to

$$\mathrm{Real}\ \ln \phi(s,b) = -\frac{\pi c^2 s^2}{8b^3 v}$$

which can be integrated analytically. We thus write for the real part

$$\ln \phi(s) = 4\pi N v \int_0^{10s(v+c)} \ln \phi(s,b)\, b\,db + \frac{\pi^2 c^2 N s}{20(v+c)}$$

If $10c/v \leqslant b \leqslant 10s(v + c)$, the approximate form of $\ln \phi(s,b)$ in this region is inserted in the integral. Note that unlike most other theories, including Lindholm's, we do not need to make an impact parameter cut-off for the real part of $\ln \phi(s)$.

For small b the integrals become difficult to evaluate numerically, and we need approximations for $\ln \phi(s,b)$. These approximations need not be too accurate since $\ln \phi(s,b)$ is multiplied by b and their product will not contribute greatly to the integral for small b. There are two approximations available, depending on the relative values of s,v,c and b. If $sv < 2b$ and if $c\pi \ll bv$, we can expand $\exp(-i\eta)$ as before and obtain

$$\ln \phi(s,b) = \frac{-i\pi cs}{2bv} - \frac{\pi c^2 s^2}{8b^3 v}$$

However as $b \to 0$ for fixed s,v,c, for small enough b neither of these conditions will be satisfied. For $b \ll sv$ we could use the Lindholm approximation

$$\ln \phi(s,b) = \tfrac{1}{2}s \left\{ \cos\left(\frac{c\pi}{bv}\right) - 1 \right\} - \tfrac{1}{2}is \sin\left(\frac{c\pi}{bv}\right).$$

but we have shown that the Lindholm result is only valid in very limited circumstances and is completely wrong whenever $c/2bv$ is integer. There are in fact three ranges of t in which approximations can be made:

i) If $t \to 0$, then

$$\eta = \frac{4c}{sv^2} + \frac{c\pi}{bv} H$$

where H is a step function whose value is 0 if $c/2bv$ is integer, and 1 otherwise, i.e.

$$\eta \simeq \frac{c\pi}{bv} \quad \text{for non-integer } c/2bv$$

$$\eta \simeq \frac{4c}{sv^2} \quad \text{for integer } c/2bv$$

(The Lindholm result is $\eta = c\pi/bv$ for all values of c,v,b,s)

ii) when $t \to \tfrac{1}{2}s$,

$$\eta \simeq \frac{c\pi}{2bv}$$

iii) when $t \to \infty$,

$$\eta \simeq \frac{cs}{v^2} \left\{ \frac{b^2}{v^2} - \frac{s^2}{4} + t^2 \right\}^{-1}$$

There is some justification in the implicit assumption made by Lindholm and Lenz that this region does not contribute significantly to the value of the whole integral. Since η is small we can expand the exponential so that that part of ln $\phi(s,b)$ arising from large t is

$$-i \frac{cs}{v^2} \int_y^\infty dt \left\{ \frac{b^2}{v^2} - \frac{s^2}{4} + t^2 \right\}^{-1} - \int_y^\infty dt \left\{ \frac{b^2}{v^2} - \frac{s^2}{4} + t^2 \right\}^{-2} \frac{c^2 s^2}{2v^4}$$

where the lower limit y is greater than but of order $\frac{1}{2}$s. The integral gives

$$\left\{ \frac{-i}{y} - \frac{1}{3y^3} \frac{cs}{2v^2} \right\} \frac{cs}{v^2}$$

and the y^3 term tends to zero as s and y tend to ∞. However the criterion for ignoring this contribution is not that it should tend to zero but that it should be smaller than the contribution from the rest of the range. For $b \ll c/2v$ these two criteria are not always the same.

Since the requirement $sv \ll b$ is always satisfied for fixed s, b as $v \to 0$, the approximation based on that requirement leads to a "statistical" result. If $c\pi < bv$ we can start with the Lindholm approximation, which we expand,

$$\ln \phi(s,b)_{\text{LINDHOLM}} = \frac{-i\pi cs}{2vb} - \frac{\pi^2 c^2 s}{4b^2 v^2}$$

c.f.

$$\ln \phi(s,b)_{\text{STAT.}} = \frac{-i\pi cs}{2vb} - \frac{\pi c^2 s^2}{8b^3 v}$$

We note that whilst the imaginary parts are identical, the real parts differ, one being proportional to s, the other to s^2. The reason for this is as follows. Since $c\pi/bv \ll 1$, $\exp(-i\eta)$ can be expanded in both cases and the integration carried out exactly to 2nd order in η to give

$$\ln \phi(s,b) = -\frac{\pi c^2}{2bv^3}\left\{\frac{sv}{b} \arctan\left(\frac{sv}{2b}\right) - \ln\left(1 + \frac{s^2v^2}{4b^2}\right)\right\} - \frac{i\pi cs}{2bv}$$

The imaginary part is thus independent of any approximation based on the value of sv/b. The behaviour of the real part is at first odd, since for $sv \ll b$ it reduces to the statistical result, but for $sv \gg b$ it does not reduce to the Lindholm result. This latter result is only obtained by ignoring the logarithmic term and by replacing the arctangent by $\pi/2$, which means that the logarithmic terms must be due to the invalid assumptions made by Lindholm and must have arisen from the terms he ignored but which we did not. Since this term appears to made a significant contribution to $\ln \phi(s,b)$ for $c\pi \ll bv$, attempts were made to obtain an analytic approximation valid over a wider range. After unsuccesful attempts to obtain one directly, the real part of the integral was evaluated numerically for various values of c/bv and different analytic forms were fitted to the calculated points using least squares. A good fit was obtained using a general form

$$I = -x_1 a \quad x_2 S\,(1 - \cos(2a\pi + x_3))$$

As before $a = c/2bv$ and $S = sv/b$. The values of x_1, x_2, x_3 are to be determined by the optimisation, and $I = 2v/\pi b$. Real $\ln \phi(s,b)$. The best fits were for the following choices for x_1, x_2 x_3:

$$I = -1{\cdot}23\ a - 0{\cdot}08\ a\ (1 - \cos(2a\pi + 0{\cdot}3\pi))\ ,\quad S = a$$

$$I = -2{\cdot}5\ a - 2{\cdot}4\ a\ (1 - \cos(2a\pi + 0{\cdot}4\pi))\ ,\quad S = 10a$$

$$I = -4\ a - 30\ a\ (1 - \cos(2a\pi)\qquad)\ ,\quad S = 100a$$

c.f.

$$I_L + I_{int} = -4a - 31a\,(1 - \cos(2a\pi)) \qquad , \quad S \gg a.$$

where I_L and I_{int} are the corresponding "Lindholm" and "integer a" solutions. There is strong justification for choosing $I_L + I_{int}$ as an approximation to I, apart from the agreement for $S \gg a > 1$, since whenever a is close to an integer value $I_{int} \gg I_L$ and if a is not nearly integer $I_L \gg I_{int}$, so that $I_{int} + I_L$ will agree with the unknown exact solution over most of the range $b \to 0$. The combination $I_L + I_{int}$ has the further advantage that if we use a stricter definition of I_L,

$$I_L = \left\{\tfrac{1}{4}S^2 - 1\right\}^{\frac{1}{2}} \left\{\exp(-2ia\pi) - 1\right\} . \quad H ,$$

where H is 1 for $s > 2$ and 0 otherwise, then $I_{int} + I_L$ has the correct asymptotic behaviour as $a \to o$ and $S \to 0$,

$$\frac{\pi b}{2v}\left\{I_L + I_{int}\right\} = -\frac{i\pi cs}{2bv} - \frac{\pi c^2 s^2}{8b^3 v}$$

in exact agreement with the statistical limit . We therefore claim that

$$I = \left\{\tfrac{1}{4}S^2 - 1\right\}^{\frac{1}{2}} \left\{\exp(-2ia\pi) - 1\right\} H$$

$$\frac{-b\pi i}{v} \sum_{m=1}^{\infty} \binom{a}{m} \frac{(2m-2)!}{(m-1)!(m-1)!} \quad \frac{(-2iS)^m}{(2i\,S)^{2m-1}}$$

and this expression, or approximations to it, are valid as $b \to 0$.

Figure 10 shows the various methods used to estimate $\ln \phi(s)$ and the regions in which they were used, as a function of b and s. The numerical integration over b was carried out using the same combination of Simpson's rule and Newton's method as in the t integral, although this was later changed to using just Simpson's rule to speed

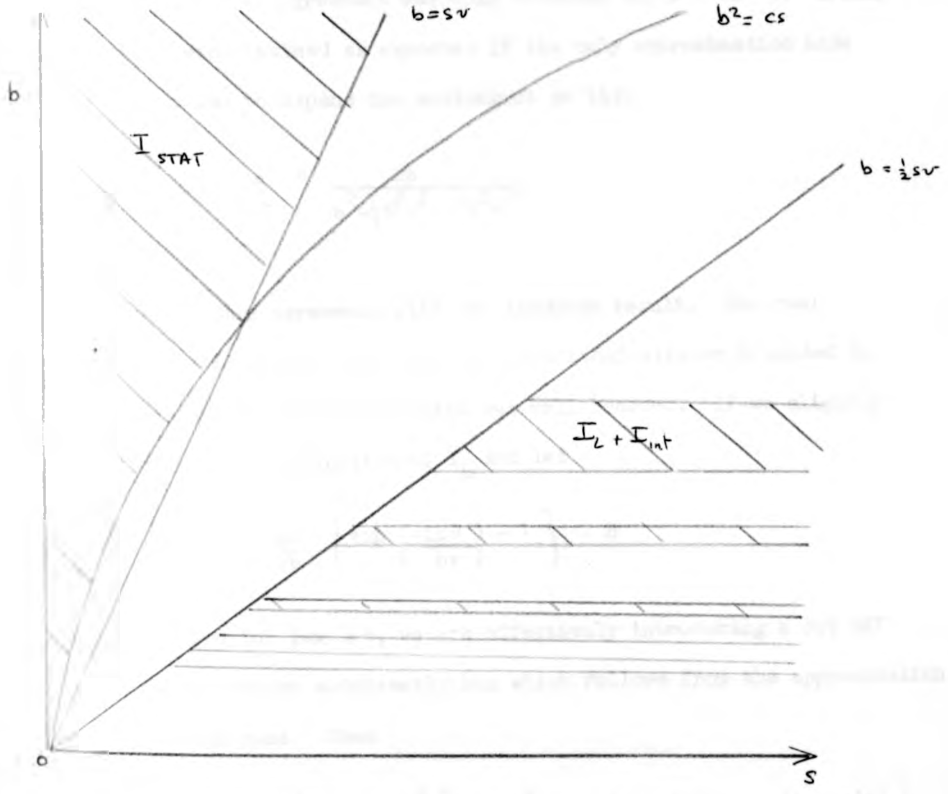

Fig 10

Regions in which approximations to I are used

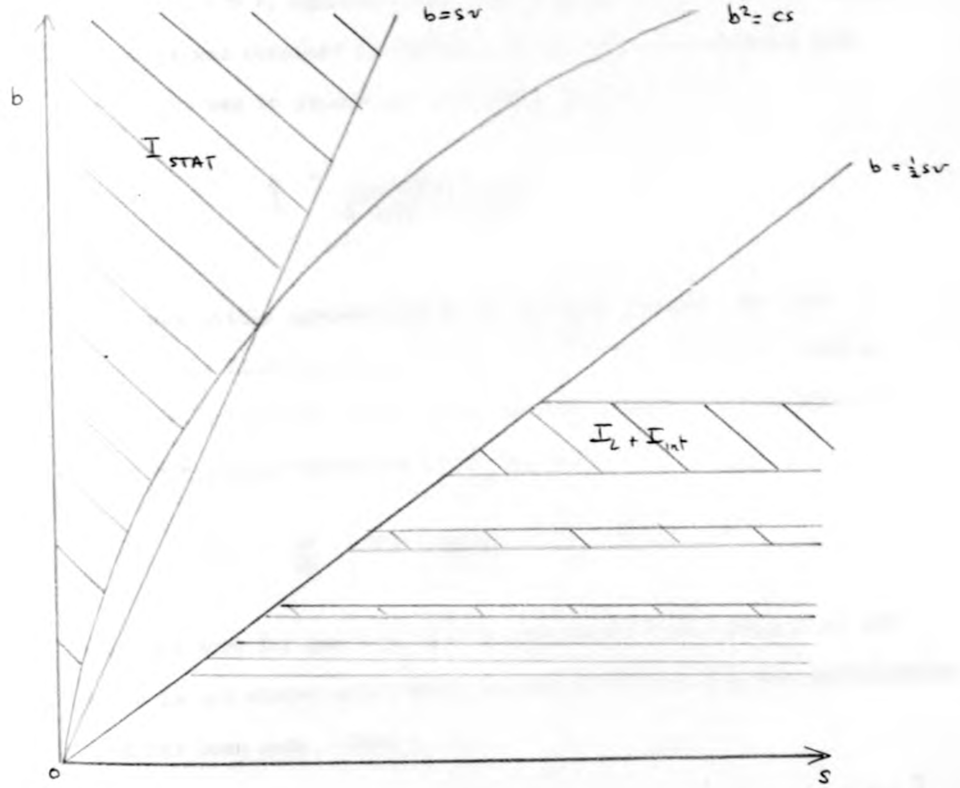

Fig 10

Regions in which approximations to I are used the computation. Only 40 steps were needed, the step sizes being chosen so that the first point was at $b = 0$ and the second was at b large enough so that severe oscillations did not occur. The results were compared and contrasted with those obtained in the statistical limit and in the Lindholm limit. The agreement with the statistical limit was poor away from the $sv = 0$ limit (e.g. for $c \simeq 1$, $v \simeq 1$, agreement was only obtained for $s < 10^{-3}$). Better agreement was obtained as expected if the only approximation made for low sv was to expand the arctangent so that

$$\ell = \frac{cs}{b^2 - \frac{1}{4}s^2v^2 + t^2v^2}$$

There was little agreement with the Lindholm result. The real part of the Lindholm limit diverged logarithmically as b tended to infinity, unlike our result which was well behaved. If we slightly relax our strict definition of I_L and let

$$I_L = \frac{sv}{2b} \left\{ \exp \left(\frac{-ic\pi}{bv} \right) - 1 \right\} \cdot H$$

which is zero for $\frac{1}{2}sv > b$, we are effectively introducing a cut off which is not chosen arbitrarily but which follows from the approximation that has been made. Then

$$\text{Real} \left\{ \ln \phi(s) \right\} = \frac{2\pi^2 c^2 sN}{2v} \left\{ \text{Ci}(u) - \frac{\sin(u)}{u} - \frac{(1-\cos(u))}{u^2} \right\}$$

where Ci is the cosine integral function and $u = 2\pi c/sv^2$. A similar expression is obtained for the imaginary part of $\ln \phi(s)$. If $u < 1$, the trigonometric function can be expanded and

$$\text{Real} \left\{ \ln \phi(s) \right\} = \frac{-2\pi^3 c^2 sN}{v} \left\{ 0{\cdot}99278 + \ln u + \frac{u^2}{24} + O(u^3) \right\}$$

$$\text{Imag} \left\{ \ln \phi(s) \right\} = -2\frac{\pi^3 c^2 sN}{v} \left\{ \frac{1}{u} - \frac{1}{4} + \frac{u}{2} + O(u^2) \right\}$$

If instead of choosing a cut-off at $b = \frac{1}{2}sv$ we had just chosen some cut-off B, then $u = \pi c/vB$ and the two equations above are identical to the solution obtained by Lindholm and quoted by Margenau and Lewis. (One exception is that where we obtain the numerical value 0·993 which is Euler's number $+\frac{1}{2}$, Margenau and Lewis quote 0·923. This could be a printing error in their paper; the original they quote from is Lindholm's thesis in Uppsala). The advantage of replacing u by a constant is that $\ln \phi(s)$ becomes proportional to s so that a Lorentzian line is obtained with width and shift equal to the real and imaginary parts of $\ln \phi(s)$. The disadvantage is that the shift is directly proportional to a cut-off radius whose definition is arbitrary. Our more careful derivation of a Lindholm-type approximation does not depend on any arbitrary cut-off, but since u is now a function of s the line profile must be evaluated numerically.

For $u < 1$ we thus used the approximations for $\ln \phi(s)$ given above having checked them against the exact expression. For $u > 1$ it was found quicker to evaluate $\ln \phi(s)$ numerically than to calculate the exponential integral functions accurately enough. The two methods however produced the same results, which was a check on the accuracy of the numerical integration.

Figures 11 shows the real and imaginary parts of $\ln \phi(s)$ obtained using I, I_s and I_L for the special case $v = 9$, $c = 9$, $4\pi N v = 1$. The "exact" numerical integration agrees with the low s "statistical" result to about 1% for $sv < 1$, although the latter has the incorrect asymptotic behaviour as $s \rightarrow 1$. There is little agreement with Lindholm except as $s \rightarrow \infty$

$$\text{Real "exact"} \longrightarrow -4{\cdot}44s + 5{\cdot}2 \quad , \quad s \rightarrow \infty$$

$$\text{Real "Lindholm"} = -4{\cdot}59s$$

If instead of choosing a cut-off at $b = \frac{1}{2}sv$ we had just chosen some cut-off B, then $u = \eta c/vB$ and the two equations above are identical to the solution obtained by Lindholm and quoted by Margenau and Lewis. (One exception is that where we obtain the numerical value 0·993 which is Euler's number $+\frac{1}{2}$, Margenau and Lewis quote 0·923. This could be a printing error in their paper; the original they quote from is Lindholm's thesis in Uppsala). The advantage of replacing u by a constant is that $\ln \phi(s)$ becomes proportional to s so that a Lorentzian line is obtained with width and shift equal to the real and imaginary parts of $\ln \phi(s)$. The disadvantage is that the shift is directly proportional to a cut-off radius whose definition is arbitrary. Our more careful derivation of a Lindholm-type approximation does not depend on any arbitrary cut-off, but since u is now a function of s the line profile must be evaluated numerically.

