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**BOOK REVIEWS**
A compact experiment to determine the efficacy of colliding macroscopic pellet fusion

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Abstract

Laboratory experiments are less than a factor of ten from the velocity required to initiate "pellet fusion" reactions. Means are proposed to close this gap.

Key words: Nuclear energy, fusion, inertial confinement.

Over the years and to the present day there has been considerable frustration with the progress made by orthodox plasma physics towards controlled thermonuclear experiments. Out of this frustration Harrison and others proposed a scheme which proports to circumvent many of the common difficulties. Briefly, the proposal is to collide solid (or gaseous) hydrogen isotope projectiles having velocities of nearly 10^4 m/s. To achieve ignition it is estimated that pellets of at least 10^{-5} kg are required.

The difficulty with such a scheme is obvious; to achieve such velocities requires conventional accelerators 10^4 meters long. Because of the theoretical uncertainty inherent in such an ignition technique the necessary experiments have not been forthcoming.

In the present paper we propose a means for producing such large and energetic projectiles and argue that it can be attempted with very modest resources. The proposed technique is to be considered a means for testing the efficacy of pellet ignition and studying the resulting physics and is not to be confused with a breakeven reactor design. However, since a thermonuclear detonation wave is initiated, in principle at least the D-T target can simply be increased in size (independently of the trigger system) to achieve an arbitrary energy yield. The basic components and geometry are shown in Fig. 1.

It is assumed that the target will have a cross-sectional radius greater than the mean free path of a thermonuclear alpha particle. At solid densities this implies cross-sectional areas of about 1 cm^2 in order for a one-dimensional ignition model to apply. In reality,
however, we expect that the target will be compressed both by impact and by a cylindrical pre-compression. (Furthermore, any residual plasma instabilities will reduce the alpha mean free path length.) Compression in this cylindrical geometry should be only slightly less effective than the spherical compressions usually assumed. In this regard it is worth comparing the minimum energy required for ignition of a spherical laser heated DT pellet, $E_L$, with that required for a tamped cylindrical pellet, $E_C$. The former scales as:

$$E_L \propto \frac{\beta^3}{\varepsilon^4 \eta^2}$$

where $\beta$ is the fusion energy gain desired, $\varepsilon$ is the efficiency of coupling in the laser energy to the plasma, and $\eta$ is the DT compression ratio. This is comparable to the scaling for cylindrical compression $E_C$:

$$E_C \propto \frac{\beta^3}{\varepsilon^4 \eta' \eta}$$

where $\eta'$ is the tamp compression ratio, we expect that $\eta' \sim \eta$.

---

**Fig. 1. a, b.** Thermonuclear experiment; A—High Explosive Fill, B—Driver, C—Accelerator Horn, D—Pellet, E—Target D-T Mix, F—Tamp, F'—Driver plates for radially compressing and tamping E, G—Flier Plate Masses.
Radial compression need be applied only at one end of the fuel stick so that ignition can occur at super-solid density and small cross-sectional area. The stick can then taper up to the steady state requirement of \(\frac{1}{2}\) to 1 cm\(^2\) (with tamp, perhaps, but no compression).

It seems reasonable to assume an ignition energy of 10 MJoules. Previously proposed fusion drivers (lasers, e\(^-\) beams, ion beams) have all involved beams of very low density and very high kinetic energy, as compared with the target thermal parameters. Under such conditions instabilities inevitably heat the plasma electrons predominantly. The confinement required (and, thence density) has then been largely determined by the time required for energy transfer from electrons to ions. This energy equilibration time actually much exceeds the energy confinement time (Lawson time) required for fusion breakeven.

In the present scheme we heat the ions directly and not the electrons. The reaction time appropriate to the thermonuclear detonation wave is:

\[
\tau = \frac{1}{n \langle \sigma v \rangle}
\]

where \(n\) is the fuel density and \(\langle \sigma v \rangle\) is the fusion reaction rate coefficient. Since the Coulomb ion-ion equilibration time is shorter than \(\tau\) (whereas the electron-ion equilibration time, \(\tau_{ei}\), is longer) the input energy will all go into an (initial) ion hot spot. Hence, we anticipate improved performance. We do not need such long confinement times or such high densities and compressions. Finally, the projectile has solid, or higher, density (i.e., the projectile is itself compressed), and hence a "beam" kinetic energy of the same order as the required final plasma temperature. Under these conditions a relatively instability-free system should be possible.

The ion temperature equation appropriate to such a thermonuclear reaction wave is just:

\[
\frac{\partial T_i}{\partial t} + u \frac{\partial T_i}{\partial x} = - \frac{2}{3} T_i \frac{\partial u}{\partial x} + \frac{2m_i}{3k_p} \mu_i \left( \frac{\partial u}{\partial x} \right)^2 + \frac{2m_i}{3k_p} \frac{\partial}{\partial x} \left( K_i \frac{\partial T_i}{\partial x} \right) + W_i + \frac{T_i - T_s}{\tau_{ei}}
\]

and the electron temperature equation is:

\[
\frac{\partial T_e}{\partial t} + u \frac{\partial T_e}{\partial x} = - \frac{2}{3} T_e \frac{\partial u}{\partial x} + \frac{2m_i}{3k_p} \mu_e \left( \frac{\partial u}{\partial x} \right)^2 + \frac{2m_i}{3k_p} \frac{\partial}{\partial x} \left( K_e \frac{\partial T_e}{\partial x} \right) + W_e + \frac{T_e - T_s}{\tau_{ei}} - A_p T_i \rho
\]

where \(u\) is the mass velocity, governed by the equation of motion:

\[
\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = - \rho^{-1} \frac{k}{m_i} \frac{\partial}{\partial x} \left[ \rho (T_i + T_e) \right] + \rho^{-1} \frac{\partial}{\partial x} \left( \left( \mu_i + \mu_e \right) \frac{\partial u}{\partial x} \right)
\]
\[ \rho \text{ is the mass density, } \mu_{e,i} \text{ are the viscosity coefficients, } K_{e,i} \text{ are the thermal conductivities and } k \text{ is Boltzmann's constant. } W_{e,i} \text{ represent the power input to ions and electrons due to fusion reactions.} \]

Once fusioning begins the fraction of the \( x \) particle energy absorbed by electrons should approach:

\[ f = \frac{32}{32 + T} \]

(where \( T \) is given in keV) and the electron temperature (along with the ion temperature) will rise to approach a steady state high temperature burn (with \( T_e \) and \( T_i \geq 10 \text{ keV} \)).

A conventional high explosive achieves a detonation wave velocity of approximately \( 10^4 \text{ m/s} \). An impedance matching driver plate (or series of layers of different materials having intermediate dispersion characteristics) might be used to couple the explosive output pulse into a tamped conical accelerator. (The energy coupling efficiency may hopefully exceed \( 20\% \)).