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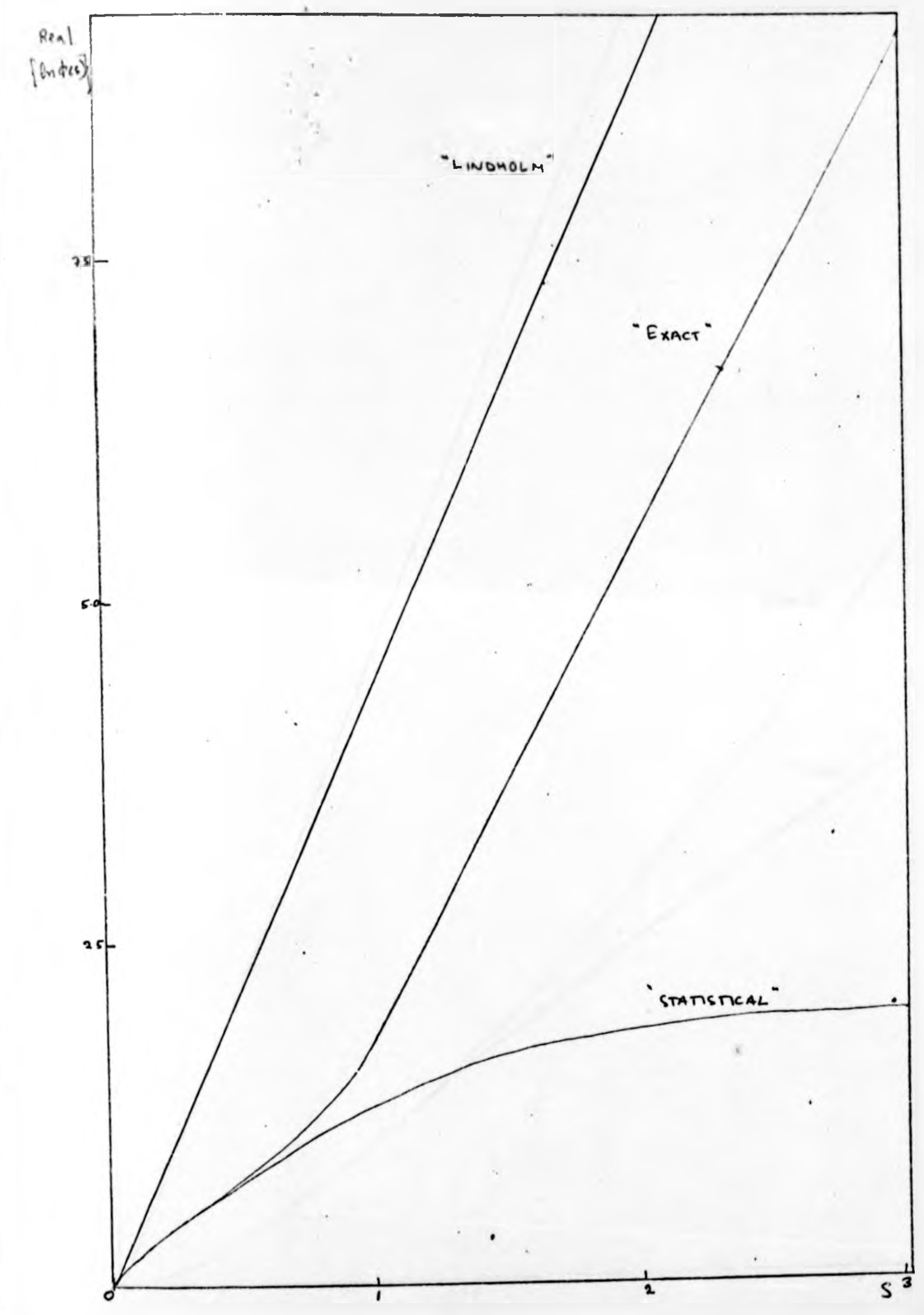

Fig 11a

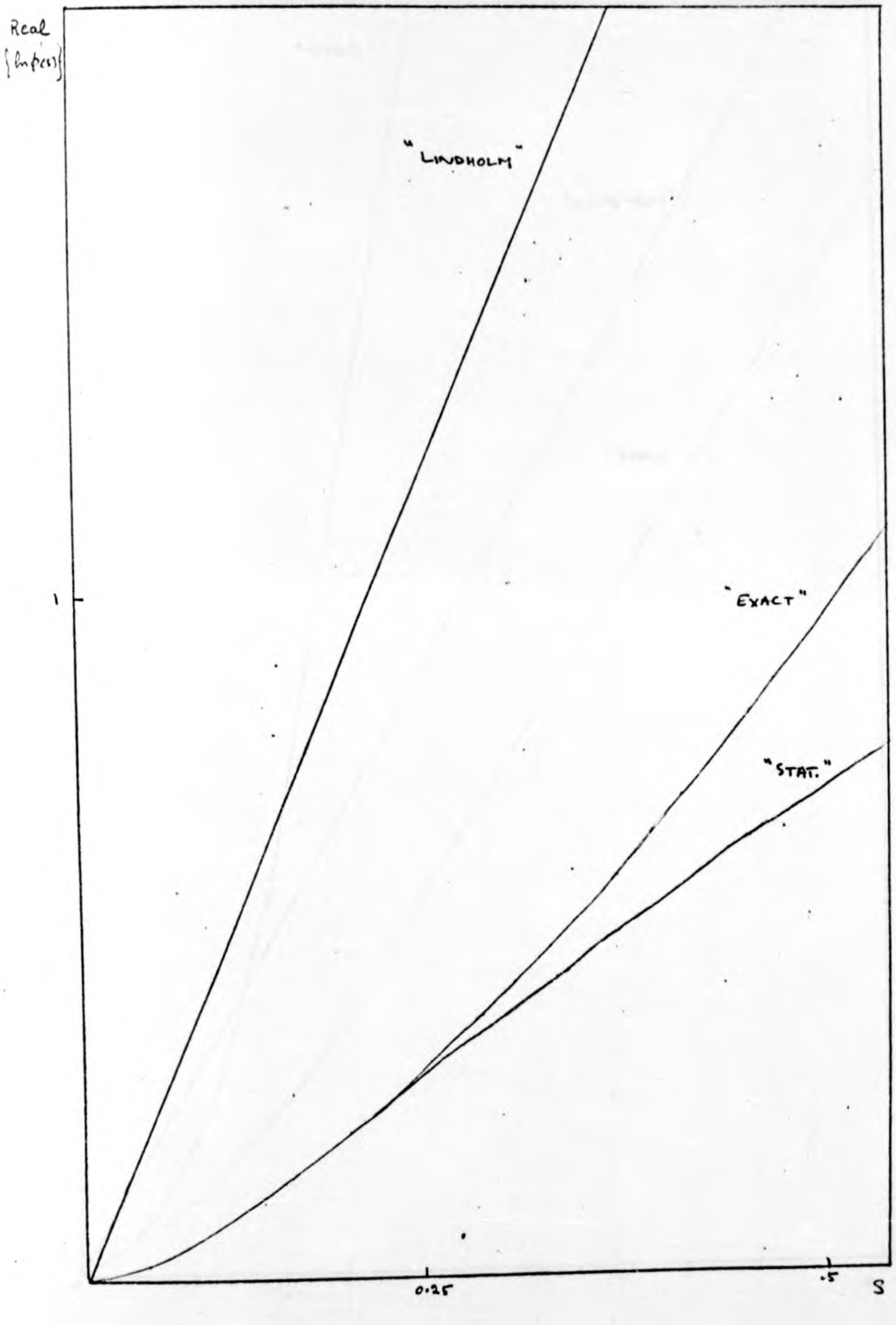

Fig 11b
Detail of 11a around s=0

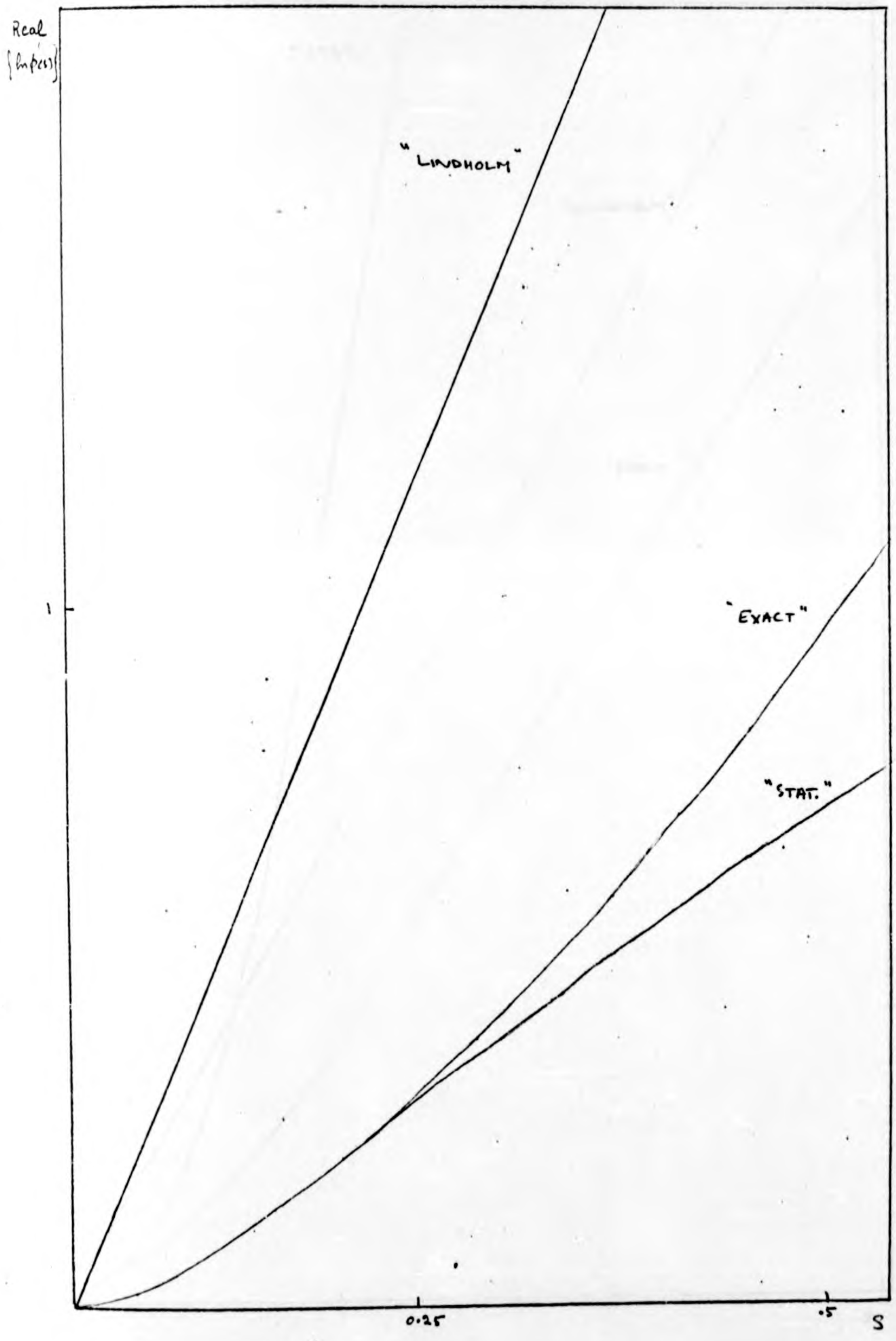

Fig 11b
Detail of 11a around s = 0

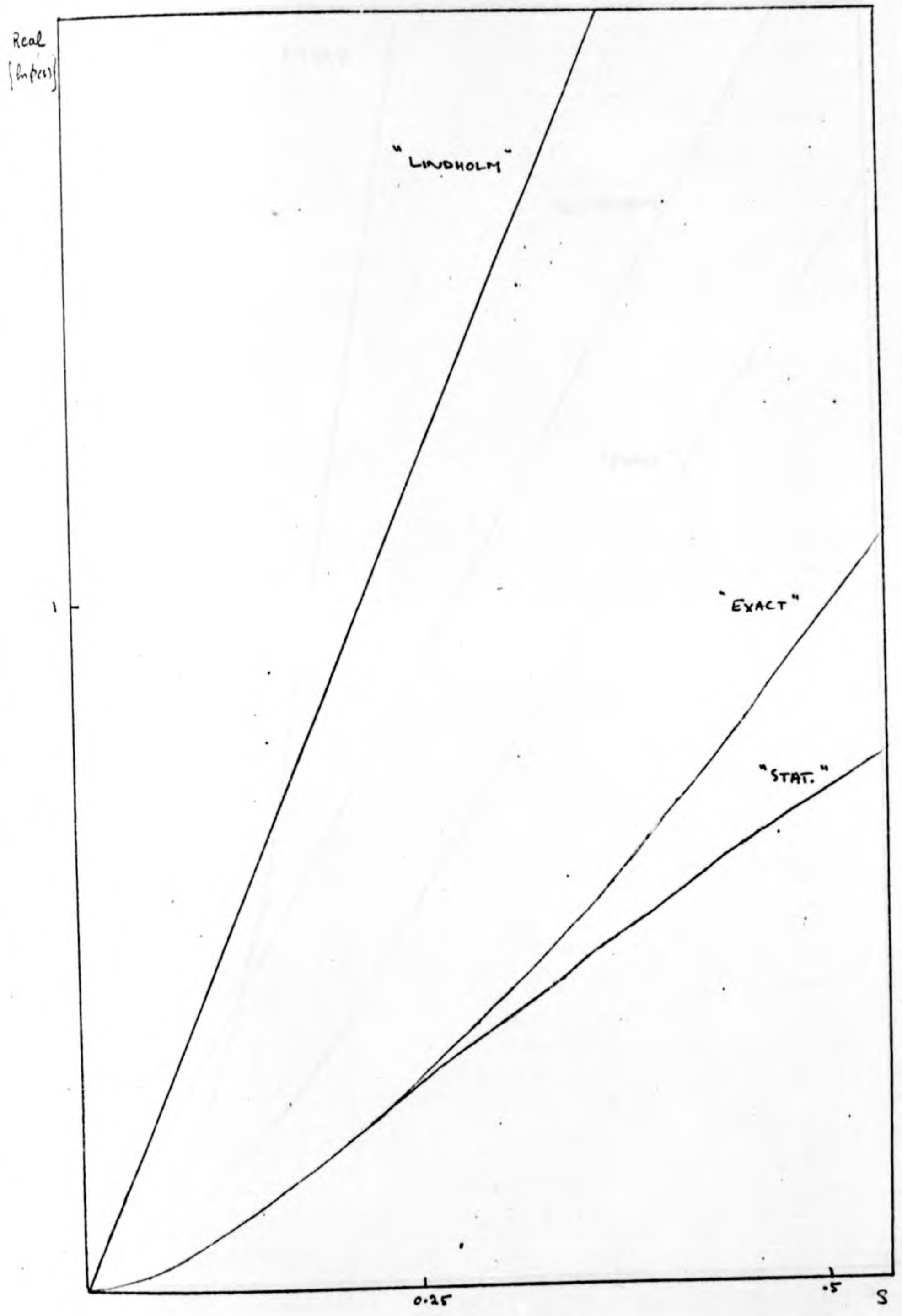

Fig 11b
Detail of 11a around s = 0

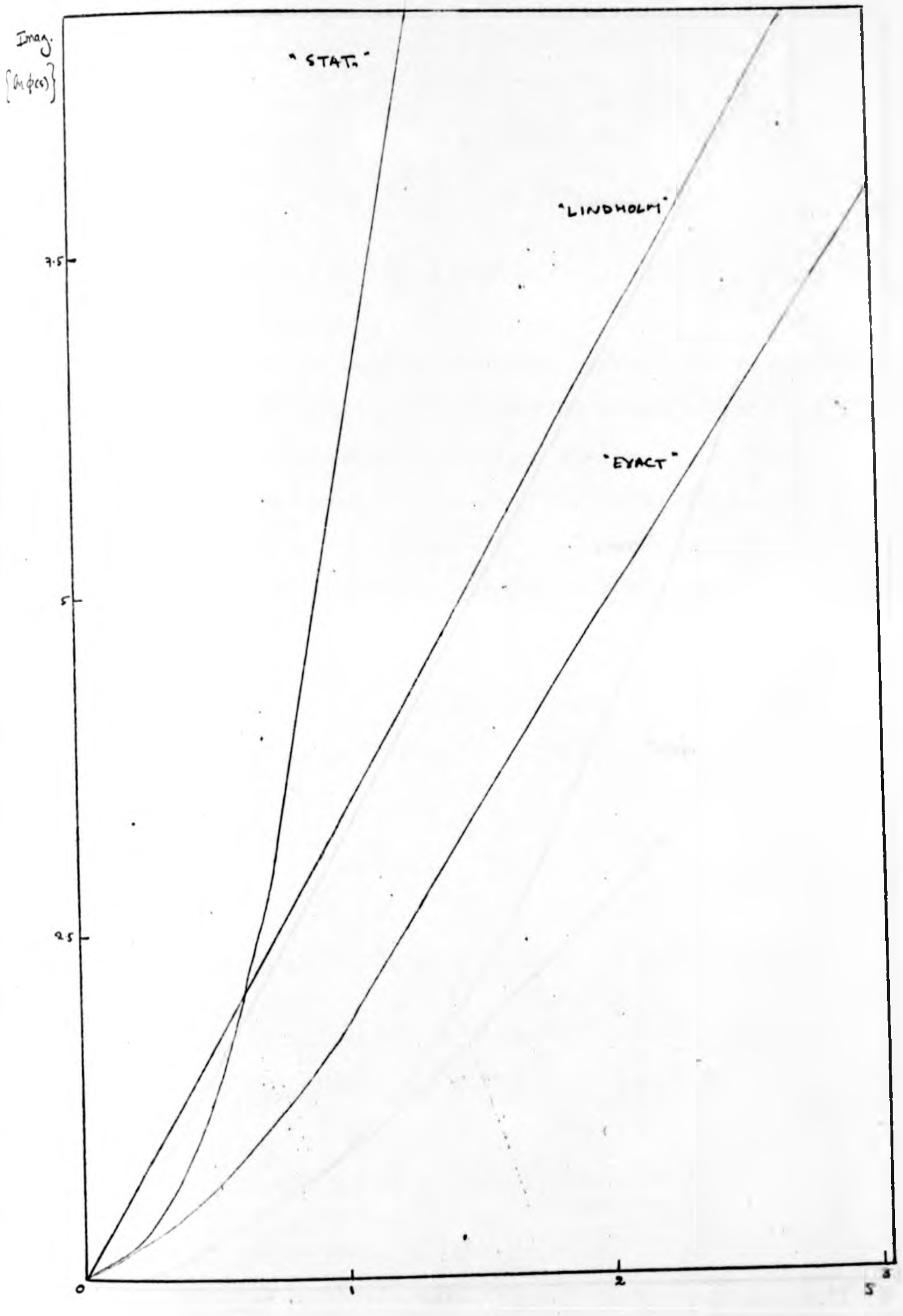

Fig 11c

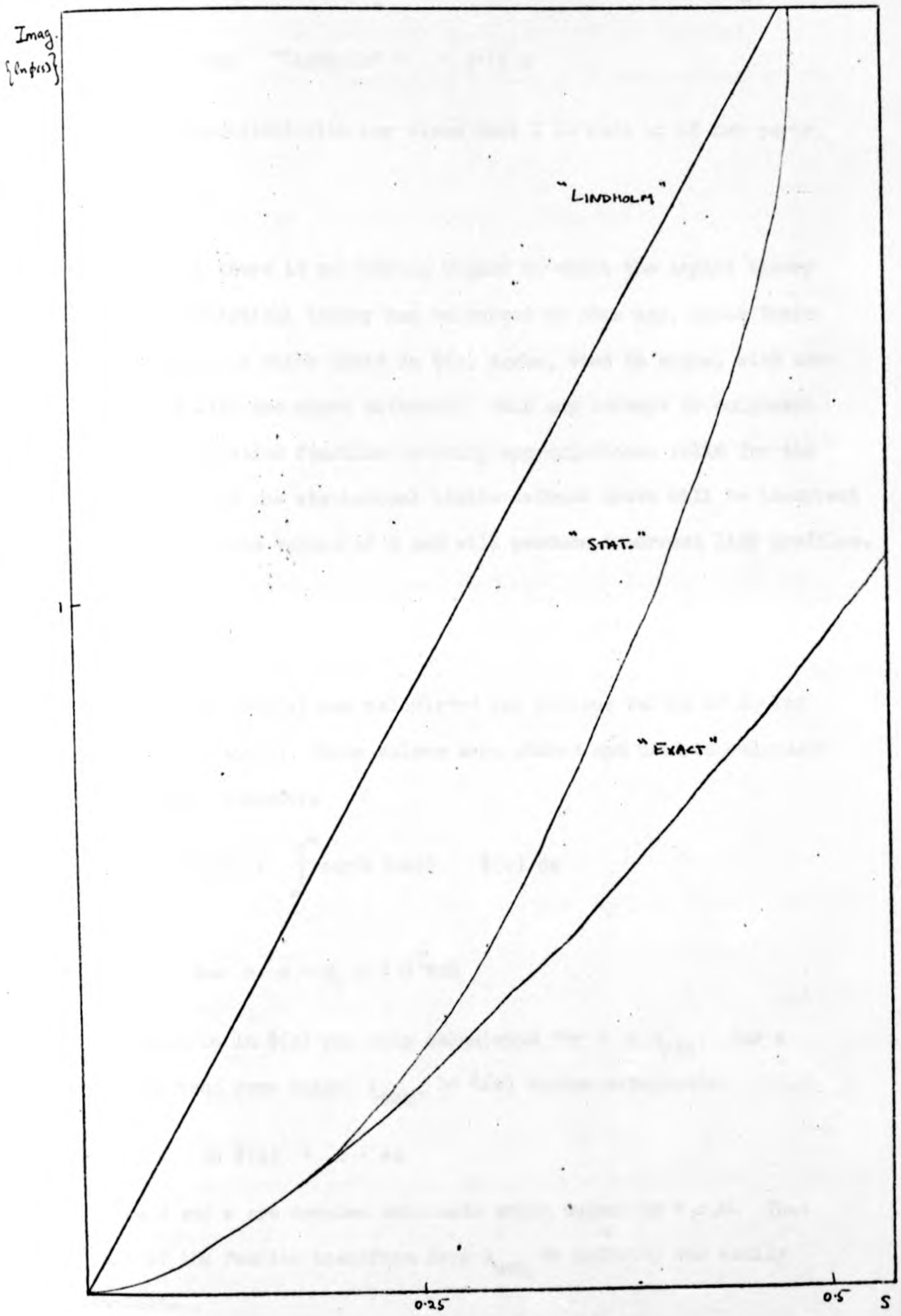

Fig 11 d

Detail of 11c around s=0

$$\text{Imag} \quad \text{"exact"} = -3{\cdot}46\, s + 3{\cdot}1 \quad , \; s \to \infty$$

$$\text{Imag} \quad \text{"Lindholm"} = -3{\cdot}15\, s$$

which is consistent with our claim that I is made up of two parts, I_L and I_{int}.

We see that there is no overlap region in which the impact theory and the statistical theory can be merged in some way, since there is no region in which their ln $\phi(s)$ agree, even in shape, with each other and with the exact solution. Thus any attempt to construct an autocorellation function by using approximations valid for the impact and for the statistical limits defined above will be incorrect for intermediate values of s and will produce incorrect line profiles.

7.3 s integral

The value of ln $\phi(s)$ was calculated for various values of s, for fixed c, N, and s. These values were stored and used to calculate the Fourier transform

$$I(w) = \int_0^\infty \exp(-i\,\Delta ws) \quad \phi(s)\, ds$$

with

$$\Delta w = w - w_o + 2\pi^2 NcB$$

The function ln $\phi(s)$ was only calculated for $s \leq s_{max}$. For s greater than some value s_{max}, ln $\phi(s)$ became asymptotic

$$\ln \phi(s) = d + es$$

where d and e are complex constants which depend on v,c,N. That part of the Fourier transform from s_{max} to infinity was easily evaluated,

$$\int_{s_{max}}^{\infty} \exp(-i\,\Delta ws) \cdot \phi(s)\, ds = \frac{-\exp\left\{ d + es_{max} - i\Delta ws_{max} \right\}}{e - i\Delta w}$$

which was added to the numerically calculated integral from 0 to s_{max}. In practice, s_{max} was chosen to be 20, and for all the cases considered the total contribution from s_{max} to infinity was at least 10 orders of magnitude smaller than that from 0 to s_{max}.

Figures 12 show the profiles obtained. They are all for particular values of $v = c = 9$ and for varying values of $4\pi Nv$. Curves were also obtained for $v = 1$ and $0{\cdot}1$, and for $c = 0{\cdot}9$ and exhibited similar behaviour. The horizontal axis has been normalised so that the peak occurs in the same place and represents the shift from $w_0 - 2\pi^2 NcB$ divided by $4\pi Nv$. On the same axes are plotted a Lindholm curve of the same physical characteristic.

For the lower densities N, the calculated profiles are wider than the Lindholm ones, the relative difference in the widths increasing as the density decreases, for fixed temperature. The opposite happens as the density increases and the Lindholm profiles overestimate the widths.

Figure 13 shows that the curves normalised to the same intensity show the slight asymmetry in the calculated profile which arises from the non-linear behaviour of $\ln \phi(s)$ on s. Figure 14 shows the shifts in more detail and shows the similarity in the curves near the peak. The anomalous behaviour of the calculated shapes starting at a distance of about twice the half-width from the centre arises from numerical errors in the calculation of the Fourier transform. These can be reduced by increasing the computational time. The Lindholm profiles in Figures 12 and 13 were obtained by plotting a Lorentzian profile with a width and shift given by Lindholm. Figure 15 shows five curves comparing this Lorentzian profile with a Lindholm profile calculated using the same integration procedure as that for our

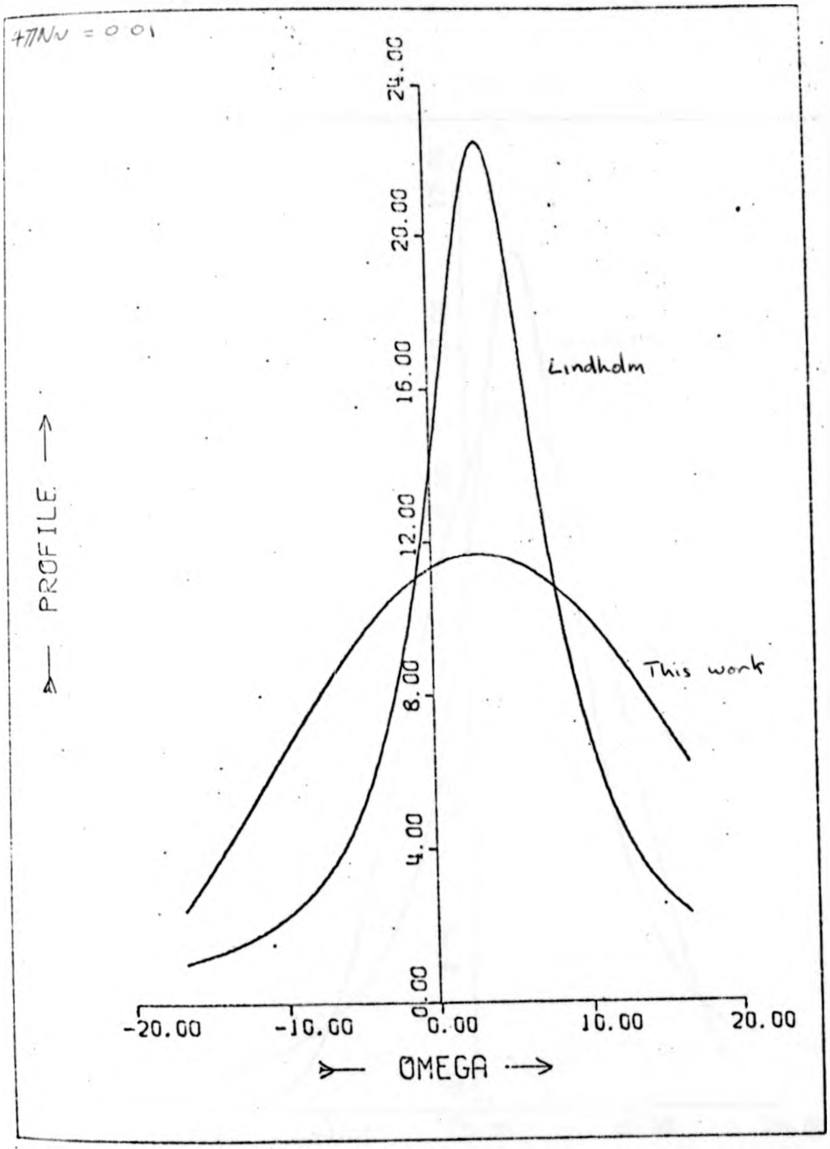
4πNν = 0.01
24.00
20.00
16.00
12.00
8.00
4.00
0.00
← PROFILE →
Lindholm
This work
-20.00
-10.00
0.00
10.00
20.00
← OMEGA →

Fig 12a

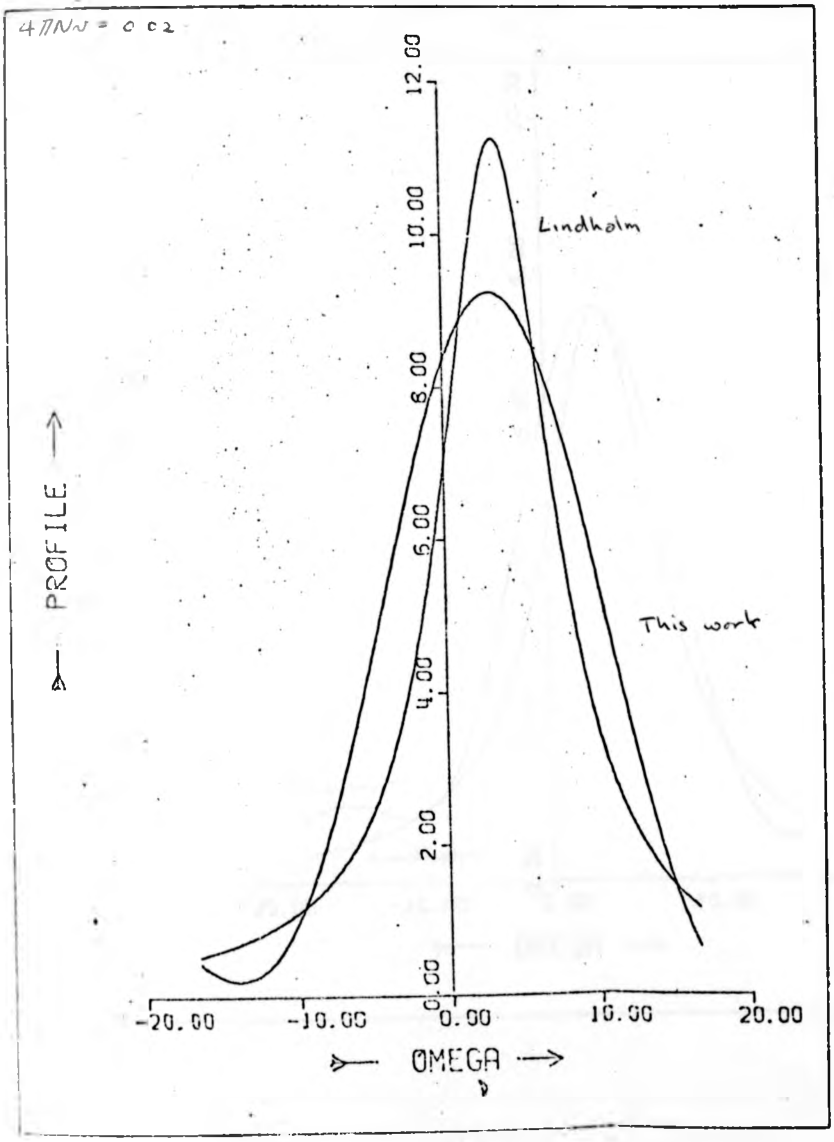
4πNw = 0.02
12.00
10.00
8.00
6.00
4.00
2.00
0.00
Lindholm
This work
PROFILE →
-20.00
-10.00
0.00
10.00
20.00
OMEGA →

Fig 12b

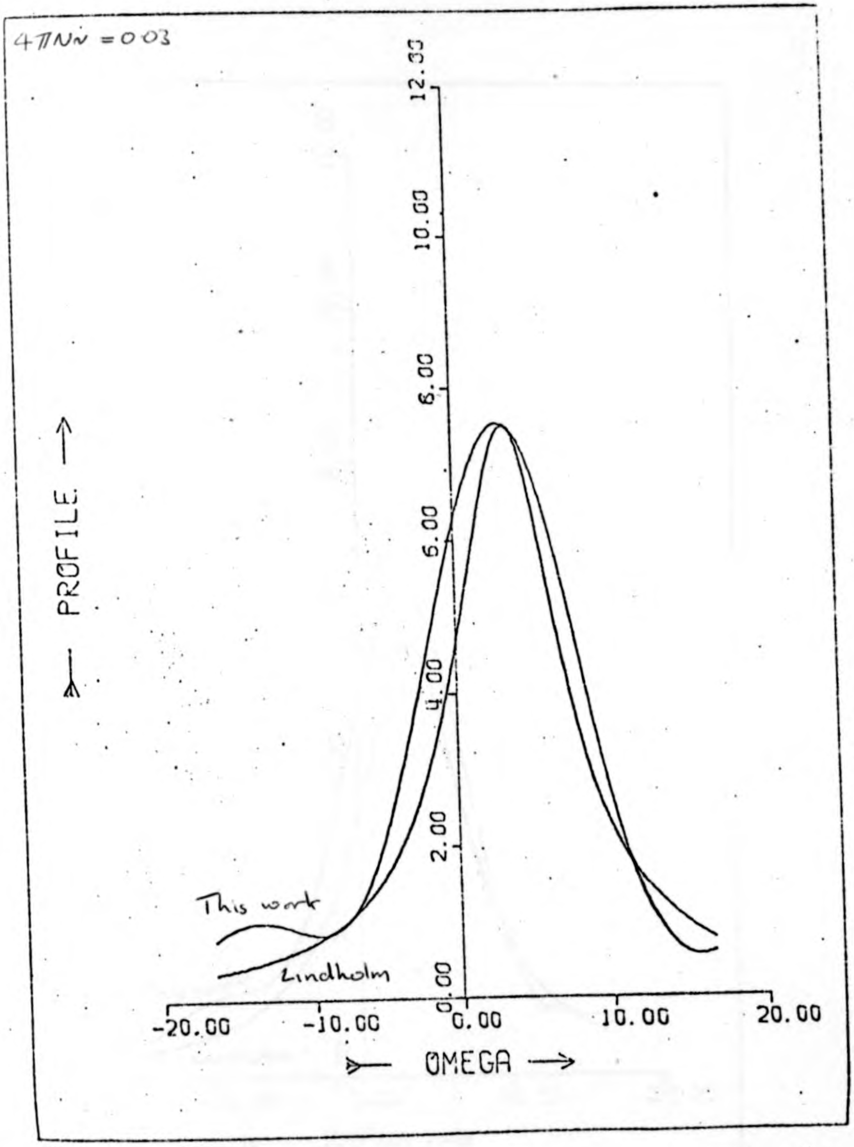
4πNv = 0.03
12.00
10.00
8.00
6.00
4.00
2.00
0.00
← PROFILE →
-20.00
-10.00
0.00
10.00
20.00
← OMEGA →
This work
Lindholm

Fig 12c

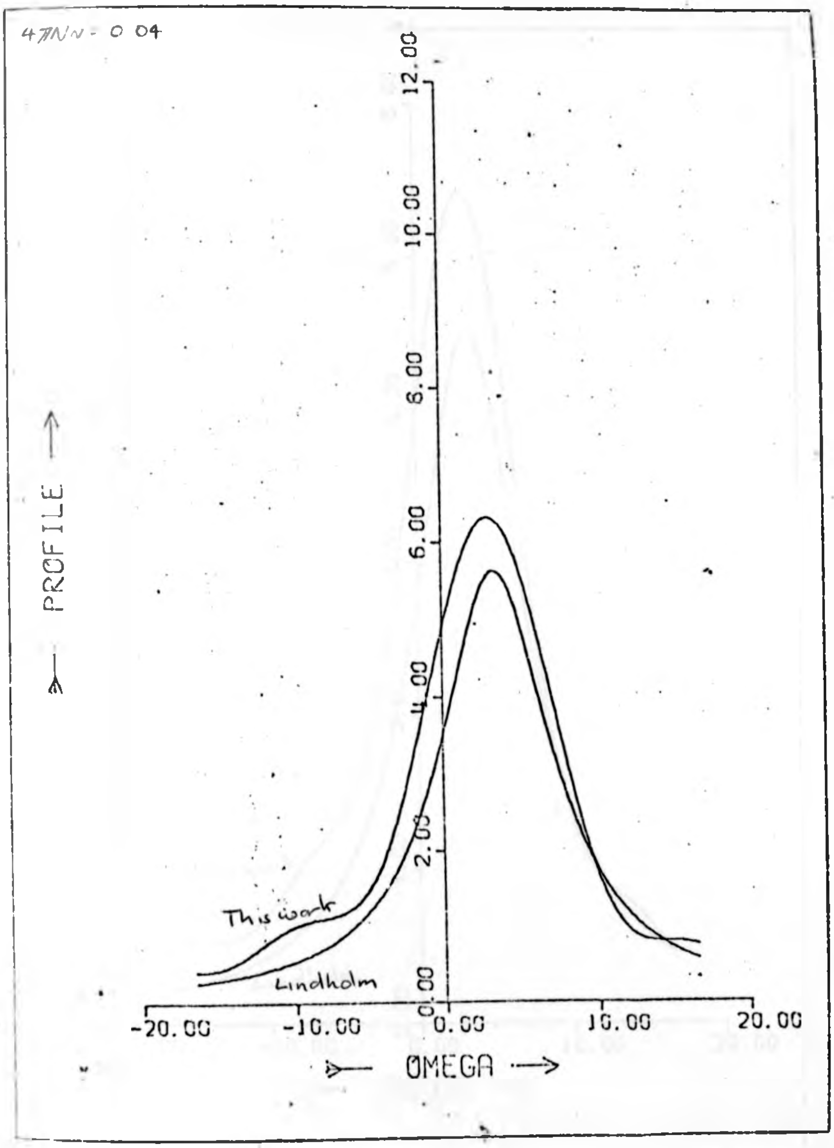
47NN-0 04
12.00
10.00
8.00
6.00
4.00
2.00
0.00
PROFILE →
This work
Lindholm
-20.00
-10.00
0.00
10.00
20.00
OMEGA →