The accelerator itself operates on the principle of an acoustic concentrator or waveguide\(^{10} \). The approximate wave equation for any horn contour can be written as:

\[ \frac{1}{S} \frac{\partial^2 p}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 p}{\partial t^2} \]  

(1)

where \( p \) is the wave pressure, \( c \) the acoustic speed, and \( S \) is the horn area, \( \pi R^2 \), with \( R \), the horn radius, a function of \( z \), the distance along the symmetry axis.

A wave launched into the wide base of the cone propagates toward the apex gaining both in intensity and speed. The fluid velocity along the axis of the horn is given by:

\[ \frac{\partial v}{\partial t} = -\frac{1}{\rho} \frac{\partial p}{\partial z} \]

(2)

where \( \rho \) is the mass density, while the approximate wave pressure can be written\(^{10} \):

\[ p \approx \frac{A}{R} \exp (\omega t - kz) \]

(3)

where \( A \) is a constant, \( t \) is time, \( \omega \) is the wave frequency, and \( k \) is the wave number.

The total alternating force exerted over an area \( S \) by an acoustic pressure \( p \) is \( pS \), so with alternating particle velocity \( u \) the acoustic power flowing becomes\(^{11} \):

\[ W = \langle up \rangle S. \]

(4)

Power balance through the accelerator demands that the alternating particle velocity at the apex (pellet position) be given by:

\[ u_e = \beta u_o \frac{R_e}{R_o} \]

(5)
where $u_0$ and $R_0$ are the initial alternating particle velocity (imposed by the explosive) and accelerator base radius, respectively, while $R_r$ is the accelerator radius at the pellet location (apex). $\beta$ is introduced to account for imperfect efficiency. Commercial ultrasonic horns (transmitting either a pulse or cw) yield beta values of about 0.7 for a multiplication of 4 to 5 times the incident sound speed.

As an acoustic disturbance approaches the apex (focus) of a cone its magnitude will increase until it reaches the structural limit of the material and the tip is "spalled" (detached and propelled) off. In plane geometry, when a sonic pulse approaches a material-vacuum interface the outermost layers spall off, taking part in the overall conservation of momentum and energy across the boundary. If the surface layer (the "pellet" in our experiment) is very weakly bound at this point (and not too thick) it can attain approximately the alternating particle velocity $u_0$. In experiments in plane geometry the precursor spall actually achieves very nearly the incident pulse velocity.

The preformed interface of dissimilar pellet and accelerator materials, plus the effect of tamping reinforcement, should facilitate ejection of the properly sized pellet mass. A material like Beryllium is assumed for the accelerator in order to provide a sound speed in excess of $10^4$ m/s and a high compressional strength. If a cylindrical driver is employed then a catenary horn shape is preferred for coupling in $u_0 \gg 10^5$ m/s.

There is an ultimate limitation on the pellet speed attainable in this device. Once the wave energy density becomes too high the compressive strength of the horn will be exceeded and the acoustic wave will be transformed into an evaporation wave. This saturation will occur at about 3 to $5 \times 10^4$ m/s.

An additional factor of $\sim 10$ might be obtained in velocity amplification if Monroe focusing is employed. Matter streams of at least $9 \times 10^4$ m/s have been achieved in the laboratory in just this way. A concave accelerator apex and pellet are needed for Monroe focusing (Fig. 1 a) and a smaller pellet aspect ratio (diameter/length) results.

One can, in fact, use any number of further stages of shaped charge acceleration. An array composed of many-shaped charges with jets all impinging upon one another at an angle (i.e., the jets all converging along a conical surface towards a focus) will lead to a second focusing and additional nonlinear acceleration.

The required pellet kinetic energy of $\lesssim 10^7$ Joules corresponds to the energy available from one or two pounds of common high explosive. An overall energy conversion efficiency, $\beta^2$, can be computed from the coupling, horn, and Monroe cavity efficiencies of references 9, 12, 4, 16 and 17. A minimum explosive fill of about 500 pounds is suggested.

It is interesting to compute the fill required for yet another, simpler, accelerator model shown in Fig. 1 b. Here the impulse of the first, explosively driven, mass is delivered
through a chain of successively lighter and, thence, faster moving flier plates until the required pellet speed is reached. The speed of the pellet is just:

\[ V = [(K)^{N}(2m_i/m_f + n_f)]^{1/N} V_0, \quad MR = m_i/m_f, \]  

where \( MR \) is the ratio of masses of the preceding and succeeding flier plates, \( N \) is the number of collisional stages employed, \( V_0 \) is the initial velocity input, and \( K \) is the coefficient of restitution of the collisions.

If it is assumed that 7 or 8 stages are used and \( K \) is about 0.9 then it is easy to show that about 1000 to 2000 pounds of explosive fill is adequate. Again we can see the importance of the compressional strength in limiting the pellet speed that can ultimately be developed by a shock focusing accelerator. In practice succeeding "flier plates" of different density materials (perhaps in the gaseous state) might be involved.

In conclusion, a prototype accelerator should be constructed out of conventional materials to determine if projectiles can be imparted with the requisite velocity via the variety of linear and nonlinear acceleration mechanisms available.

This can be accomplished with a sub-scale system at very low cost. If the result is promising then a full scale model should be built and an ignition experiment attempted.

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Ambient boundary layer flow as a mechanism for diverting plasma impurities

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Abstract
A model of a toroidal plasma boundary layer is described which need not be restricted by the assumption of uniform plasma-limiter contact. Within this model a simple impurity divertor system is suggested.

Key words: Fusion, Tokamaks, plasma boundary layers.

1. Introduction
The adverse effects arising from plasma impurities (particularly high Z impurities) are well known. Impurities lead to an energy drain on the plasma via enhanced radiation, may influence the disruptive instability, and classically, impurities transport to the plasma center. With regard to fusion, impurities are critical. A simplified balance of the fusion alpha power generated against the bremsstrahlung radiation loss (neglecting other loss mechanisms) indicates, for example, that an impurity yielding \( Z_{\text{eff}} = 4.3 \) would prevent ignition in a \( D-T \) plasma for any temperature.

Various sources of contamination have been identified: weakly bound residual gases and solids collected on the first wall from previous discharges, atoms sputtered or evaporated from the limiter and first wall during a discharge, and material liberated due to gross damage or blistering.

One suggested means of reducing impurities is the magnetic divertor scheme\(^1\) which seeks to divert the outer field lines of the plasma from the main chamber of the system. Presumably any sputtered material would be contained in this layer, and hence the impurities are removed from the system. The divertor concept to be explored here, seeks to modify (enhance) the natural divertor effect of the parallel field plasma transport which may already be present in the boundary flow region\(^2\) and terminate this
flow at a suitably designed impurity dump. This is in contrast to the impurity flow
reversal concept of Ohkawa and Burrell which seeks to modify (reverse) the radial
transport of the impurities.