Fig 12 d

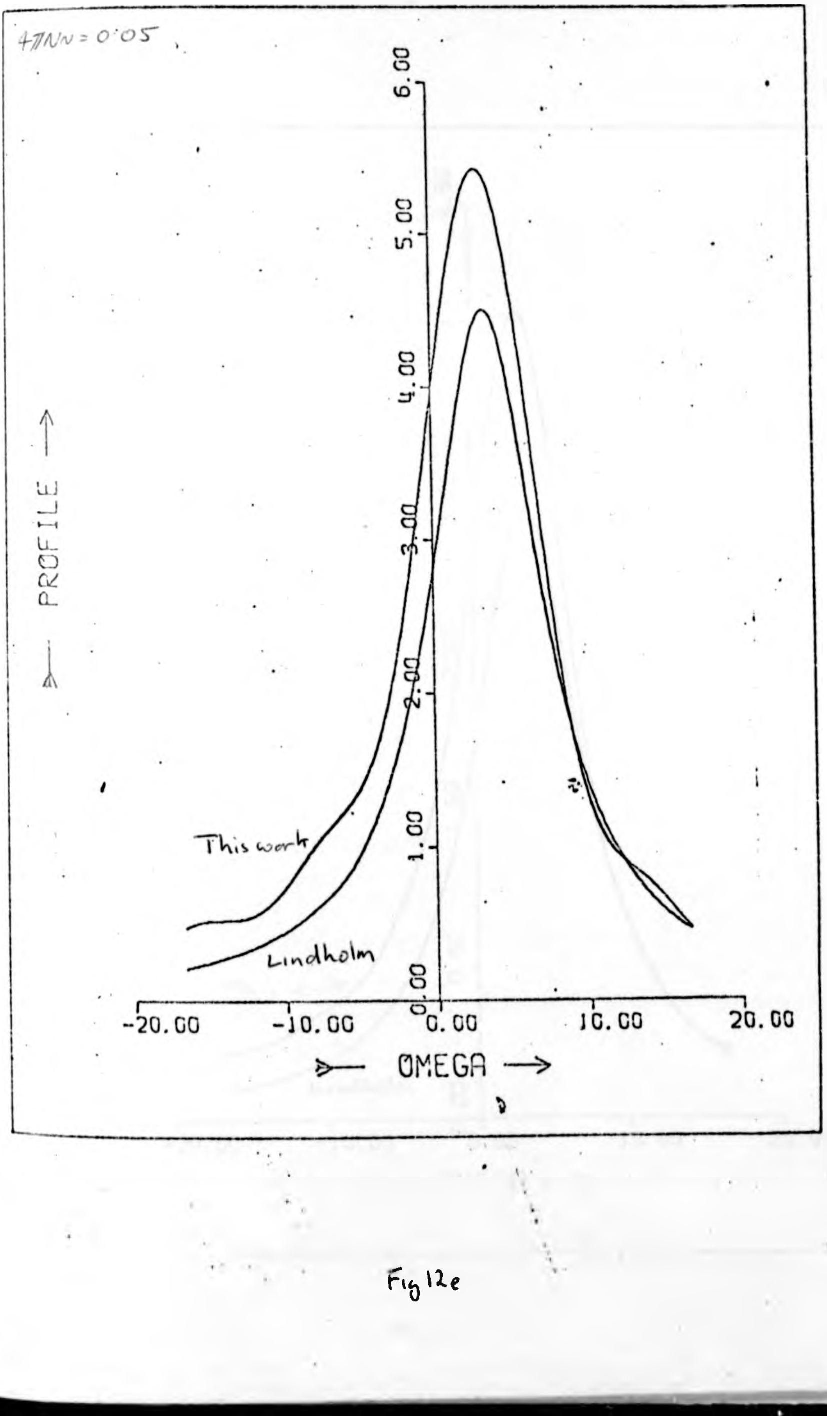
4πNν = 0·05
PROFILE →
6.00
5.00
4.00
3.00
2.00
1.00
0.00
-20.00
-10.00
0.00
10.00
20.00
OMEGA →
This work
Lindholm

Fig 12e

4U/Nv = 0 07

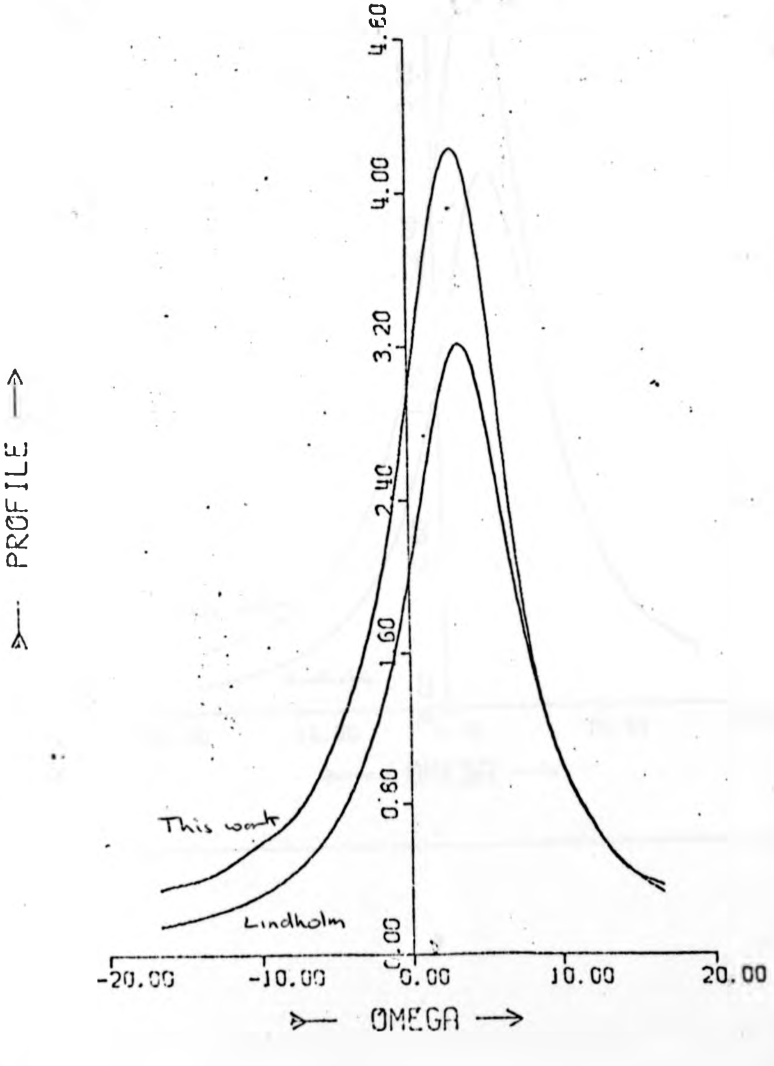

Fig 12 f

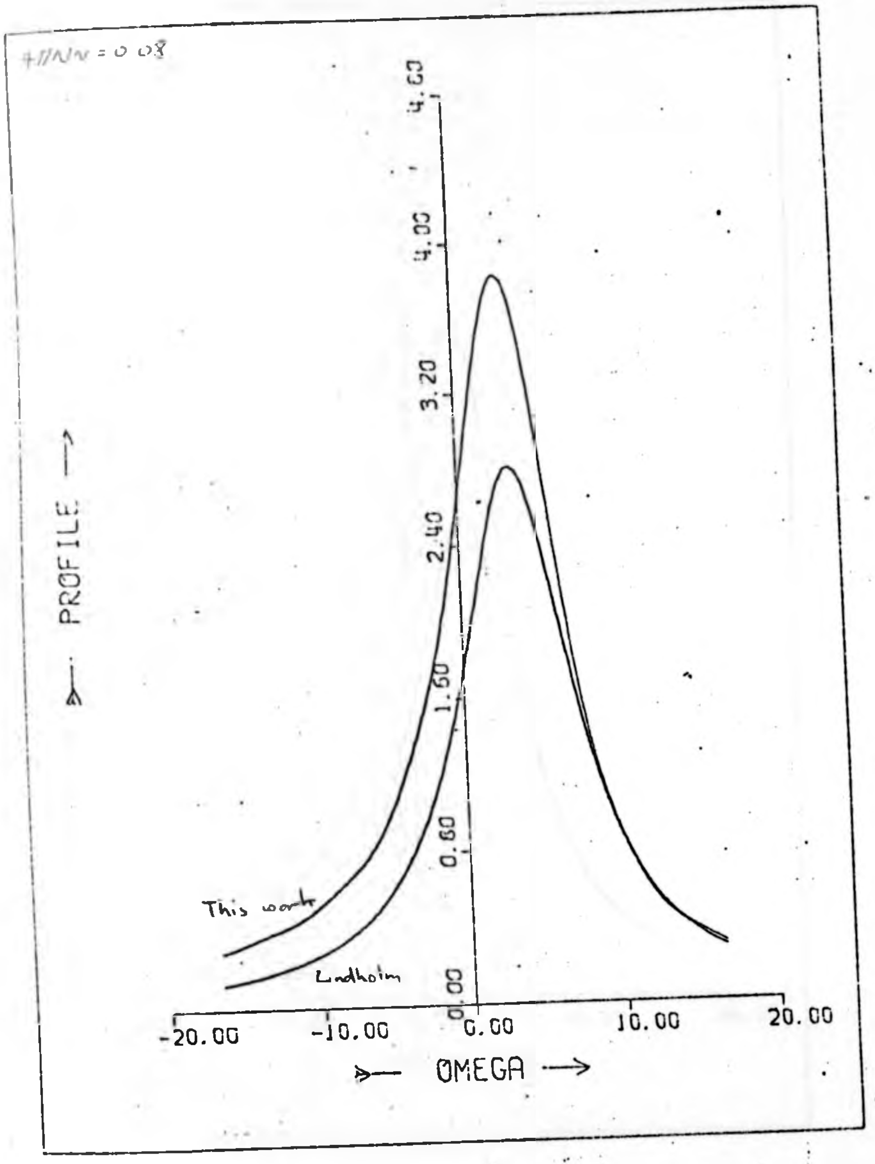
4Π/N/N = 0.08
PROFILE
0.00
0.80
1.60
2.40
3.20
4.00
4.80
This work
Lindholm
-20.00
-10.00
0.00
10.00
20.00
OMEGA

Fig 12g

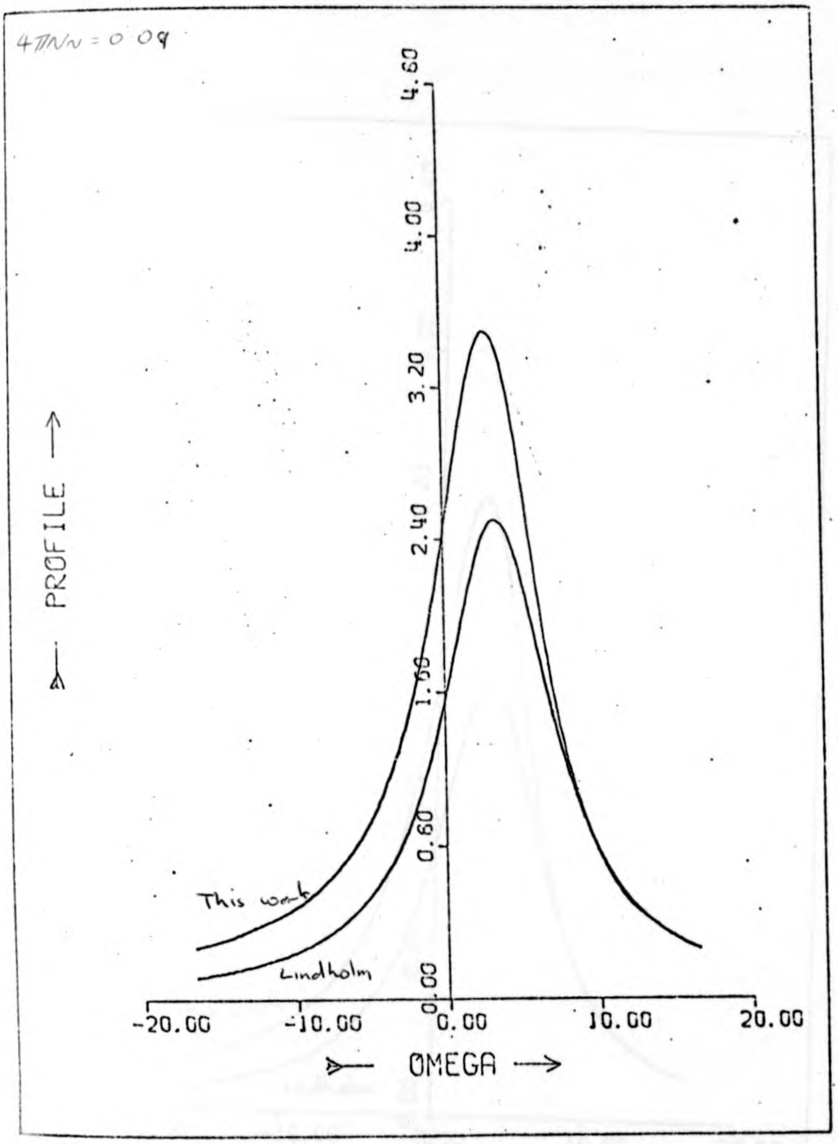
$4\pi N v = 0.09$
PROFILE
0.00
0.80
1.60
2.40
3.20
4.00
4.80
This work
Lindholm
-20.00
-10.00
0.00
10.00
20.00
OMEGA

Fig 12 h

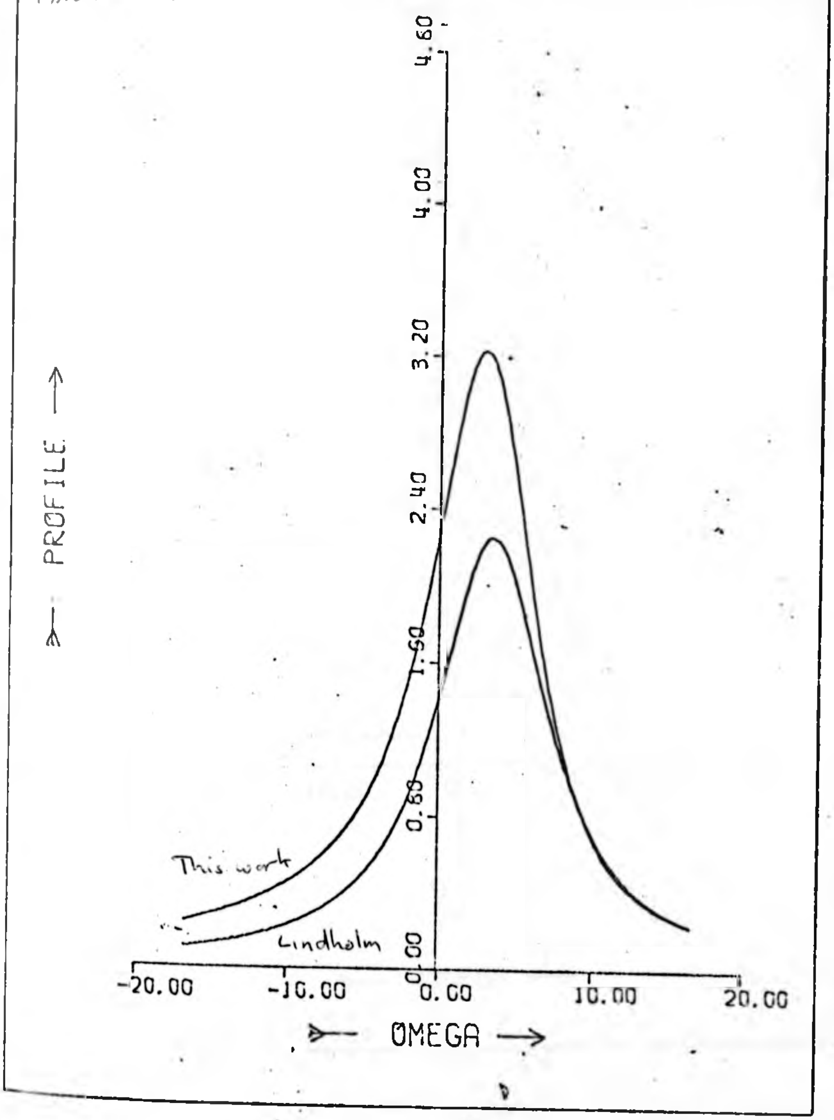
4πN'v = 0 1
PROFILE
0.00
0.80
1.60
2.40
3.20
4.00
4.80
This work
Lindholm
-20.00
-10.00
0.00
10.00
20.00
OMEGA

Fig 12 :

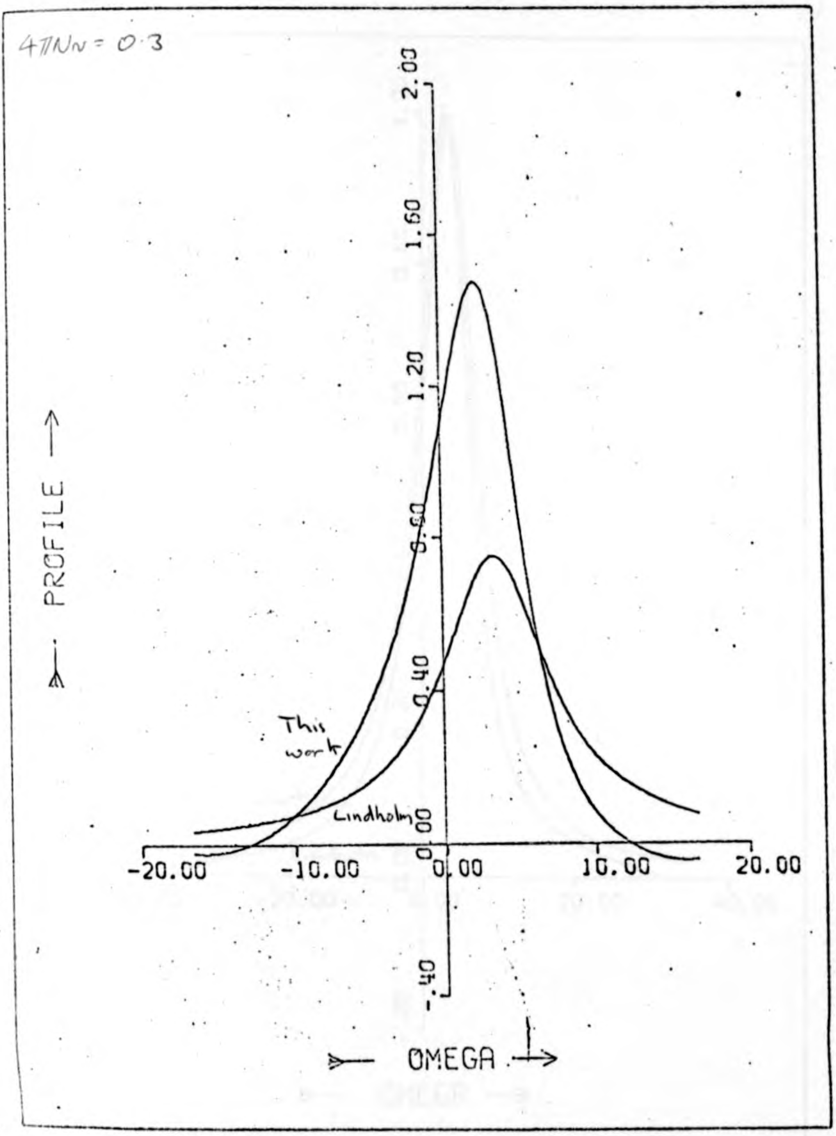
4πNν = 0·3
PROFILE →
OMEGA →
2.00
1.60
1.20
0.80
0.40
0.00
-.40
-20.00
-10.00
0.00
10.00
20.00
This work
Lindholm

Fig 12 g

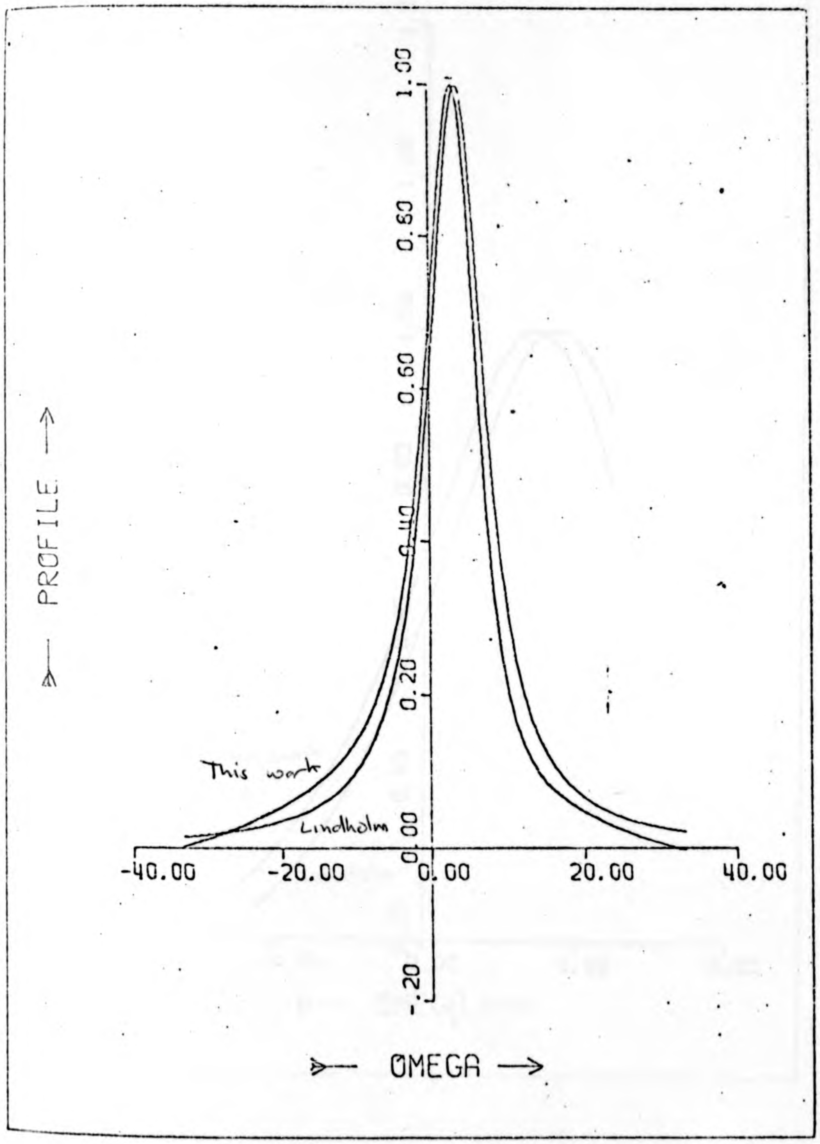
PROFILE →
OMEGA →
1.00
0.80
0.60
0.40
0.20
0.00
-.20
-40.00
-20.00
0.00
20.00
40.00
This work
Lindholm

Fig 13

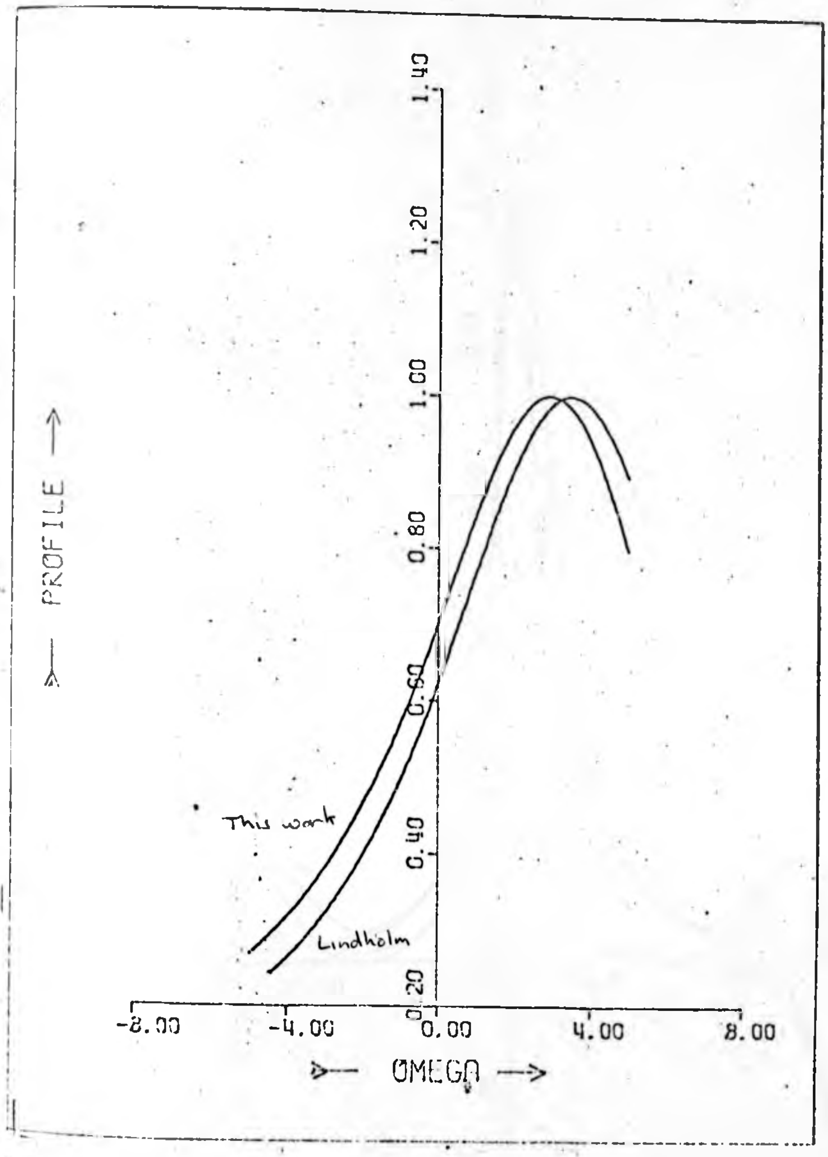
PROFILE →
1.40
1.20
1.00
0.80
0.60
0.40
0.20
-8.00
-4.00
0.00
4.00
8.00
OMEGA →
This work
Lindholm

Fig 14

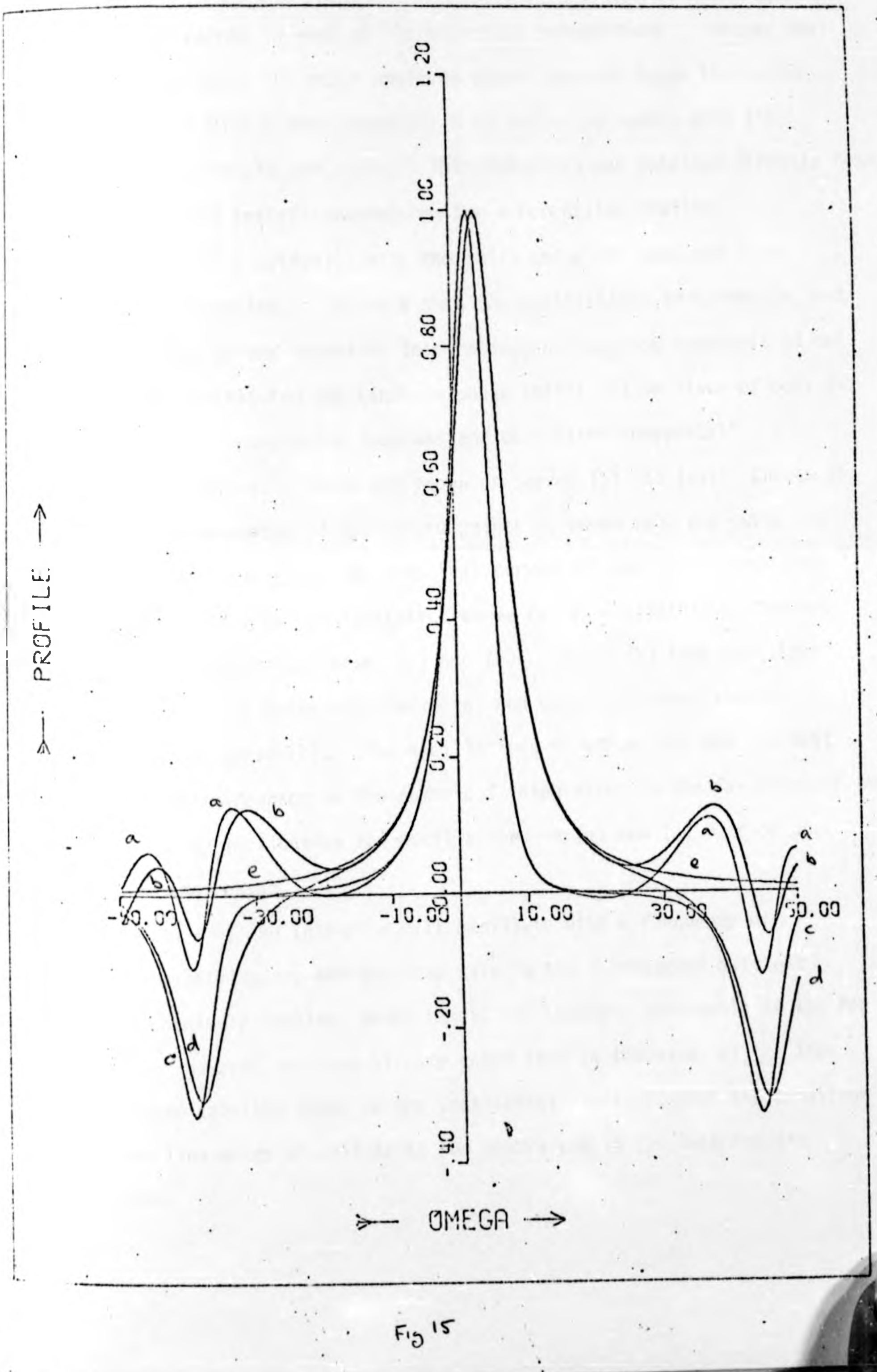
1.20
1.00
0.80
0.60
0.40
0.20
0.00
-.20
-.40
-50.00
-30.00
-10.00
10.00
30.00
50.00
a
b
c
d
e
PROFILE
OMEGA

Fig 15

profile. Curve (a) is our profile calculated numerically by the method already described. Curve (c) is our profile evaluated using more quadrature points in each of the numerical integrations. We see that as expected curve (c) stays positive over a greater range than curve (a) and that within that range it is in better agreement with the Lorentzian Lindholm curve (e). This curve (e) was obtained directly from the normalised analytic expression for a Lorentzian profile, $1/\{(\Delta w\text{-shift})^2 + (\text{width})^2\}$ with the shift and width obtained from Lindholm's formulae. To check that the oscillations in curves (a) and (c) were due to the numerical integration and were not intrinsic to our theory we substituted the Lindholm phase shifts (η) in place of ours in the numerical integration programs and calculated "numerical" Lindholm profiles. These are shown as curves (b) and (d). Curves (b) used the same number of quadrature points as curve (a), and curve (d) the same as curve (c). We note that curves (b) and (d) diverge from each other and from the "analytic" curve (e) approximately as far out of the line centre as curves (a) and (c). Curve (b) then oscillates approximately in phase with curve (a) and curve (d) shows similar behaviour to curve (c). The oscillations in curves (b) and (d) must arise from inaccuracy in the numerical integration in the far wings of the line, and by implication the oscillations in (a) and (c) must be due to the same reason.

As $\Delta w \to \infty$, the integrand will oscillate with a frequency of approximately $2\pi/\Delta w$, and the step size in the s integrand must get correspondingly smaller, which limits the accuracy obtainable in the far wings. However, we have already shown that in the wings of the line our exact solution tends to the statistical limit, so that the behaviour of the line wings as well as in the centre and in the intermediate regions.

CHAPTER VIII

CONCLUSION

In the first part of this work we considered the application of classical mechanics to the motion of a particle in a simple Harmonic, a Morse, and a Coulomb potential. We then applied two correspondence principles to obtain approximations to various quantum mechanical matrix elements in these potentials. We made use of the ambiguity in the correspondence principle definition of n_c to show that although the simplest (?) choice $n_c = n + \frac{1}{2}s$ produced results which might be acceptable in the absence of quantum mechanical results for n of order 5 and above, and $s < n$, a heuristically chosen expression for n_c for each potential produced results which could be used for all values of n. For the Coulomb potential we further calculated quantities such as the dipole moment and the oscillator strength which, apart from showing agreement with their quantum mechanical counterparts, are relatively simple in form and should be used for high quantum numbers where the quantum mechanical calculations are cumbersome and tabulated values are not available.

In the second part we applied classical methods to the broadening of spectral lines. We presented a general theory valid for high quantum numbers (Appendix III) whenever classical perturbation theory was valid. This has a wider range of validity than quantum mechanical line broadening theories which assume quantum mechanical perturbation theory. The theory reduces in the line wings to the statistical result of Margenau, but its behaviour in the line centre shows severe limitations in the work of Lindholm. Working in terms of the autocorellation function we showed that our results tended to the statistical result as s → o and to an asymptote with a similar though not identical gradient as Lindholms as s → ∞.

The line profiles obtained were compared with the Lorentzian Lindholm profile and the half-widths were found to be far more sensitive to the physical parameters of temperature and pressure than the Lindholm theory would indicate.

APPENDIX I

STATISTICAL THEORY

The problem of the broadening of spectral lines due to the presence of perturbers can be approached from a different direction. The radiating atom is in an external field. A spectral line arising from a transition between energy levels E_2 and E_1 has a frequency proportional to $E_2 - E_1$. In the presence of an external field each of these energy levels changes. In the presence of only one perturber they are functions of the atom/perturber separation, and the radiation frequency thus depends on this separation. If the perturbers are quasi-static (i.e. do not significantly change their position during any time of interest) then it is possible to calculate the probability of various perturber distributions, and hence obtain the frequency associated with each distribution.

In a series of papers in the 1930's Margenau developed the Statistical theory from the general qualitative arguments above to a sophisticated detailed theory. In 1955, with Meyerott, he showed the formal similarity between his theory and an alternative approach hy Holtzmark. The Holtzmark theory is well described in the review paper of Margenau and Lewis, but the Margenau theory is best described in the original papers.

For one perturber, the result obtained was , for a volume V ,

$$\phi(s) = 1 - \frac{1}{V} \int_0^R \left\{ \exp(-i\Delta\omega(r)\, s) - 1 \right\} 4\pi r^2 \, dr$$

and for NV perturbers,

$$\ln \phi(s) = 4\pi N \int_0^\infty \left\{ \exp\,(-i\Delta\omega(r)s) - 1 \right\} r^2 \, dr.$$

In the wings of a line, when the static approximation is valid, the probability of finding a particle near the atom is small, and it may be a reasonable approximation to consider only the interaction with the closest perturber. This is the "nearest neighbour" approximation. The probability of finding one particle in the interval dr and no particles within r is

$$w(r)\, dr = \exp\,(-4/3\pi r^3 N) \quad N\, 4\pi r^2 \, dr$$

Choosing $\Delta\omega_o$ to be the mean shift corresponding to the average interparticle separation $n^{-1/3}$, it can be shown that the profile is

$$I(w) = \frac{1}{k}\left(\frac{\Delta\omega_o}{\Delta\omega}\right)^{(k+3)/k} \exp\left\{ -\left(\frac{\Delta\omega_o}{\Delta\omega}\right)^{3/k} \right\} \frac{1}{\Delta\omega_o}$$

for $\Delta\omega = c/r^k$. This formula is found to be correct sufficiently far in the line wings.