The plasma boundary-limiter shadow region contains a natural flow of plasma along
field lines toward the limiter. This region may serve as a shield to absorb wall evolved
impurities (for example, by sputtering or desorption) and to absorb high energy charge
exchange neutrals from the hot plasma core (thus reducing sputtering). Section 2 will
define some parameters relevant to the shadow region, in particular, the thickness of the
flow layer. To be absorbed in this region an impurity must be ionized, and to be effi-
ciently removed from the system (before transporting into the hot plasma) the impu-
ritiy must flow with the plasma to a suitably prepared dump (i.e., be collisionally pumped
by the plasma). Section 3 will examine the conditions that ionization and collisional
pumping impose on the flow region as well as requirements for the dump. Section 4
will consider external modification of the shadow region to enhance the flow by adding
density and/or energy. Also to be discussed are ways of modifying the limiter design
so as to take advantage of the natural divertor effect. Section 5 will consider imple-
mentation of this experiment on ISX.

2. Characterization of the limiter-shadow region

Ohkawa, Waltz and Burrell have considered a model for a Tokamak boundary in
uniform contact with a limiter. The limiter of a Tokamak defines a current channel
and loosely defines a plasma boundary. However, plasma continues to diffuse radially
past this point into the limiter-shadow region defined to be between the limiter radius
and wall radius. There is no current in the shadow but the plasma may flow electro-
statically along the field lines to the limiter at a speed expected to be some fraction, \( \alpha \),
of the local sound speed,

\[
c_s = \left( \frac{2T_e}{A m_p} \right)^{1/2}
\]

where \( T_e \) is the electron temperature, \( m_p \) is the ion mass, and \( A \) is the ion mass number.
\( T_e \) is usually greater than the ion temperature in this region. If not then \( T_e \) is replaced
by the ion temperature.

The value of \( \alpha \) will depend on collisional effects (the fast escaping electrons may be
attenuated by ionizing collisions, \( 1 - n_e \sigma v_{e} t_0 \) being the fraction of fast electrons still
able to reach the limiter), magnetic mirroring (e.g., as one enters a magnetic divertor)
and the boundary conditions at the limiter (i.e., electrically grounded, biased, or floated)
and in the plasma (which is only approximately modelled in one dimension). Experi-
ments in the FM-1 divertor have confirmed the existence of this flow and have deter-
mined \( \alpha \approx 1/3 \) (limiter was electrically connected to the wall). In other experiments
\( \alpha \) has been found to be as low as \( 1/12 \).

Further evidence for a plasma flow comes from TFR experiments which indicate
most particle recycling on the limiter (though most of the energy went to the wall via
radiation). In clean ATC discharges most energy deposition was on the limiter via thermal conduction (which also indicates particle flow). T-3 experiments found that gas recycling from the limiter was an order of magnitude greater than recycling from an equal area of wall; however, the limiter recycling represented only 10-20% of the total particle recycling from the wall and limiter combined. Thus, there is evidence of plasma flow in the shadow, but also evidence of a relatively thick flow layer.

An estimate of the width of the flow layer may be obtained by considering the parallel flow and perpendicular diffusion. In a time \( t_0 \), an ion will flow parallel to the magnetic field a distance \( l_\parallel \) and, in the same time, will transport radially a distance \( l_\perp \) depending on the radial transport coefficient \( D_\perp \). Hence,

\[
t_0 = \frac{l_\parallel}{ac_s} = \frac{P_\parallel}{D_\perp} \tag{1}
\]

\[
l_\perp = \left( \frac{l_\parallel D_\perp}{ac_s} \right)^{1/2}.
\]

The boundary layer is known to be highly turbulent and one expects very rapid cross-field transport in this region. Whereas the more quiescent Tokamak interior has a transport which is perhaps one hundred times less than Bohm the boundary layer will probably have \( D_\perp \) close to the Bohm value:

\[
D_\perp \approx D_B = T_e/16eB.
\]

This assumption is widely adopted and seems to be in reasonable agreement with experiments performed in the boundary layer\(^{15}\).

Then we have

\[
l_\perp = 2 \times 10^{-3} \left( \frac{l_\parallel}{aB} \right)^{1/2} (A T_e)^{1/11}
\]

(2)

where MKS units are used and \( T_e \) is in eV.

Although \( B \) is several Tesla in both current and projected experiments \( l_\parallel \) and \( T_e \) are less well determined. \( l_\parallel \) depends critically on the particular type of limiter (or divertor) and the uniformity of contact that the plasma has with the limiter. For an ideal poloidal limiter, with uniform plasma contact, a boundary field line intersects the limiter once each transit around the torus and hence a distance \( 2\pi R \). However, in the shadow flow region, the plasma will tend to flow the shortest distance to the limit which, by symmetry, indicates a null flow plane at the azimuth opposite the limiter. This reduces the distance to about \( l_\parallel = \pi R \) for the ideal poloidal limiter. In practice, however, the limiter may not be ideal. In the T-3 device\(^{10}\) which had a diaphragm-type limiter the plasma was found to ride only on the outside edge of the limiter. Therefore \( l_\parallel \) could be significantly longer. Obviously, \( l_\parallel \) will depend on the programming of field coils in any real machine.

An ideal toroidal limiter will have \( l_\parallel \sim \pi R q \) with \( q \) the safety factor. For a rod limiter (such as used in Doublet II) \( l_\parallel \) could become even longer. In the DITE
experiment a field line is diverted about once every ten transits and hence \( I_{\parallel} \sim 20\pi R \). The ideal poloidal limiter then represents a lower bound on \( I_{\parallel} \), and in general \( I_{\parallel} \sim C\pi R \) where \( C \approx 2 \) or 3 to 20.

If the limiter contact is reduced in comparison with \( q \) (i.e., plasma-limiter contact length \( < 2\pi rq \), with \( r \) the minor plasma radius) some field lines will (in an ideal, non-rotating plasma) never reach the limiter. Particles on these field lines will not experience any flow and will, theoretically, have to diffuse radially to the wall. Such an example is given in Fig. 1.

![Fig. 1. Inhomogeneous plasma boundary flow. \( q = 2 \), limiter contact length = \( \pi a/2 \). Azimuthal stripes: radially thicker, stagnant band; toroidal stripes: radially thin boundary flow band.](image)

Such a situation might arise due to poor plasma-limiter contact or if one reduces the limiter size (contact) intentionally in order to increase \( I_{\parallel} \). (We will see later why one would want to increase \( I_{\parallel} \) in some machines.) In reality, of course, shear and poloidal \( E \times B \) driven plasma rotation will act to reduce this effect, as will microinstabilities, localizing its maximum impact to toroidal and azimuthal positions nearest to the limiter-plasma contact points. Still, significant variations in boundary layer thickness may be produced and our estimates of \( I_{\parallel} \) must be taken as averages. This phenomenon should be explored experimentally and may have impact on such things as RF coupling to the plasma boundary.