APPENDIX II

AII.1 Infinite Series

We outline here attempts to obtain analytic forms of ln $\phi(s,b)$ and ln $\phi(s)$. We first evaluate

$$\ln \phi(s,b) = \int_0^\infty dt_o \left\{ \exp(-i\eta) - 1 \right\}$$

$$\eta = 2a \left\{ \arctan\left(\frac{S}{1 + T^2 - \frac{1}{4}S^2} \right) + H\pi \right\}$$

$$S = \frac{vs}{b}, \quad T = \frac{vt_o}{b}, \quad a = \frac{c}{2bv}$$

$$H = 1 \text{ if } 1 + T^2 - \tfrac{1}{4}S^2 < 0$$

$$= 0 \text{ otherwise.}$$

Using the fact that

$$\exp(-2ix) = 1 - \frac{2i\tan(x)}{1 + i\tan(x)}$$

we can write

$$\exp(-i\eta) = \left\{ 1 - \frac{2iS}{1 + T^2 - \frac{1}{4}S^2 + iS} \right\}^a \exp(-2ia\pi H)$$

This can be expanded in a series which is infinite for non-integer values of "a", but has "a" terms if "a" is integer. (The convergence of the infinite series has to be established by considering the real and imaginary parts separately, each part being made up of two infinite series). So,

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$$\ln \phi(s,b) = \int_{c}^{\infty} dt_0 \left\{ \exp(-i\eta) - 1 \right\}$$

$$\eta = 2a \left\{ \arctan\left(\frac{S}{1 + T^2 - \frac{1}{4}S^2} \right) + H\pi \right\}$$

$$S = \frac{vs}{b}, \quad T = \frac{vt_0}{b}, \quad a = \frac{c}{2bv}$$

$$H = 1 \text{ if } 1 + T^2 - \tfrac{1}{4}S^2 < 0$$

$$= 0 \text{ otherwise.}$$

Using the fact that

$$\exp(-2ix) = 1 - \frac{2i\tan(x)}{1 + i\tan(x)}$$

we can write

$$\exp(-i\eta) = \left\{ 1 - \frac{2iS}{1 + T^2 - \frac{1}{4}S^2 + iS} \right\}^a \exp(-2ia\pi H)$$

This can be expanded in a series which is infinite for non-integer values of "a", but has "a" terms if "a" is integer. (The convergence of the infinite series has to be established by considering the real and imaginary parts separately, each part being made up of two infinite series). So,

APPENDIX II

AII.1 Infinite Series

We outline here attempts to obtain analytic forms of ln $\phi(s,b)$ and ln $\phi(s)$. We first evaluate

$$\ln \phi(s,b) = \int_{c}^{\infty} dt_o \left\{ \exp(-i\eta) - 1 \right\}$$

$$\eta = 2a \left\{ \arctan\left(\frac{S}{1 + T^2 - \frac{1}{4}S^2} \right) + H\pi \right\}$$

$$S = \frac{vs}{b}, \quad T = \frac{vt_o}{b}, \quad a = \frac{c}{2bv}$$

$$H = 1 \text{ if } 1 + T^2 - \tfrac{1}{4}S^2 < 0$$

$$= 0 \text{ otherwise.}$$

Using the fact that

$$\exp(-2ix) = 1 - \frac{2i\tan(x)}{1 + i\tan(x)}$$

we can write

$$\exp(-i\eta) = \left\{ 1 - \frac{2iS}{1 + T^2 - \frac{1}{4}S^2 + iS} \right\}^a \exp(-2ia\pi H)$$

This can be expanded in a series which is infinite for non-integer values of "a", but has "a" terms if "a" is integer. (The convergence of the infinite series has to be established by considering the real and imaginary parts separately, each part being made up of two infinite series). So,

$$\ln \phi(s,b) = \int_0^\infty dt_0 \left\{ \exp(-2ia\pi H) - 1 \right\} + \int_0^\infty dt_0 \quad \exp(-2ia\pi H) \sum_{m=1} \binom{a}{m} \left\{ \frac{-2iS}{1 + T^2 - \frac{1}{4}S^2 + iS} \right\}^m$$

which can be written

$$\ln \phi(s,b) = (\tfrac{1}{4}S^2 - 1)^{\frac{1}{2}} \; H(\tfrac{1}{4}S^2 - 1) \left\{ \exp(-2ia\pi) - 1 \right\}$$
$$+ \sum_{m=1} \binom{a}{m} \int_0^\infty dt_0 \frac{(-2iS)^m}{(1 + T^2 - \frac{1}{4}S^2 + iS)^m}$$
$$+ \sum_{m=1} \binom{a}{m} \left\{ \exp(-2ia\pi) - 1 \right\} H(\tfrac{1}{4}S^2 - 1) \int_0^{\sqrt{\frac{1}{4}S^2 - 1}} dt_0 \frac{(-2iS)^m}{(1+T^2-\frac{1}{4}S^2+iS)^m}$$

with $H(\frac{1}{4}S^2-1) = 1$ if $S > 2$

$= 0$ if $S \leqslant 2$

We shall refer to the first term as the "Lindholm" term, L, to the second as the "Integer" term, I, and to the third as the cross term, X.

We note that the "Lindholm" term only reduces to the equation obtained by Lindholm for $S \gg 2$; it differs in that it is zero whenever S is less than 2. The integer term has been evaluated in the main text,

$$I = 2\pi \sum_{m=1} \binom{a}{m} \frac{(2m-2)!}{(m-1)!(m-1)!} \quad \frac{(2iS)^m}{(2i-S)^{2m-1}}$$

we call this term "integer" because it is the only non-zero term when "a" is integer. When "a" is not integer, we can approximate the infinite series by a closed form approximation. Since

$$\frac{2iaS}{(2i-S)} \left\{ 1 + \frac{2iS}{(2i-S)^2} \right\}^{a-1} = \sum_{m=1} \binom{a}{m} \frac{m(2iS)^m}{(2i-S)^{2m-1}}$$

which only differs from I in the factor m compared with $(2m-2)!/(m-1)!(m-1)!$ (these take the values 1, 2, 3, 4, ... as opposed to 1, 2, 6, 20) we use this as an approximation to I. The disagreement for higher orders of m will only be significant whenever S is approximately 2.

The cross term can be written in terms of X(m) where

$$X = \sum_{m=1} \binom{a}{m} \left\{ \exp(-2ia\pi) - 1 \right\} H(\tfrac{1}{4}S^2 - 1) \quad X(m),$$

$$X(m) = \int_0^{\sqrt{\frac{1}{4}S^2-1}} dt_0 \, \frac{(-2iS)^m}{(1 + T^2 - \frac{1}{4}S^2 + iS)^m}$$

and

$$X(1) = \left\{ \frac{-2iS}{S-2i} \right\} \left\{ \tfrac{1}{2}\ln(-1 + \tfrac{1}{2}S^2 + \tfrac{1}{2}S^2 \sqrt{1-4/S^2}) - i \arctan \left(\sqrt{\tfrac{1}{4}S^2 - 1} \right) \right\}$$

$$X(2) = \frac{8iS}{(S-2i)^2} \sqrt{\tfrac{1}{4}S^2 - 1} - \frac{2iS}{(S-2i)^2} X(1)$$

and it can be shown that

$$X(m) = H(\tfrac{1}{4}S^2-1) \sqrt{\tfrac{1}{4}S^2-1} \left\{ \exp(-2ia\pi) - 1 \right\} \sum_{m=1} \binom{a}{m} 2^m H(2-m)$$

$$\times \sum_{k=0}^{m-2} \frac{(2m-3)!!}{(2m-3-2k)!!} \frac{(m-k-2)!}{(m-1)!} \left\{ \frac{-2iS}{(S-2i)^2} \right\}^k$$

$$+ \; X(1) \, H(\tfrac{1}{4}S^2-1) \left\{ \exp(-2ia\pi) - 1 \right\} \sum_{m=1} \binom{a}{m} \frac{(2m-3)!!}{(m-1)!} \left\{ \frac{4iS}{(S-2i)^2} \right\}^{m-1}$$

Our claim that $\ln \phi(s,b)$ could be written as a sum of the "integer" and the "Lindholm" term will be justified if the cross term is small when $S > 2$. The check was not made due to the difficulty in evaluating

X numerically, and the greater difficulty in estimating it analytically.

Having obtained a complete exact solution to ln $\phi(s,b)$, we next try to integrate it with respect to b^2; we write

$$\ln \phi(s) = 4\pi N v \, (I_b + L_b + X_b) \quad ,$$

$$I_b = \int_0^\infty b\,db \; I$$

$$L_b = \int_0^\infty b\,db \; L$$

$$X_b = \int_0^\infty b\,db \; X$$

No significant progress was made with X_b.

After some analysis, we can obtain the real and imaginary parts of L_b

$$\mathrm{Real}\left\{L_b\right\} = -\left(\frac{c\pi}{v}\right)^3 \sum_{k=0}^{\infty} \binom{\frac{1}{2}}{k} \frac{u^{2k-2}}{(2k+2)!} \left\{ \left[\sum_{n=0}^{k} (-1)^{n+1} \frac{(2n+1)!}{u^{2n+1}} \right] \cos u \right.$$

$$\left. - \left[\sum_{n=0}^{k} (-i)^{n+1} \frac{(2n)!}{u^{2n}} \right] \sin u - u\,\mathrm{Ci}(u) + (2k+1)! \, \frac{(-1)^k}{u^{2k+1}} \right\}$$

and

$$\mathrm{Imag}\left\{L_b\right\} = -\left(\frac{c\pi}{v}\right)^3 \sum_{k=0}^{\infty} \binom{\frac{1}{2}}{k} \frac{u^{2k-2}}{(2k+2)!} \left\{ \left[\sum_{n=0}^{k} (-1)^{n+1} \frac{(2n)!}{u^{2n}} \right] \cos u \right.$$

$$\left. - \left[\sum_{k=0}^{\infty} (-1)^{n+1} \frac{(2n+1)!}{u^{2n+1}} \right] \sin u - u\,\mathrm{Si}(u) \right\}$$

with $u = \dfrac{2c\pi}{sv^2}$

These expressions can be written in various ways, and asymptotic forms can be obtained using the limiting approximations for the Sine and Cosine integral functions, Si(x) and Ci(x). Since, as $u \rightarrow \infty$

$$uCi(u) \simeq \left[\sum_{n=0}^{\infty} (-1)^{n+1} \frac{(2n+1)!}{u^{2n+1}} \right] \cos u - \left[\sum_{n=0}^{\infty} (-1)^{n+1} \frac{(2n)!}{u^{2n}} \right] \sin u$$

we can express the then dominant term in the expression for Real$\{L_b\}$ as

$$\text{Real} \{I_b\} = \left(\frac{c\pi}{v}\right)^3 \frac{1}{3u^3} \quad , \quad u \rightarrow \infty \; , \quad s \rightarrow 0$$

and similarly

$$\text{Real} \{I_b\} = -\left(\frac{c\pi}{v}\right)^3 \ln\left(\frac{1}{u}\right) \cdot \frac{1}{2u} \, , \quad u \rightarrow 0, \; s \rightarrow \infty$$

$$\text{Imag} \{I_b\} = -\left(\frac{c\pi}{v}\right)^3 \frac{\pi}{4u^2} \quad , \quad u \rightarrow 0, \; s \rightarrow \infty$$

The imaginary part of I_b has no simple expression in the limit $s \rightarrow 0$. We reiterate an important advantage of this general solution over Lindholm's: we have not had to introduce ad hoc cut-offs in the impact parameter since a cut-off is implicit in the presence of $H(\frac{1}{4}S^2-1)$ in the solution for $\ln \phi(s,b)$.

The solution of I_b depends on integrating

$$I_b = \sum_{m=1}^{\infty} A_m \int_0^{\infty} \frac{dx}{x^4} \frac{(x/u)^m}{(2i-x/u)^{2m-1}} \binom{x}{m}$$

$$A_m = \left(\frac{c\pi}{v}\right)^3 (iu)^{m-1} \frac{(2m-2)!}{(m-1)!(m-1)!}$$

which was done for m = 1,2,3,4. The series generated appeared very slow to converge, and at this stage the entire approach was abandonned.

AII.2 Split Ranges

The major stumbling block in many approaches was the different behaviour of the integrand in different regions. A method was developed to consider the integral as a sum of integrals over different ranges.

Writing the integrand in the form

$$\left\{1 - \frac{2iX}{1+iX}\right\}^{a} \exp\left\{-2ia\pi H\right\}$$

$$X = S/(1 + T^2 - \tfrac{1}{4}S^2)$$

the criterion for using a binomial expansion is that

$$\frac{3S^2}{(1 + T^2 - \frac{1}{4}S^2)^2} < 1$$

This will be satisfied if $S < 4 - 2\sqrt{3}$ for all values of T. If S lies between $4 \pm 2\sqrt{3}$ it will not be satisfied if

$$\tfrac{1}{4}S^2 - 1 + \sqrt{3}\,S \geqslant T^2$$

and if $S \geqslant 4 + 2\sqrt{3}$ it will not be satisfied if

$$\tfrac{1}{4}S^2 - 1 + \sqrt{3}\,S \geqslant T^2 \geqslant \tfrac{1}{4}S^2 + 1 - \sqrt{3}\,S$$

We therefore consider ln $\phi(s,b)$ for three ranges of S,

$$S < 4 - 2\sqrt{3}$$

$$4 - 2\sqrt{3} \leqslant S < 4 + 2\sqrt{3}$$

$$4 + 2\sqrt{3} \leqslant S$$

We consider these in order.

(i) $S < 4 - 2\sqrt{3}$

In this case we obtain what we have called the "integer a" solution.

(ii) $4 - 2\sqrt{3} \leqslant S < 4 + 2\sqrt{3}$

$$\ln \phi(s,b) = \frac{b}{v} \left\{ I_1 + I_2 \right\}$$

$$I_1 = \int_0^y \frac{v}{b} dt \left\{ e^{-i\eta} - 1 \right\}$$

$$I_2 = \int_y^\infty \frac{v}{b} dt \sum_{m=1}^{\infty} \binom{a}{m} \left\{ \frac{-2iS}{1+T^2-\frac{1}{4}S^2+iS} \right\}^m$$

and $y = \left\{ \frac{1}{4}S^2 - 1 + \sqrt{3}\ S \right\}^{\frac{1}{2}}$.

The value of y is 0 when $S = 4 - 2\sqrt{3}$. We find that

$$I_2 = \sum_{m=1}^{\infty} \binom{a}{m} (-2iS)^m \left\{ \frac{(2m-2)!}{(m-1)!(m-1)!} \frac{2}{(2i-S)^{2m-1}} \left[\pi + \arctan\left(y + \tfrac{1}{2}iyS\right) \right] \right.$$

$$+ H(m-2)\, y \sum_{k=0}^{m-2} \frac{(2m-3)!!}{(2m-2k-3)!!} \frac{(m-k-2)!}{(m-1)!} \frac{1}{2^{k+1}} \frac{1}{(\frac{1}{4}S^2-1+iS)^{k+1}}$$

$$\left. + \frac{1}{(\sqrt{3}S+iS)^{m-k-1}} \right\}$$

In evaluating I_2 we have to consider three more ranges of S. If $2 < S < 4 + 2\sqrt{3}$,

$$I_2 = \sum_m \binom{a}{m} (-2iS)^m \sum_k \binom{-m}{k} \left\{ 1 - \tfrac{1}{4}S^2 + iS \right\}^{-m-k} \frac{1}{2k+1} \left\{ (\tfrac{1}{4}S^2 - 1)^{k+\frac{1}{2}} \right.$$

$$\left. \times \left(\exp(-2ia\pi) - 1\right) + L_1^{k+\frac{1}{2}} \right\}$$

$$+ \sum_m \binom{a}{m} (-2iS)^m \sum_k \binom{-m}{k} \left\{ 1 - \tfrac{1}{4}S^2 + iS \right\}^k \frac{1}{1-2m-2k} \left\{ L_2^{-m-k+\frac{1}{2}} - L_1^{-m-k+\frac{1}{2}} \right\}$$

$$- L_2^{\frac{1}{2}}$$

If $2/\sqrt{3} < S < 2$

$$I_2 = \sum \binom{a}{m} (-2iS)^m \sum_k \binom{-m}{k} \left\{1 - \tfrac{1}{4}S^2 + iS\right\}^{-m-k} \frac{1}{2k+1} L_1^{k+\frac{1}{2}}$$

$$+ \sum \binom{a}{m} (-2iS)^m \sum_k \binom{-m}{k} \left\{1 - \tfrac{1}{4}S^2 + iS\right\}^{k} \frac{1}{1-2m-2k} \left\{L_2^{-m-k-\frac{1}{2}} - L_1^{-m-k-\frac{1}{2}}\right\}$$

$$- L_2^{\frac{1}{2}}$$

and if $4 - 2\sqrt{3} < S < 2/\sqrt{3}$

$$I_2 = \sum \binom{a}{m} (-2iS)^m \sum_k \binom{-m}{k} \left\{1 - \tfrac{1}{4}S^2 + iS\right\}^{-m-k} \frac{1}{2k+1} L_2^{k+\frac{1}{2}}$$

$$- L_2^{\frac{1}{2}}$$

In all these equations L_1 and L_2 are limits of integration,

$$L_1 = 1 + \tfrac{1}{2}S^2$$

$$L_2 = \tfrac{1}{4}S^2 - 1 + \sqrt{3}\, S = y^2$$

(iii) $4 + 2\sqrt{3} \leqslant S$

As we have done in the previous case, we consider $\ln \phi(s)$ as a sum of integrals over different ranges.

$$\ln \phi(s,b) = \frac{b}{v} (J_1 + J_2 + J_3)$$

$$J_1 = \frac{v}{b} \int_0^{L_3^{\frac{1}{2}}} dt \quad \mathrm{Exp}$$

$$J_2 = \frac{v}{b} \int_{L_3^{\frac{1}{2}}}^{L_2^{\frac{1}{2}}} dt \quad \left\{ \exp(-i\eta) - 1 \right\}$$

$$J_3 = \int_{L_2^{\frac{1}{2}}}^{\infty} dt \quad \mathrm{Exp}$$

where Exp indicates that a binomial expansion can be used, and

$$L_3^{\,2} = \tfrac{1}{4}S^2 - 1 - \sqrt{3}\,S.$$

The expressions for J_1, J_2, J_3 are as follows:

$$J_1 = -e^{2ia\pi} \sum_{m=1}^{\infty} \binom{a}{m} (-2iS)^m \left\{ \frac{(2m-2)!}{(m-1)!(m-1)!} \; \frac{2}{(2i+S)^{2m-1}} \quad \arctan\left[(i+iS)L_3^{\frac{1}{2}}\right] \right.$$

$$+ \frac{L_3^{\frac{1}{2}}}{(2m-1)} \sum_{k=0}^{m-2} \frac{(2m-1)!!}{(2m-2k-3)!!} \; \frac{(m-k-2)!}{(m-1)!} \; \frac{2^{k-1}}{(2i+S)^{2k+2}} \quad \frac{1}{(i-\sqrt{3})^{m-k-1}} \; *$$

$$\left. \frac{1}{S^{m-k-1}} \right\}$$

$$J_3 = \sum_{m=1}^{\infty} \binom{a}{m} (-2iS)^m \; I_2$$

$$J_2 = \sum_{m=0}^{\infty} \binom{a}{m} (-2iS)^m \sum_{k=0}^{\infty} \binom{m}{k} (1-\tfrac{1}{4}S^2+iS)^{-m-k} \; \frac{1}{2k+1} \left\{ (\tfrac{1}{4}S^2-1)^{k+\frac{1}{2}} (e^{2ia\pi}-1) \right.$$

$$\left. + L_1^{\,k+\frac{1}{2}} - L_3^{\,k+\frac{1}{2}} \right\}$$

$$+ \sum_{m=0}^{\infty} \binom{a}{m} (-2iS)^m \sum_{k=0}^{\infty} \binom{m}{k} (1-\tfrac{1}{4}S^2+iS)^k \; \frac{1}{-2m-2k+1} \left\{ L_2^{\,-m-k+\frac{1}{2}} - L_1^{\,-m-k+\frac{1}{2}} \right\}$$

$$+ \left\{ L_3^{\frac{1}{2}} - L_2^{\frac{1}{2}} \right\}$$

After some numerical and analytical attempts to evaluate $\ln \phi(s)$, this attempt was also abandonned.