The flow thickness (averaged), \( I_{\perp} \), is only weakly dependent on \( T_e \) and not at all on density; however, it will be useful to know the values of \( n \) and \( T_e \) in the shadow region. Unfortunately, there is little consistent experimental data on this region. Extrapolation of measurements on T-316, TFR\(^8\) and ATC\(^9\) indicate density \( \sim 10^{17} \) to \( 10^{18} \) m\(^{-3}\) and \( T_e \sim 1 \) to \( 100 \) eV. This indicates the need for specific shadow region measurements. Recent PLT\(^1\) values are \( T_e = 5 \) eV and \( n_e = 10^{18} \) m\(^{-3}\).

We can now estimate a value of \( I_{\parallel} \). Assuming \( I_{\perp} = \pi R \) with \( R = 4 \) m, \( B = 3T \), \( a = 1/3 \), \( A = 1 \), and \( T_e = 10 \) eV, then \( I_{\parallel} \sim 1.17 \) cm. If \( I_{\parallel} \) were, in fact, about 10
times longer (which can certainly be achieved on DITE), then $l_\perp \sim 4 \text{ cm}$. A smaller value of $\alpha$ can probably also be achieved.

Certainly the shadow gap, $l_p$, must be greater than $l_\perp$ to insure particle recycling on the limiter. The long path length ($l_p$) in T-3 (due to plasma contact only on a small section of limiter) may have increased $l_\perp$ enough to account for the wall recycling observed.

3. **Boundary layer conditions for impurity pumping**

Having characterized the boundary layer, we must now determine whether conditions there are suitable for naturally removing impurities. Three essential requirements are that the flow layer ionize the impurities, collisionally pump them to the limiter (or dumping mechanism), and that the impurity dump prevent re-entry of the impurities into the system. The ionization mean free path is given by

$$\lambda = \frac{V_0}{n \langle \sigma v \rangle_{\text{ionize}}}$$

where $n$ is the local plasma density, $V_0$ the impurity entry speed, and $\langle \sigma v \rangle_{\text{ionize}}$ the electron-impurity ionization rate coefficient. To insure ionization of the impurities in the flow layer, it is necessary that $l_\perp > \lambda$, i.e.,

$$nl_\perp > \frac{V_0}{\langle \sigma v \rangle_{\text{ionize}}}.$$  \hspace{1cm} (3)

Sputtered impurities have an energy of the order of a few eV$^{13}$ leading to $V_0 \sim$ few times $10^3 \text{ m/sec}$ for impurities. For hydrogen at $10 \text{ eV}$, $(V_0 \sim 10^4 \text{ m/sec})$, $\langle \sigma v \rangle \sim 2 \times 10^{-14} \text{ m}^2/\text{sec}^{14}$ and with $l_\perp \sim 0.05 \text{ m}$ then we need $n > 10^{18} \text{ m}^{-3}$. Alternatively, if $n = 10^{18} \text{ m}^{-3}$ then we need $l_\perp > 0.5 \text{ m}$. Higher mass number impurities relax this condition somewhat to $n > 10^{18} \text{ m}^{-3}$ but even then the condition is only marginally satisfied in the shadow region. Certainly increasing $l_\perp$ would relax the ionization condition but there may be other limiting criteria. $l_\perp$ must be increased too which may lead to MHD stability problems. Artificially increasing the density will be discussed in Section 4.

Once ionized, the impurities will flow along the field in the boundary, but it is desired that they reach the limiter before cross-field diffusion carries them into the hot plasma. Hence it is necessary that they flow in the same direction as the plasma so as to achieve the shortest path length to the limiter. This places restrictions on the frequency of collisions made by impurities with the plasma.

We tacitly assume a collisional boundary with regard to the parallel motion, and it is of interest to examine the collision lengths for electrons, ions and impurities. These are

$$\lambda_e \sim \lambda_i \sim 1.4 \times 10^{13} \frac{T_e}{nL}$$

$$\lambda_\perp \sim 10^{13} A^{113} T_i^{312} T_\perp^{1/2}/(Z^2 nL)$$
where \( L \) is the Coulomb Logarithm and \( Z \) is the impurity charge. With \( n = 10^{18} \text{m}^{-3} \), \( T = 10 \text{ eV} \) and \( L = 13 \) then \( \lambda_\ast \sim \lambda_\parallel \sim l \text{ meter} \) and \( \lambda_\parallel \sim 3/4 A^{1/2}/Z^2 \sim 1 \text{ meter} \) for \( Z = 1 \). Since \( l_\parallel \) is many meters collisionality seems a good assumption. Although the boundary temperature is low there may be significant second and third ionization of impurities, hence leading to \( \lambda_\parallel \sim \text{few cm} \).

The steady state force balance equation for the impurities colliding with ions is, in one dimension:

\[
0 = - \frac{K_n T_i}{\delta} - \nu \eta i m_i (s V_i - V_f)
\]

where \( \nu \eta i \) is the impurity-ion collision frequency, \( \delta \) is the pressure gradient scale length, \( s \) denotes the sign of the impurity velocity, \( V_f \), and \( K \) is the sign of the pressure gradient. If \( s > 0 \),

or

\[
\nu \eta i > \frac{K T_i e}{m_i V_f \delta}
\]

(where \( T_i \) is now in eV) then impurities will be "collisionally pumped" by the interaction with the plasma flow. This pumping action will drive the impurities under the limiter and into the neutral gas pumping region. It will also serve to prevent back-streaming from the vacuum pumps.

If

\[
T_i \sim T, \quad m_i \sim A m_e, \quad K = 1, \quad \delta = l_\parallel/2, \quad V_f = a c_
\]

then

\[
\nu \eta i > \frac{2 T_i e}{A m_e a c_\parallel l_\parallel}
\]

using

\[
\nu \eta i = 2 \times 10^{-13} n_i Z^2/(AT_i^{3/2})
\]

yields

\[
n_i l_\parallel > 10^{16} T_i^{6/2}/(T_s^{3/2} Z^2 a)
\]

for \( T = 10 \text{ eV}, \: Z = 1, \: a = 1/3, \) and \( l_\parallel = 10 \text{ meters} \):

\[
n_i > 3 \times 10^{17} \text{m}^{-3}.
\]

This condition is only slightly different from the condition on density imposed before, although the ionization condition is ultimately the more restrictive one.

Finally, the limiter itself must be modified. If the impurities merely strike and bounce off they may be injected into the plasma. Furthermore, they may sputter new impurities.
4. Modifications in the boundary region

As was seen in the previous section, the natural divertor appears to be marginal. Although the effect probably occurs to some extent in present Tokamaks, no attempt is made to take advantage of or augment the impurity pumping. The pumping ducts are not even located near the limiter in most machines. (Of course this is not true for magnetic divertor Tokamaks where the limiter is the neutralizer plate and certainly is differentially pumped.) For a Tokamak with magnetic divertor one may want to increase \( l_L \) by removing one or more of the neutralizer plates so as to increase \( l_r \).

The external addition of density to the limiter shadow would be particularly complex. Ideally, plasma (or gas and energy) would be introduced at the limiter radius and would not transport into the central plasma. The creation of a density peak in the shadow region would be particularly advantageous in holding the impurities in the flow region. In Princeton's TFTR it is hoped to create inverted profiles transiently in order to extract impurities.

If the application of RF power with gas injection still upsets the overall energy balance then simple enhancement of the existing boundary layer may only occur transiently. Of course, if sufficient gap space is available, \( l_r > \) several \( l_L \), there is another way to create a dense shielding plasma. Well beyond the existing flow layer the "vacuum" region can be filled by an externally injected plasma of thickness \( \sim 2l_L \) and arbitrary density. Again, with \( l_r \) large this external shell will exist nearly independent of the interior plasma and natural boundary. Both flows will then exhaust to a magnetic divertor or other suitable impurity dump (see the discussion of the "capped limiter" to follow).

The power required to ionize injected gas can be estimated from

\[
P = \frac{3}{2} nT (I_o) (2\pi a) (2\pi R) a \rho l_r.
\]

For \( n = 10^{18} \text{ m}^{-3} \), \( T = 10 \text{ eV} \), \( I_o = 20 \text{ cm} \), \( a = 1 \text{ m} \), \( R = 3 \text{ m} \), \( l_L \approx 100 \text{ m} \), \( a \ll 1/3 \) we get \( P \approx 5 \text{ kWatts} \).

Since about 90% of the boundary energy in Tokamaks is lost to recombination radiation, etc., we would probably need closer to 50 kilowatts in practice. Still, this could easily be provided, and the requirement does not depend strongly on machine size since we are creating only a thin, cold plasma shell. (A cold dense shell might produce only low energy charge exchange neutrals which would be unable to sputter the wall materials.)

As we have mentioned several times, the design of the limiter-impurity dump is very important since the contaminants must physically be removed from the system. A magnetic divertor may be desired but requires substantial energy and tampering with the confining field configuration.

Whereas the magnetic divertor removes the limiter to a remote, differentially pumped chamber it is also possible to bring differential pumping to the limiter and leave the field
configuration unchanged. One way to attack this problem is to employ a "capped" of "T" shaped limiter such as that shown in Fig. 2. The cap assumed is to be larger than the duct which pumps it and located close to the wall. The ionization length for impurities should be smaller than the cap radius to prevent neutral impurities from escaping the pumping region. (And, of course, vacuum pumping must be adequate to remove the neutral buildup.) This restriction gives a limiter diameter of perhaps one meter. Such a size is, in fact, smaller than the limiter area needed for adequate cooling in reactor-scale Tokamaks. Condition 5 assures that pumping will also take place under the limiter.

Gettering the neutralizer plate has been suggested but may be ineffective at high operating temperatures. Contouring the neutralizer plate to reflect the neutrals toward the duct may also be of some value.

Since the object of the capped limiter would be to locally remove the flow layer the usual plasma-limiter particle recycling would be reduced. This is observed in the DITE device, and necessitates the addition of new (clean) gas by external means. Of course gas will find it hard to enter through the shielding layer, hence refueling would be through a hole in the limiter. At first sight we may expect that the total vacuum pumping requirements have been increased. However, virtually all of the gas is returned (as plasma, flowing fast) to, and under the limiter. For this reason no impedance is seen by the pumps during a discharge. (Pump down in air will be inhibited of course.)

The edge of the limiter cap will necessarily intercept part of the flow layer. This thickness must be as cool and small as possible, relative to \( I_d \), to reduce sputtering and yet thick enough to withstand the thermal load. If cooling is effective between discharges, then thermal diffusion is the limiting parameter. Heat deposited on the plate can diffuse, in time \( t_p \), to a depth:

\[
d = (D_{th} t_p)^{1/2}
\]
where

\[ D_{th} = K/(\rho C_p) \]

with \( K \) the thermal conductivity of the material, \( \rho \) its density, and \( C_p \) the specific heat at constant pressure. For tungsten or molybdenum, \( D_{th} = 0.5 \text{ cm}^2/\text{sec} \) and hence for a discharge of less than a second duration a cap about 0.5 cm thick is probably adequate anyway.

The fraction of the flow intercepted by the edge is \( f \sim 2d/l_\perp \) or, with \( l_\perp \sim 3 \text{ cm}, f \sim 1/3 \). Perhaps half this would re-enter the plasma. Hopefully, if we can create an external shielding plasma impurities would ionize far out and all pass under the cap. One can then hope to make and cool the edge so that it will inject relatively little contamination.

\section{5. Implementation and testing on ISX}

A project to test these ideas seems ideally matched to the objectives outlined for the Impurity Study Experiment (ISX) of General Atomic Co. and Oak Ridge National Laboratory. A satisfactory experimental test of the divertor action, however, may be difficult on a relatively small, low density Tokamak. Assuming a limiter shadow characterized by \( n = 10^{10} \text{ m}^{-3} \) and \( T = 10 \text{ eV} \) and toroidal limiter and \( q = 4 \) then \( l_\perp = 11 \text{ m} \) and \( l_\parallel = 0.015 \text{ m} \). The impurity pumping condition is satisfied (eqn. 5) but the ionization condition is not. Two approaches to an experiment can be suggested: 1. We can inject a preionized impurity and study the subsequent divertor action. 2. Restrict the studies to the injection of slow, readily ionizable tracers.

A problem common to all small scale experiments is that the important plasma parameters, density, temperature, and size, are all scaled down from reactor values while the impurity reflux characteristics, velocity and ionization rate, remain almost unchanged. A measured puff of room temperature Argon or Xenon tracer might help to restore the scaling since the impurity influx velocity would be reduced. In this case, \( n l_\perp > 10^{16} \text{ m}^{-2} \). We might also seek to replace the ISX limiter to modify \( I_\perp \). To study the removal as well as pumping we would have to instal a capped limiter.

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On the distribution of the eigenvalues of a matrix differential operator

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Abstract

The paper deals with the nature of the spectrum associated with a type of second-order matrix differential operator with certain boundary conditions. It is found that under certain conditions satisfied by the coefficients of the differential system, the spectrum is discrete. Some results are then obtained giving distributions of the eigenvalues on the real axis. The method employed depends, among others, upon some of the ideas and techniques of E. C. Titchmarsh.

Key words: Differential operator, eigenvalue problem, Hilbert space, Dirichlet (Neumann) problem, Spectrum—discrete, continuous, point continuous, Green's matrix, meromorphic function, pseudomonotonic, variation of the eigenvalues, distribution of the eigenvalues, convex downwards.

1. Introduction

Let \( I: a < x < b \) be an interval on the real line: \( a = -\infty, b = \infty \) or both being allowed. Let \( C^0(I) = C(I) \) be the set of all real-valued continuous functions on \( I \) and \( C^k(I), k = 1, 2, \ldots, \) denote the set of those \( f \in C(I) \) for which \( f^{(k)} \in C(I) \).