AII.3 Fourier Expansion

The last method we shall describe was in some ways the most successful even though it did not lead to an expression for $\phi(s)$. Since much of the work previously described used Fourier expansion, we expanded

$$\exp(-iaX) = \sum_n' A_n(a) \exp(-inX)$$

with $$X = 2 \arctan (T+\tfrac{1}{2}S) - 2 \arctan (T-\tfrac{1}{2}S)$$

from which

$$\exp(-iaX) - 1 = \sum_n \frac{\mathrm{Sin}(n-a)\pi}{(n-a)\pi} \left\{ \exp(-inX) - 1 \right\}$$

and we now have an infinite series of what we called "integer a" solutions.

Useful approximations can be made by writing $a = N - \epsilon$, with $0 \leqslant \epsilon \leqslant 1$. Then

$$\exp(-iaX) - 1 = \sum_n (-1)^{n-N} \frac{\sin \epsilon\pi}{(n-N+\epsilon)\pi} \left\{ \exp(-inX) - 1 \right\}$$

The approximation we make is to assume, perhaps incorrectly, that the dominant terms in the expansion are those for which $(n-N+\epsilon)$ is small, so that the only terms we select from the expansion are those corresponding to $n = N$ and $n = N - 1$,

i.e. $$\exp(-iaX) - 1 = \pm \frac{\sin\epsilon\pi}{\epsilon\pi} \left\{ \exp(-iNX) - 1 \right\} \pm \frac{\sin\epsilon\pi}{(1-\epsilon)\pi} \left\{ \exp(-i(N-1)X) - 1 \right\}$$

and

$$\ln \phi(s,b) = \pm 2\pi i \frac{b}{v} \sum_{m=1}^{N} \binom{N}{m} \frac{(2m-2)!}{(m-1)!(m-1)!} \frac{(2iS)^{m}}{(2i-S)^{2m-1}}$$

$$\pm 2\pi i \frac{b}{v} \sum_{m=1}^{N-1} \binom{N-1}{m} \frac{(2m-2)!}{(m-1)!(m-1)!} \frac{(2iS)^{m}}{(2i-S)^{2m-1}}$$

Although this solution appears simple, there are difficulties arising from the definition of N, and the initial assumption cannot be rigorously justified if ϵ is about $\frac{1}{2}$.

and

$$\ln \phi(s,b) = \pm 2\pi i \,\frac{b}{v} \sum_{m=1}^{N} \binom{N}{m} \frac{(2m-2)!}{(m-1)!(m-1)!} \, \frac{(2iS)^{m}}{(2i-S)^{2m-1}}$$

$$\pm 2\pi i \,\frac{b}{v} \sum_{m=1}^{N-1} \binom{N-1}{m} \frac{(2m-2)!}{(m-1)!(m-1)!} \, \frac{(2iS)^{m}}{(2i-S)^{2m-1}}$$

Although this solution appears simple, there are difficulties arising from the definition of N, and the initial assumption cannot be rigorously justified if ϵ is about $\frac{1}{2}$.

APPENDIX III

Regions of validity and Merging of Spectral Lines

Apart from the approximations mentioned in the text, the line profiles obtained will cease to have any meaning for high enough values of n. Highly excited states have relatively small energy separation, and broadening of the levels causes them to merge.

This merging of states was first considered by Inglis and Teller (1939), and their method was revised and commented on by Unsold (1948). We have shown that for hydrogen the energy levels are given by

$$E_n = \frac{-e^2}{2a_o n^2}$$

where a_o is the first Bohr radius, so that the separation of energy levels for high n is

$$\Delta E_n = \frac{e^2}{a_o n^3}$$

When the splitting is of the order of $\frac{1}{2}\Delta E_n$, the levels will merge.

In the case of statistical broadening, the splitting in the linear Stark effect for the extreme components is

$$3/2ea_o n^2 F$$

for a field F. The electric field is generally assumed small, and Inglis and Teller chose an ionic field of $3{\cdot}7\ e^2\ n^{2/3}$ and obtained the following equation forthe highest observable state n_{max},

$$\log_{10} N = 23{\cdot}3 - 7{\cdot}5 \log_{10} n_{max}.$$

(This formula has often been used to determine the ion density N). They also showed that starting with the Lindholm approximation and substituting

$$c = \frac{e^2 a_o n^2}{\hbar}$$

and

$$mv^2 = 3kT ,$$

the effect of electrons has to be taken into consideration when

$$T < \frac{5 \times 10^5 \ K}{n_{max}}$$

(although this criterion should be treated with some caution, based as it is on the Lindholm calculations). There will thus be a limit dependent on temperature and density beyond which no spectral lines will be observed.

Before this limit is reached, one of the major approximations in the theory may break down. Using cross sections obtained from the correspondence principle, G. Peach has shown in some unpublished work that beyond a certain quantum number, inelastic collisions will dominate the line broadening process. This value of the quantum number also depends on the physical situation, but for the cases considered was of order 100 or less.

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Matrix elements and correspondence principles

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Abstract. Heisenberg's form of the correspondence principle for non-relativistic matrix elements has been used to evaluate matrix elements for various potentials. These are compared with available quantum mechanical results to check the general validity of the use of classical mechanics and correspondence principles in the derivation of quantum mechanical expressions.

Using a one dimensional harmonic oscillator potential, matrix elements of the form $\langle n|q^m|n+s\rangle$ and $\langle n|p^m|n+s\rangle$ are worked out. A Morse potential is then considered and the matrix elements for position, momentum, and kinetic energy are evaluated. Using a Coulomb potential a similar procedure is used for functions of various position coordinates, from which dipole and quadrupole moments from transitions between n, l states are calculated.

The agreement with quantum mechanics is found to be generally good, and in some cases identical results are obtained.

1. Introduction

There are many problems in the physics of excited states which have no exact analytic solutions. For highly excited states, we can apply the correspondence principle and use classical mechanics. The classical solution will tend to the exact quantum mechanical solution in the limit of high quantum number (n), but there is some uncertainty as to the exact range of validity of this approximation, and its application to intermediate or even low quantum numbers is not *a priori* justified.

The purpose of this paper is to examine this range of validity and to demonstrate how correspondence principle solutions can be used away from the high n limit, so that classical techniques may be used more effectively where no exact quantum mechanical solutions are available. Of course detailed comparisons between quantum and correspondence solutions can only be made when both are known, so we consider here cases where exact quantum solutions are available, derive the correspondence solution, and compare the two over a wide range of quantum numbers.

Section 2 is a brief introduction to the standard classical theories and to the correspondence principles used. In § 3, this theory is applied to a one-dimensional harmonic oscillator potential to evaluate matrix elements of various powers of position and momentum. In § 4 this is repeated for a Morse potential and in § 5 for a Coulomb potential. At all stages results are compared with available quantum mechanical results. Section 6 is a summary of the comparisons.

2. Theory

The classical theory of action and angle variables is well documented (Corben and Stehle 1960, Goldstein 1959), if q and p are the initial values of position and momentum, then

$$I = \frac{1}{2\pi}\oint p\,\mathrm{d}q \tag{1}$$

$$w = \frac{\partial}{\partial I}\int p(I)\,\mathrm{d}q. \tag{2}$$

We follow the notation of Landau and Lifshitz (1960) and replace the usual action variable J by $J = J/2\pi$. The angle variable w then varies between 0 and 2π and $w = \omega t + \text{constant}$, ω being the classical frequency.

Sommerfeld assumed that

$$I = nh \tag{3}$$

with n = integer, so that the energy of the system is quantized. The second fundamental assumption of the old quantum theory (see Jammer 1966), formulated by Bohr, is that in the limit where successive stationary states differ little from each other,

$$\omega_{nn} = \frac{(E_n - E_{n'})}{h} \to s\omega \tag{4}$$

where ω_{nn} is the observed quantal frequency, and $s = n' - n$. A few years later, Heisenberg (1949) made a similar correspondence between matrix elements and Fourier coefficients.

If we expand

$$q(t) = \sum_s q_s \mathrm{e}^{\mathrm{i}s\omega t} \tag{5}$$

then Heisenberg's form of correspondence is that

$$\langle n|q(t)|n+s\rangle = q_s.$$

In general, equation (4) is only true in the limit of high n and low s. It is a question of practical importance as to whether or not there exists a more accurate approximation than is afforded by the classical *limit*. A fruitful approach is to notice that the limit necessarily does not distinguish between initial and final parameters, and to employ an *ad hoc* approximation that does. Any such attempt must of course be in agreement with the physical situation under consideration, and this problem in the case of the Coulomb potential has been investigated by Wentzel (1924) and more recently by Biedenharn and Brussaard (1965). Thus, for a transition between two states with quantum numbers n and $n+s$, the quantizing equation becomes

$$I = n_c h$$

and

$$n_c = f(n, n+s).$$

We shall show that good agreement is obtained for high n values between quantum mechanical and correspondence matrix elements by letting

$$n_c = n + \tfrac{1}{2}s \tag{6}$$

however, much better results are obtained over a large range of n values by comparing the correspondence and quantal results for simple cases at low n values, and adjusting n_c to agree at these low values. This particular choice of n_c will vary from potential to potential, but for each potential will give better agreement than equation (6). In some cases, a judicious choice of n_c reproduces quantal results for all values of n.

3. Simple harmonic potential

For a one-dimensional harmonic potential, $E = \omega I$, and

$$q = \left(\frac{2I}{\omega}\right)^{1/2} \cos \omega t. \tag{7}$$

Comparing equations (5) and (7), we infer that the only non-zero Fourier components are those with $s = \pm 1$, that is,

$$\langle n|q|n+1\rangle = \langle n|q|n-1\rangle = \left(\frac{\hbar\mu}{2\omega}n_c\right)^{1/2}.$$

This does not distinguish between upward and downward transitions, and would mean that the transitions $\langle n+1| \rightarrow |n\rangle$ and $\langle n| \rightarrow |n-1\rangle$ produced identical results, which is certainly false. Thus, on physical grounds, the substitution for n_c will have to differentiate between upward and downward transitions. Equation (7) can be raised to any integer power λ; for a general $\lambda > 0$, a similar procedure results in

$$\langle n|q^\lambda|n+s\rangle = \left(\frac{\hbar\mu}{2\omega}n_c\right)^{\lambda/2} \frac{\lambda!}{\{\frac{1}{2}(\lambda-s)\}!\{\frac{1}{2}(\lambda+s)\}!}$$

with the values of s restricted to

$$s = \lambda - 2j \qquad j = 0, 1, \ldots \lambda.$$

The simple harmonic oscillator is symmetric in position and conjugate momentum, p. The latter can be obtained by differentiating equation (7) with respect to time, and the correspondence matrix element is

$$\langle n|p^\lambda|n+s\rangle = \mathrm{i}^{2\lambda-s}\mu^\lambda\left(\frac{\hbar\omega}{2}n_c\right)^{\lambda/2} \frac{\lambda!}{\{\frac{1}{2}(\lambda-s)\}!\{\frac{1}{2}(\lambda+s)\}!} \tag{8}$$

with similar restrictions on s and λ. We now have to define n_c in terms of n and s, and this definition is very much an individual matter. There is an infinite class of valid definitions which produce results which obey Bohr's correspondence principle and agree with quantum mechanics in the limit $s/n \rightarrow 0$; the theory does not tell us which to choose to obtain results away from this limit. The simplest choice would be to let n_c equal the mean of n and $n+s$, that is,

$$n_c = n + \tfrac{1}{2}s.$$

From table 1, we see that using this substitution the quantal and correspondence results agree to $\sim(50/n)\%$.

We now use a pragmatic approach and choose the substitution which gives the best agreement with quantum mechanics over the whole matrix. Comparing in table 1

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Table 1. Comparison of correspondence and quantum mechanical values for the matrix elements of p^λ, $\lambda = 1, 2, 3, 4$. $A = i\mu\frac{1}{2}(h\omega)^{1/2}$. The substitution $(n_c)^s = (n+s)!/n!$, $s \neq 0$; $n_c = n+\frac{1}{2}$, $s = 0$, gives identical results for all terms except the three marked (*)

Matrix element	Correspondence value	Quantum mechanical value
$\langle n\|p\|n+1\rangle$	$An_c^{1/2}$	$A(n+1)^{1/2}$
$\langle n\|p\|n-1\rangle$	$-An_c^{1/2}$	$A(n)^{1/2}$
$\langle n\|p^2\|n+2\rangle$	A^2n_c	$A^2\{(n+1)(n+2)\}^{1/2}$
$\langle n\|p^2\|n\rangle$	$-2A^2n_c$	$-2A^2(n+\frac{1}{2})$
$\langle n\|p^2\|n-2\rangle$	A^2n_c	$A^2\{n(n-1)\}^{1/2}$
$\langle n\|p^3\|n+3\rangle$	$A^3n_c^{3/2}$	$A^3\{(n+1)(n+2)(n+3)\}^{1/2}$
$\langle n\|p^3\|n+1\rangle$	$-3A^3n_c^{3/2}$	$-3A^3(n+1)^{3/2}$
$\langle n\|p^3\|n-1\rangle$	$3A^3n_c^{3/2}$	$3A^2n^{3/2}$
$\langle n\|p^3\|n-3\rangle$	$-A^3n_c^{3/2}$	$-A^3\{n(n-1)(n-2)\}^{1/2}$
$\langle n\|p^4\|n+4\rangle$	$A^4n_c^2$	$A^4\{(n+1)(n+2)(n+3)(n+4)\}^{1/2}$
*$\langle n\|p^4\|n+2\rangle$	$-4A^4n_c^2$	$-4A^4(n+\frac{3}{2})\{(n+1)(n+2)\}^{1/2}$
*$\langle n\|p^4\|n\rangle$	$6A^4n_c^2$	$6A^4(n^2+n+\frac{1}{2})$
*$\langle n\|p^4\|n-2\rangle$	$-4A^4n_c^2$	$-4A^4(n-\frac{1}{2})\{n(n-1)\}^{1/2}$
$\langle n\|p^4\|n-4\rangle$	$A^4n_c^2$	$A^4\{n(n-1)(n-2)(n-3)\}^{1/2}$

the correspondence matrix elements with the quantum mechanical ones (Wilson *et al* 1955) we find that the best choice is

$$n_c^s = \frac{(n+s)!}{n!} \qquad s \neq 0. \tag{9a}$$

Expanding this for $s/n \to 0$,

$$n_c = n+\tfrac{1}{2}s+\tfrac{1}{2}$$

that is,

$$n_c = n+\tfrac{1}{2} \qquad s = 0. \tag{9b}$$

Substituting equations (9*a*) and (9*b*) in equation (8) for $\lambda = 1, 2, 3$, the two sets of results are identical for all values of n and s, that is, the two matrices are identical. For $\lambda \geqslant 4$, only elements of the form $\langle n|p^\lambda|n\pm\lambda\rangle$ are identical; the rest agree to $<50/n^2\,\%$. For example, $\langle n|p^4|n\rangle_Q = 6A^4(n^2+n+\frac{1}{2})$, whereas $\langle n|p^4|n\rangle_c = 6A^4(n^2+n+\frac{1}{4})$; for $n = 10$, these agree to 0·226%. (This was first noticed by Bell and Guggenheim (1936) in their calculations of mean values of dipole moments.) It is not yet understood why some correspondence matrix elements and their quantum mechanical counterparts are identical, and others are only nearly equal. The explanation probably involves correspondence identities (Norcliffe and Percival 1968a, b).

The results of this paper have been used by Clark and Dickinson (1971), who used the correspondence principle for strongly coupled states (Percival and Richards 1970c) to obtain approximate transition probabilities for a forced harmonic oscillator. They formally and numerically show that the correspondence principle result has a much larger range of validity than the first order perturbation approximation, even for 0 → 1 transitions.

4. Morse potential

The Morse potential is one of the best approximations for all values of q for the diatomic molecule. It is a one-dimensional potential defined by

$$V(q) = D[1-\exp\{-a(q-q_e)\}]^2$$

D being the dissociation energy, a a constant, and q_e corresponding to the bottom of the potential well.

If the energy of the system is E_n, and we define $t = a^{-1}h^{-1}(2\mu D)^{1/2}$ then

$$1-\frac{E_n}{D} = \left(1-\frac{n_c}{t}\right)^2$$

that is

$$\frac{E_n}{D} = \frac{n_c}{t}\left(2-\frac{n_c}{t}\right).$$

The parameter t is in fact a number of the order of (but greater than) the maximum number of bound states the potential will support. As in the case of the harmonic oscillator, replacing n_c by $n+\frac{1}{2}$ gives the quota result (Herzberg 1950).

The frequency ω is found to be

$$\omega = a^2h\mu^{-1}(t-n_c).$$

Defining Q to be the displacement from the bottom of the potential well, that is, $Q = q-q_e$, we find that

$$aQ = \ln\left(1+\sqrt{\frac{E}{D}}\sin w\right)-\ln\left(1-\frac{E}{D}\right). \tag{10}$$

Thus Q is a periodic function of w, and can be expanded in a Fourier series, the coefficients of which are

$$\langle n|Q|n+s\rangle = \frac{-i^s}{as}\left(n_c^s\frac{1}{(2t-n_c)^s}\right)^{1/2}. \tag{11}$$

Herman and Schuler (1953) used quantum mechanics to obtain this matrix element, and their expression can be written in the form

$$\langle n|Q|n+s\rangle = \frac{-1}{as}\left(\frac{(n+s)!}{n!}\,\frac{(2t-n-1-s)!}{(2t-n-1)!}\right)^{1/2} \times\left(\frac{(t-n-s-\frac{1}{2})(t-n-\frac{1}{2})}{\{(t-n-s)/2^{-1/2}\}\{(t-n-s)/2^{-1/2}\}}\right)^{1/2}. \tag{12}$$

For $s \ll t-n$, the last $(\;)^{1/2}$ tends to unity. Table 2 compares correspondence and quantum mechanical values of $a^2s^2|\langle n|Q|n+s\rangle|^2$, for $t = 50$, that is, for a potential with about 48 bound states. The correspondence matrix elements are first calculated using a mean value for n_c; comparison with the quantum mechanical values shows that there is an order of magnitude agreement for large s/n, which improves considerably when $s/n < 1$.

Comparing equations (11) and (12), it would seem reasonable to choose, for a particular value of n_c, that from equation (9*a*). This was the particular value chosen for the harmonic potential. Table 2 shows that much better agreement is obtained if equation (9*a*) is used.

Table 2. Comparison of quantum mechanical and correspondence values of $a^2s^2|\langle n|Q|n+s\rangle|^2$ in a Morse potential, with $t = 50$

Transition $n \rightarrow n+s$	Quantum mechanical value	Correspondence value $n_c = n+s/2$	Percentage difference	Correspondence value $(n_c)^s = (n+s)!/n!$	Percentage difference
1–2	0·020406	0·015228	34·0	0·020408	−0·0109
3–4	0·041662	0·036269	14·9	0·041667	−0·0118
7–8	0·086944	0·081081	7·23	0·86957	−0·0142
15–16	0·19044	0·18343	3·82	0·19048	−0·0216
1–4	$2·6272 \times 10^{-5}$	$1·6858 \times 10^{-5}$	55·8	$2·6203 \times 10^{-5}$	0·266
1–12	$1·053 \times 10^{-13}$	$1·833 \times 10^{-13}$	−42·5	$0·963 \times 10^{-13}$	9·37
3–6	$1·398 \times 10^{-4}$	$1·046 \times 10^{-4}$	33·6	$1·397 \times 10^{-4}$	0·1131
5–10	$4·575 \times 10^{-6}$	$3·504 \times 10^{-6}$	30·5	$4·557 \times 10^{-6}$	0·397

4.1. *Momentum in Morse potential*

The conjugate momentum p can be simply obtained by differentiating equation (10) with respect to time. If $\alpha^2 = E/D$, that is $\alpha < 1$,

$$p = \frac{\mu\alpha\omega}{a}\frac{\cos w}{1+\alpha\sin w}$$

the Fourier transform of which gives

$$\begin{aligned}\langle n|p|n+s\rangle &= \mathrm{i}^{s-2}\frac{\mu\omega}{a}\left(\frac{n_c}{2t-n_c}\right)^{s/2} &\qquad s \neq 0\\ &= 0 &\qquad s = 0.\end{aligned}$$

The matrix of p^2 is of more interest, and the correspondence matrix elements for p^2 can be compared with the quantum mechanical results of Greenwalt and Dickinson (1969)†. For diagonal elements we find that the two expressions are identical, that is we have a correspondence identity:

$$\langle n|p^2|n\rangle = a^2\hbar^2 n_c(t-n_c) \qquad n_c = n+\tfrac{1}{2}.$$

For off diagonal elements the quantal expression can be simplified and written in the form

$$\begin{aligned}\langle n|p^2|n+s\rangle_Q = &\left\{(-1)^s a^2\hbar^2\left(\frac{(n+s)}{n!}\right)^{1/2}\right\}\\ &\times\left((t-n-\tfrac{1}{2})(t-n-s-\tfrac{1}{2})\frac{(2t-n-s-1)!}{(2t-n-1)!}\right)^{1/2}\\ &\times(t(s-1)-s(n+\tfrac{1}{2}+\tfrac{1}{2}s)\end{aligned}$$

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† A factor of ½ has been omitted from one term of equation (6) of that paper, as confirmed by A S Dickinson (private communication).

which can be compared with the correspondence expression

$$\langle n|p^2|n+s\rangle_c = [(-i)^s a^2 h^2 n_c^{s/2}]\left((t-n_c)(t-n_c)\frac{1}{(2t-n_c)^s}\right)^{1/2}(t(s-1)-sn_c).$$

We could use the 'mean value' n_c, and equation (9*a*) as usual gives a good agreement. However, it was found that once the terms in the square bracket had been equated, even better agreement was obtained by using the expansion of equation (9*a*),

$$n_c = n+\tfrac{1}{2}s+\tfrac{1}{2}.$$

Figure 1 shows the agreement between the two equations when this course of action is followed. The agreement is surprisingly good for $s/n \gg 1$.

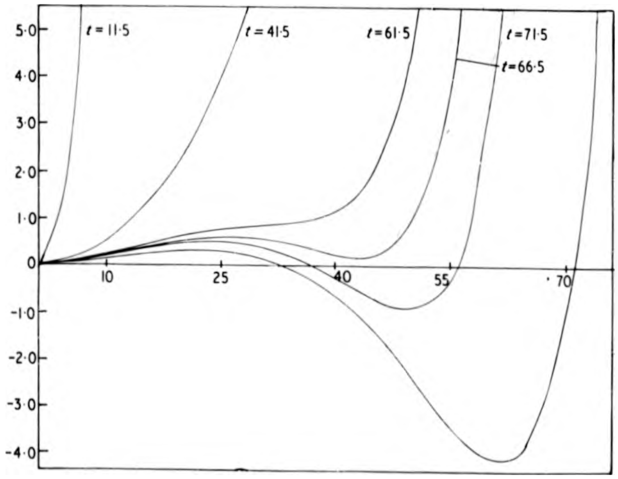

Figure 1. Percentage difference between quantum mechanical and adjusted correspondence matrix elements for momentum squared in a Morse potential, plotted against the final quantum number. The initial quantum number = 1 and the percentage = $(C-Q/C)\times 100$.

5. Coulomb potential

We now consider the case of an atom consisting of a nucleus of infinite mass, of charge Ze, only one electron, and with quantum numbers n, l, m. The electron describes an ellipse of semi-axis $a(=a_0n^2)$ (Born 1927) with the nucleus at one of the foci. The eccentric anomaly, u is defined by

$$r(t) = a(1-\epsilon\cos u)$$

$$\left.\frac{1}{-n_c)^s}\right)^{1/2}(t(s-1)-sn_c).$$

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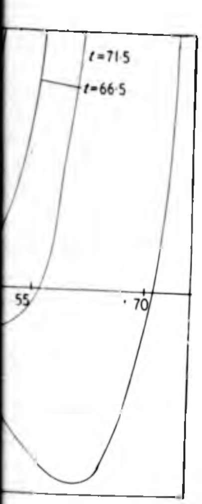

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r being the distance from the nucleus to the electron, and ϵ the eccentricity defined by

$$\epsilon^2 = 1-\frac{l^2}{n^2}. \tag{13}$$

Then

$$w = u-\epsilon \sin u.$$

We shall consider transitions between n, l, m levels. A function of three independent variables, describing a system with three degrees of freedom, can be expanded into a three-dimensional Fourier series. By analogy with the previous potentials, we expand the position coordinates (x, y, z) in the angle variables w, ψ, and ϕ (see Born), that is,

$$x(w,\psi,\phi) = \sum_{s,\Delta l,\Delta m} x_{n,l,m}^{n+s,l+\Delta l,m+\Delta m} \exp \mathrm{i}(sw+\Delta l\psi+\Delta m\phi)$$

etc, then obtain the matrix element for the transition by evaluating the Fourier coefficients. The properties of the integrals give selection rules for Δl and Δm:

For the x and y coefficients

$$\Delta l = \pm 1 \qquad \Delta m = \pm 1$$

for the z coefficient

$$\Delta l = \pm 1 \qquad \Delta m = 0.$$

The three matrix elements can be written in the form

$$\begin{aligned}
\langle n, l, m|x|n+s, l+\Delta l, m+\Delta m\rangle &= \frac{\Delta l}{4}\left(1+\frac{\Delta m\, m}{\Delta l\, l}\right) R_{n,l}^{n+s,l+\Delta l} \\
\langle n, l, m|y|n+s, l+\Delta l, m+\Delta m\rangle &= -\mathrm{i}\Delta m\frac{\Delta l}{4}\left(1+\frac{\Delta m m}{\Delta l l}\right) R_{n,l}^{n+s,l+\Delta l} \\
\langle n, l, m|z|n+s, l+\Delta l, m\rangle &= -\frac{\mathrm{i}}{2}\left(1-\frac{m^2}{l^2}\right)^{1/2} R_{n,l}^{n+s,l+\Delta l}
\end{aligned} \tag{14}$$

where

$$R_{n,l}^{n+s,l+\Delta l} = a\frac{\Delta l}{s}\left(J_s'(s\epsilon)+\Delta l\frac{(1-\epsilon^2)^{1/2}}{\epsilon}J_s(s\epsilon)\right) \tag{15}$$

is the dipole moment between states n, l and $n+s$, $l+\Delta l$. The eccentricity is now

$$\epsilon^2 = 1-\frac{l_c^2}{n_c^2}$$

and l_c and n_c have yet to be defined. There are again an infinite number of valid choices, and choosing $l_c = l$, $n_c = \bar{n}$ gives results which are close to the quantum mechanical ones. A heuristic approach leads to

$$\begin{aligned}
l_c &= \max(l, l+\Delta l) \\
n_c &= n(n+s)/(n+\tfrac{1}{2}s)
\end{aligned}$$

as these provide good agreement between quantal and correspondence results for higher values of $\Delta l/l$ and $\Delta n/n$.

For $s = 0$, the matrix elements for x, y, z are again given by equation (14), this time with

$$R_{n,l}^{n,l+\Delta l} = \tfrac{3}{2}\epsilon a$$

that is

$$R_{n,l}^{n,l-1} = R_{n,l-1}^{n,l} = \tfrac{3}{2}n(n^2 - l^2)^{1/2}.$$

This is identical to the quantum mechanical result (Bethe and Salpeter 1957).

5.1. *Oscillator strengths*

The matrix elements for x, y, z can be used in the determination of $f_{n,l}^{n',l'}$, the oscillator strengths between highly excited states for hydrogenic atoms. For the x component

$$(f_{n,l}^{n',l'}) = \frac{2\mu}{3h}\,\omega_{n'n}\left(\sum_m |\langle n, l, m|x|n'l'm'\rangle|^2\right)_{\substack{\text{averaged}\\ \text{over } m}}$$

where the frequency of the emitted radiation is given by equation (4), and the classical frequency ω by

$$\omega = \frac{4\pi Ry}{n_c^3}.$$

Summing the x, y, z components,

$$f_{n,l}^{n+s,l+\Delta l} = \frac{n_c}{3s}\left(J_s'(s\epsilon) + \Delta l\frac{(1-\epsilon^2)^{1/2}}{\epsilon}J_s(s\epsilon)\right)^2.$$

To check the validity of this equation, we can work out the averaged oscillator strength, $\overline{f_{nn'}}$, by summing over final l states and averaging over initial l states; this average can then be compared with independently obtained results. Summing and averaging,

$$\overline{f_{n'n}} \simeq \frac{4}{3}n_c\frac{J_s(s)J_s'(s)}{s^2}. \tag{16}$$

If we let $n_c = n$, this is just the result obtained by Mezger (1968). About the same time, Menzel (1968) worked out an asymptotic quantum mechanical expression,

$$\overline{f_{n'n}} = \frac{4}{3}(n + \tfrac{3}{2}s)\frac{J_s(s)J_s'(s)}{s^2}.$$

To obtain detailed balancing, we use a method outlined by Percival and Richards (1970a) and multiply the right hand side of equation (16) by $(1 + s/n)$, so that

$$\overline{f_{n'n}} = \frac{4}{3}\,\frac{(n+s)^2}{n+(s/2)}\,\frac{J_s(s)J_s'(s)}{s^2}$$

which is the result quoted by Percival and Richards (1970b), and which has the same asymptotic behaviour as the Menzel result.

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Table 3. Comparison of correspondence and quantum mechanical numerical values of various dipole moments squared for a Coulomb potential

Transition	Quantum mechanical	Correspondence value $n_c = n+s/2$	Percentage difference	Correspondence value $n_c = n(n+s)/(n+\frac{1}{2})$	Percentage difference
2s–3p	9·393	11·022	17·31	9·720	3·48
4s–5p	72·553	76·395	5·30	73·181	0·86(5)
6s–7p	274·19	281·22	2·56	275·25	0·38(5)
4p–5d	121·86	127·86	4·92	123·18	1·083
4d–5f	197·83	207·00	4·64	200·46	1·33
(13, 7)–(20, 8)	39·51	47·18	19·4	37·96	−3·93

5.2. *Numerical comparison with quantum theory*

For numerical calculations, equation (15) is best written as

$$R_{n,l}^{n+s,l+\Delta l} = \frac{n_c^2}{2s}\Delta l\left\{\left(1+\Delta l\frac{l_c}{n_c}\right)J_{s-1}(s\epsilon)+\left(1-\Delta l\frac{l_c}{n_c}\right)J_{s+1}(s\epsilon)\right\}.$$

Numerical values of $(R_{n,l}^{n+s,l+\Delta l})^2$ were computed using $n_c = n(n+s)/(n+\frac{1}{2}s)$ and compared with the quantum mechanical results of Green *et al* (1957) which were for all values of $n, n+s \leqslant 20$. The following points emerged:

(i) The difference between the two sets of values decreased as s/n decreased, l remaining constant. This is just Bohr's correspondence principle.

(ii) This difference also decreased with decreasing l/n, that is, as the eccentricity increased, for fixed s. The worst errors occurred for the highest transitions, that is, when $l = n-1$: $6g-10f$ is less than 1% out whereas $6h-10g$ is 13% out.

If we apply the strict condition that $s(l+1)/n < 1$, the greatest difference should be less than 3·5% for all values of n. If we only restrict $s/n < 1$ and $(l+1)/n < 1$, differences of 10% may be found amongst the higher s/n and $(l+1)/n$ values. In general, there is good agreement for high values of n.

5.3. *Quadrupole moments*

The complete expansion of the radiation field produced by a system of moving charges contains not only terms described as electric dipole radiation but also terms described as electric quadrupole, octupole, ... radiation. These too can be evaluated using the correspondence principle. The matrix elements for quadrupole radiation are of the form

$$\langle n, l, m|xy|n+s, l+\Delta l, m+\Delta m\rangle.$$

The selection rules for the quantum numbers l and m follow from equation (13) in a similar way as that for dipole radiation. For the xy elements, for example,

$$\Delta l = 0, \pm 2$$

$$\Delta m = \pm 2$$

for $\Delta l = 0, \Delta m = \pm 2$,

$$\langle n, l, m|xy|n+s, l, m\pm 2\rangle = \pm\left(1-\frac{m^2}{l^2}\right)\frac{J_s(s\epsilon)}{s^2}$$

for $\Delta l = \pm 2$, $\Delta m = \pm 2$

$$\begin{aligned}\langle n, l, m|xy|n+s, l+\Delta l, m+\Delta m\rangle = {} & \frac{1}{s\epsilon^2}\frac{2}{\Delta m}\left(1+\frac{\Delta m}{\Delta l}\frac{m}{l}\right)^2 \\ & \times\left(\frac{(1-(\epsilon/2)^2)}{\epsilon}J_s(s\epsilon)-s(1-\epsilon^2)J_s'(s\epsilon)\right) \\ & +(1-\epsilon^2)^{1/2}\frac{1}{s\epsilon^2}\frac{4}{\Delta m\Delta l}\left(1-\frac{m}{l}\right)^2 \\ & \times\left(\frac{s(1-\epsilon^2)}{\epsilon}J_s(s\epsilon)-J_s'(s\epsilon)\right).\end{aligned}$$

As mentioned above, higher order terms could also be evaluated by this method if they were required.

6. Conclusion

Classical mechanics has been used in conjunction with Bohr and Heisenberg's form of the correspondence principles to derive matrix elements of position and momentum in various potentials. In the case of off diagonal elements, the quantization condition is not well defined. If the quantizing number used in the classical equations is equated to the mean of the upper and lower quantum numbers of the transition, results are obtained which agree with available quantum mechanical results for $s/n \ll 1$, but which are inaccurate for $s/n \sim 1$. Better results are obtained by comparing analytic or numerical values of certain simple quantum expressions with their classical counterparts, and choosing n_c to give good agreement between the two. This particular choice of n_c varies from potential to potential: in the case of the harmonic and Morse potentials (which are closely related for low n), we chose $(n_c)^s = (n+s)!/n!$, whereas in the case of the Coulomb potentials good results were obtained using $n_c = n(n+s)/(n+\frac{1}{2}s)$.

The success of the above theory in obtaining valid results for these three potentials seems to indicate that this technique could be applied to any potential for which formal quantum mechanical solutions are difficult to obtain, for high values of n. The disagreement with the exact quantum mechanical solution should be at most of order s/n, using $n_c = n+\frac{1}{2}s$, and far less than this if a particular value for n_c is found for the potential. The results obtained should be much more accurate for high n values than those obtained by the usual extrapolation techniques.

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$$\frac{m}{l}\bigg)^2$$

$$)^2\big) J_s(s\epsilon)-s(1-\epsilon^2)J_s'(s\epsilon)\bigg)$$

$$\frac{1}{s\epsilon^2}\,\frac{4}{\Delta m\Delta l}\bigg(1-\frac{m}{l}\bigg)^2$$

$$J_s(s\epsilon)-J_s'(s\epsilon)\bigg).$$

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