Consider the differential operator

\[
M = \begin{pmatrix} -D^2 + p & q \\ q & -D^2 + r \end{pmatrix}, \quad D \equiv \frac{d}{dx},
\]

where \( p, q, r \in C^1(I) \); \( p, q, r \) are absolutely continuous over any compact sub-interval of \( I \) for \( x \in I \).

Let the basic Hilbert space be \( \mathcal{H} = L^2(a, b) \) and let \( \mathcal{D} \) represent the set of all \( f \equiv \begin{pmatrix} f_1 \\ f_2 \end{pmatrix} \in \mathcal{H} \) such that (i) \( f \in C^1(I) \); (ii) \( f' \) absolutely continuous on every compact sub-interval of \( I \); \( f' \in A.C \) and (iii) \( Mf \in \mathcal{H} \). We say that \( f \in \mathcal{D}_n \) if \( f \in \mathcal{H} \) satisfies the conditions (i) and (ii).
Let \( \mathcal{C} \) be the set of complex numbers and \( \lambda \in \mathcal{C} \); then
\[
M \phi = \lambda \phi,
\]
where \( \phi = \begin{pmatrix} u \\ v \end{pmatrix} \in \mathcal{D} \), with some prescribed boundary conditions, gives rise to an eigenvalue problem both in the finite as well as in the singular case considered by Chakravarty\(^1\), \(^2\).

Let \( a < \alpha < x < \beta < b \) and let the solution \( \phi = \{u, v\} \) of (1.2) satisfy at \( \alpha \) and \( \beta \) either
\[
\begin{align*}
\begin{cases}
\phi(\alpha) = \psi(\alpha) = 0, \\
\phi(\beta) = \psi(\beta) = 0.
\end{cases}
\end{align*}
\]

or
\[
\begin{align*}
\begin{cases}
\phi'(\alpha) = \psi'(\alpha) = 0, \\
\phi'(\beta) = \psi'(\beta) = 0.
\end{cases}
\end{align*}
\]

The eigenvalue problems (1.2)-(1.3) and (1.2)-(1.4) will henceforth be designated as the Dirichlet problem and the Neumann problem respectively over the interval \((a, \beta)\).

The purpose of the present paper is to obtain certain conditions on \( p, q, r \) so that the spectrum of the given differential system may be discrete over \( I \) and then to obtain certain estimates giving the distribution of the eigenvalues on \( I \).

The spectrum \( \sigma(\lambda) \) of the system (1.2)-(1.3) or (1.2)-(1.4) may be defined as the set of \( \lambda \) values contributing to the expansion formula. It has been established by Chakravarty\(^2\) (p. 403), that there exists at least a pair of linearly independent \( \mathcal{C}^2 \) solutions of the system (1.2)-(1.3) or (1.2)-(1.4) given by
\[
\begin{align*}
\begin{cases}
\psi_k(x, \lambda) = m_{k1}(\lambda) \phi_k + m_{k2}(\lambda) \psi_k + \theta_k, \\
m_{k1} = m_{jk}.
\end{cases}
\end{align*}
\]

where \( \phi_k \equiv \phi_k(0/x, \lambda), j = 1, 2 \) are the "boundary condition vectors" at \( x = 0 \) (for definition see Chakravarty\(^1\), p. 137) and \( \theta_k \equiv \theta_k(0/x, \lambda) \) are determined from \([\phi, \theta_j] = \delta_{ij}\), \([\theta_k, \theta_k] = 0, \delta_{ij}\), the Kronecker delta; \( \phi_j, \theta_j \) entire functions of \( \lambda \).

By closely following the analysis given in Chaudhuri and Everitt\(^3\) (pp. 95–119), it can be shown that the spectrum of the given system may be characterised by the properties of the matrix
\[
(m_{ij}) \equiv \begin{pmatrix}
m_{11} & m_{12} \\
m_{21} & m_{22}
\end{pmatrix}
\]
If $\lambda = \mu + iv$, then the spectrum is

(i) discrete, if and only if $m_{ij}(\lambda)$ are all meromorphic, i.e., the matrix $(m_{ij})$ is meromorphic;

(ii) continuous, if and only if \( \lim_{\mu \to 0} m_{ij}(\lambda) \) tends to a continuous, non-vanishing function, bounded for all $\mu \in (\mu_1, \mu_2)$; and

(iii) point-continuous, if and only if \( \lim_{\mu \to 0} m_{ij}(\lambda) \) tends to infinity, but \( \lim_{\mu \to 0} m_{ij}(\mu) \) is a continuous, non-vanishing function in $N'(\mu)$, the deleted neighbourhood of $\mu$. Finally, $\mu$ does not belong to the spectrum, if and only if \( \lim_{\mu \to 0} m_{ij}(\lambda) = 0 \).

In discussions involving the eigenvalue problems, Green’s matrix plays a very prominent role. The discussion of the Green’s matrix for the finite integral $(a, b)$ occurs in Chakravarty$^1$ (p. 148). For the singular case the Green’s matrix is defined by

$$ G(x, y, \lambda) = \begin{cases} \mathcal{G}(x, y, \lambda), & y < x \\ \mathcal{G}(y, x, \lambda), & y > x \end{cases} $$

where $\mathcal{G}(x, y, \lambda)$ is the matrix with elements $G_{ij}(x, y, \lambda) = (\psi^T_j(x, \lambda), A_i(y))$, the inner product of the vector $\psi^T_j(x, \lambda)$ (the transpose of $\psi_j(x, \lambda)$) and the $i$th column vector $A_i(y)$ of

$$ A(y) = \begin{pmatrix} x_1 & y_1 \\ x_2 & y_2 \end{pmatrix}, \{x_i, y_i\} = \phi_j(0|y, \lambda), $$

the boundary condition vector at $y = 0$. See Chakravarty$^2$ (p. 403). Also Sen Gupta$^6$ (p. 91).

It follows that since $\phi_j$, $\theta_j$ are entire functions of $\lambda$, $G(x, y, \lambda)$ is meromorphic, if and only if, the matrix $(1.6)$ is meromorphic. This property of the Green’s matrix will be utilised in our discussion.

The present analysis depends upon the ideas and techniques as developed by Titchmarsh$^7$ for problems of second-order partial differential equations and employed by Chaudhuri and Everitt$^1$ (pp. 185–209) in solving corresponding problems on a type of fourth-order differential equations.

2. Notations

In what follows we use the following notations.

The accent denotes differentiation with respect to $x$;

$P$ stands for the matrix $P = \begin{pmatrix} p & q \\ q & r \end{pmatrix}$;

$P_i$, being that in which the elements $p, q, r$ are replaced by $p_i, q_i, r_i$;
When \( a = 0 \): we write \( D_\alpha(f, g) = D_\alpha(f, g, P) \).

\[
\langle f, g \rangle_{a, b} = \int_a^b \langle f, g \rangle \, dt, \quad \|f\|_{a, b}^2 = \langle f, f \rangle_{a, b};
\]

\[
(F, G, P) = f'_a g'_a - f'_b g'_b = pf_1 g_1 - qf_2 g_2 + qf_1 g_1.
\]

where

\[
F = \begin{pmatrix} f_1 & f_2 \\ f'_1 & f'_2 \end{pmatrix} = \begin{pmatrix} f & f' \end{pmatrix}, \quad f' = \{f'_1, f'_2\},
\]

with a similar notation for \( G \).

\[
D_\varepsilon(f, g) = D_\varepsilon(f, g, P) = \int_a^b (F, G, P) \, dt, \quad \varepsilon = (a, b);
\]

When \( a = 0 \), we write \( D_\varepsilon(f, g) = D_\varepsilon(f, g, P) \) for \( D_\varepsilon(f, g, P) \).

When \( \varepsilon = (0, \infty) \), we define \( D(f, g) = D(f, g, P) = \lim_{b \to \infty} D_b(f, g, P) \).

If \( \varepsilon = (x', x) \), where \( x', x \) are points on the real axis, we write \( D_{x', x}(f, g) = D_{x', x}(f, g, P) \) for \( D_{x', x}(f, g, P) \).

\( E \) represents the unit matrix \( \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \).

We note that if \( \rho > 0 \) and \( \det P > 0 \), \( D_b(f) \) is always positive, \((F, F, P)\) being positive definite.

3. Properties of \( D_\varepsilon(f, g) \) for the finite interval \([0, b]\)

Let \( \lambda_n = \lambda_n(b) \) and \( \psi_n(x) = \psi_n(b, x) \) denote respectively the eigenvalue and the eigenvector for the Dirichlet (Neumann) problem enunciated in Art. 1. Then some of the properties of \( D_\varepsilon(f, g) \) are contained in the following lemmas.

Lemma 3.1: For the Dirichlet (Neumann) problem,

(i) \( D_b(\psi_m, \psi_n) = \delta_{mn} \delta_{mn} \), where \( \delta_{mn} \) is the Kronecker delta.

(ii) \( D_b(\alpha \psi_m + \beta \psi_n) = \begin{cases} \alpha^2 \lambda_m + \beta^2 \lambda_n, & m \neq n; \\ \alpha \lambda_m + \beta \lambda_n, & m = n; \end{cases} \) \( \alpha \), \( \beta \) constants.

Lemma 3.2: If \( \rho > c \) and \( \det (P - cE) > 0 \), \( c \), a positive real constant, then the eigenvalues for the Dirichlet (Neumann) problem are greater than or equal to \( c \).

We have

\[
D_b(\psi_n) = D_b(\psi_n, \psi_n, P) = D_b(\psi_n, \psi_n, P - cE) + c \int_0^b |\psi_n|^2 \, dt.
\]
The lemma follows, since the integral in the first expression on the right is positive definite and
\[ \int_0^b |\psi_n|^2 \, dt = 1. \]

**Lemma 3.3:** Let (i) \( f(x) = \{f_1, f_2\} \in \mathcal{D} \) (ii) \( f(0) = f(b) = 0 \). Then if
\[ c_m = \int_0^b (\psi_m, f) \, dt \]
be the Fourier co-efficient of \( f \) for the Dirichlet problem,
\[ D_b (f, \psi_m) = \lambda_m c_m. \tag{3.1} \]
If further (iii) \( p > 0 \) and \( \det P > 0 \), then
\[ D_b (f) \geq \sum_{n=0}^{\infty} \lambda_n c_n^2. \tag{3.2} \]
Results (3.1) and (3.2) also hold for the Neumann problem, but now the condition (ii) is not required.

Since, on integration by parts
\[ D_b (f, \psi_m) = \int_0^b (M\psi_m, f) \, dt + \left[ (\psi_m, f) \right]_0^b, \]
(3.1) follows on utilizing \( M\psi_m = \lambda_m \psi_m \).

To prove (3.2) we observe that by virtue of the condition (iii), \( D_b (F) \geq 0 \) for every vector \( F \in \mathcal{D} \). Hence
\[ 0 \leq D_b \left[ f - \sum_{n=0}^m c_n \psi_n \right] = D_b \left[ f - \sum_{n=0}^m c_n \psi_n, f - \sum_{n=0}^m c_n \psi_n, P \right] \]
\[ = D_b (f) - 2 \sum_{n=0}^m c_n D_b (f, \psi_n) + \sum_{n=0}^m c_n^2 D_b (\psi_n, \psi_n) + 2 \sum_{n \neq m} c_n c_m D_b (\psi_m, \psi_n) \]
\[ = D_b (f) - \sum_{n=0}^m \lambda_n c_n^2, \]
by lemma 3.1 (i) and the result (3.1).

(3.2) therefore follows.

**Lemma 3.4:** If (i) \( f \in \mathcal{D} \) (ii) \( f(0) = f(b) = 0 \) and if \( c_n \) is the Fourier co-efficient of \( f \), then
\[ D_b (f) = \sum_{n=0}^{\infty} \lambda_n c_n^2. \]
Let \( \tilde{c}_n \) be the Fourier co-efficient of \( \tilde{f} = Mf \).

Then by the Parseval theorem,

\[
\int_0^b (f, \tilde{f}) \, dt = \sum_{n=0}^{\infty} c_n \tilde{c}_n = \sum_{n=0}^{\infty} \lambda_n c_n^2.
\]

where \( \tilde{c}_n = \lambda_n c_n \), by Chakravarty \(^4\), Lemma 3 (p. 150).

By integration by parts,

\[
\int_0^b (f, \tilde{f}) \, dt = - (f, f|_0^b) + D_b (f, f, P) = D_b (f), \quad \text{by the condition (ii).}
\]

The result therefore follows.

If \( d_n \) be the Fourier co-efficient of \( g(x) \equiv \{g_1, g_2\} \), where \( g \) satisfies conditions similar to those of \( f \) in the above lemma, it follows similarly that

\[
D_b (f, g) = \sum_{n=0}^{\infty} \lambda_n c_n d_n.
\]

4. Extension to infinite interval (Spectrum assumed wholly discrete)

The Dirichlet and the Neumann problem for the infinite interval \([0, \infty)\) takes respectively the form

\[
\begin{align*}
M\phi &= i\phi \\
u(0) &= v(0) = 0
\end{align*}
\]

and

\[
\begin{align*}
M\phi &= i\phi \\
u'(0) &= v'(0) = 0
\end{align*}
\]

where

\[
I: \quad 0 \leq x < \infty.
\]

The eigenvector \( \psi_m \equiv \{\psi_{1m}, \psi_{2m}\} \) corresponding to the eigenvalue \( \lambda_m \) is integrable square at infinity.

It follows by integration by parts and using the relation

\[
M\psi_m = \lambda_m \psi_m
\]

where necessary, that

\[
\int_0^b (\psi_m, \psi_m^*) \, dt = [(\psi_m, \psi_m^*)]_0^b - \int_0^b |\psi_m'|^2 \, dt.
\]
Substituting for $\psi''$ from the differential system it follows, for both the Dirichlet and the Neumann problem, that

$$D_{x} (\psi_{n}, \psi_{n}, P) = (\psi_{n} (x), \psi'_{n} (x)) + \lambda_{n} \int_{0}^{x} |\psi_{n}|^{2} \, dx.$$ Integrating first with respect to $x$ over $(0, X)$ and then again integrating the result so obtained with respect to $X$ over $(0, R)$, we obtain, after some easy reductions, that

$$\int_{0}^{R} (\psi_{n}, \hat{\psi}_{n}, P) \left(1 - \frac{t}{R}\right)^{2} \, dt = \frac{1}{R^{2}} \int_{0}^{R} |\psi_{n}|^{2} \, dx + \lambda_{n} \int_{0}^{R} \left(1 - \frac{t}{R}\right)^{2} |\psi_{n}|^{2} \, dt,$$

where

$$\hat{\psi}_{n} = \begin{pmatrix} \psi_{n} \\ \psi'_{n} \end{pmatrix}.$$ By making $R$ tend to infinity, it follows that $D(\psi_{n}) = \lambda_{n}$. Similarly

$$D(\psi_{m}, \psi_{n}) = 0, \text{ if } m \neq n.$$ Let $\mathcal{B}_{1}$ be associated with the Hilbert space $\mathcal{H}_{1} = \mathcal{L}^{2} [0, \infty)$ in the same way as $\mathcal{B}$ is associated with $\mathcal{H} = \mathcal{L}^{2} (a, b)$.

Then

$$\int_{0}^{R} \left(1 - \frac{t}{R}\right) (f, M \psi_{n}) \, dt = \int_{0}^{R} \left(1 - \frac{t}{R}\right) (F, \hat{\psi}_{n}, P) \, dt - \frac{1}{R} \int_{0}^{R} (f, \psi_{n}^{*}) \, dt,$$

$f \in \mathcal{B}_{1}$, $[f(0) = 0$ for the Dirichlet problem].

It follows, on making $R$ tend to infinity, that

$$D(f, \psi_{n}) = \lambda_{n} \psi_{n},$$

where $\psi_{n}$ is the Fourier coefficient of $f$.

If, moreover, $p, q, r \in M$, if $p, q, r$ satisfy the conditions similar to those stated in Chakravarty (Theorem II, p. 404), viz.,

$$D(f) \geq \sum_{n=0}^{\infty} \lambda_{n} \psi_{n}.$$
(i) either \(|p + r| + |q| \leq Q(x)\) or \(|p|, |q|, |r| \leq Q(x)\)

where \(Q(x) \in C^1(I), \ I : 0 \leq x < \infty\) and \(Q(x) \geq \delta > 0;\)

(ii) \(\lim_{t \to \infty} |Q'(x)/Q''(x)| < \infty, \ c \leq 3/2: \)

(iii) \(F(x) = \int_{-\infty}^{x} \{Q(t)\}^{-1/2} \, dt\) tends to infinity as \(x\) tends to infinity.

Or,

if \(p, q, r\) satisfy (i) where \(Q(x)\) is continuous, monotone non-decreasing and

\(\int_{-\infty}^{\infty} \{Q(2t)\}^{-1/2} \, dt\) divergent.

If \(p, q, r \in \mathcal{M}\), we have \(\tilde{c}_n = \lambda_n c_n\), where \(\tilde{c}_n\) is the Fourier co-efficient of \(\tilde{f} = Mf\) (Chakravarty\(^4\), p. 413).

It follows by the Parseval theorem that

\[
\int_{0}^{\infty} (f, \tilde{f}) \, dx = \sum_{n=0}^{\infty} \lambda_n c_n^2.
\]

Now, as before,

\[
\int_{0}^{R} \left(1 - \frac{t}{R}\right)(f, \tilde{f}) \, dt = \int_{0}^{R} \left(1 - \frac{t}{R}\right)(F, F, P) \, dt - \frac{1}{R} \int_{0}^{R} (f, f') \, dt,
\]

\(f(0) = 0.\)

Therefore by making \(R\) tend to infinity, it follows that

\[
D(f) = \int_{0}^{\infty} (f, \tilde{f}) \, dt.
\]  \(\text{(4.3)}\)

Hence

\[
D(f) = \sum_{n=0}^{\infty} \lambda_n c_n^2, \text{ if } f \in \mathcal{D}_1, \ p, \ q, \ r \in \mathcal{M} \text{ and } f(0) = 0.
\]

If, in addition, \(g \in \mathcal{D}_2, \ g(0) = 0\), it follows in a similar manner that

\[
D(f, g) = \sum_{n=0}^{\infty} \lambda_n c_n d_n,
\]

where \(d_n\) is the Fourier co-efficient of \(g\).
5. **Extension to the case when the spectrum is possibly continuous**

We define the $H$-matrix by

\[
H(x, y; \mu) = \begin{cases} 
\lim_{\nu \to 0} \int G(x, y, \lambda) d\sigma, & \mu > 0; \\
-\lim_{\nu \to 0} \int G(x, y, \lambda) d\sigma, & \mu < 0; \\
0, & \mu = 0;
\end{cases}
\]

where $\lambda = \sigma + iv$ and $G(x, y, \lambda)$ is the Green's matrix in the singular case $[0, \infty]$. Then closely following the analysis as given in Titchmarsh’s (pp. 41--55), it follows that:

Each element of $H(x, y; \mu) \in L^2[0, \infty)$, for fixed $x$.

\[
F(x, \mu, f) = F(x, \mu) = \{ F_1(x, \mu), F_2(x, \mu) \} = \int_0^\infty H^T(y, x; \mu) f(y) dy \in L^2(0, \infty)
\]

for every $\mu$, if $f \in L^2[0, \infty)$.

If

\[
J_b(f, g, \mu) = \frac{1}{\pi} \langle F(y, \mu, f), g(y) \rangle_{0, \infty}, \quad J(f, g, \mu) = \frac{1}{\pi} \langle F(y, \mu, f), g(y) \rangle_{0, \infty}
\]

where

$g \in L^2[0, \infty)$ and $J(f, \mu) = J(f, f, \mu),$

then $J(f, \lambda)$ is non-decreasing:

\[
| J(f, g, \beta) - J(f, g, \alpha) |^2 \leq \| F \|_{0, \infty} \| g \|_{0, \infty}. \tag{5.1}
\]

Also, if $f \in D_\alpha$, $p, q, r \in \mathbb{M}$, $g \in D_\alpha$, then

\[
\langle \tilde{f}, g \rangle_{0, \infty} = \int_{-\infty}^\infty \lambda^r dJ(f, g, \lambda), \quad \lambda \text{ real.} \tag{5.2}
\]

[For discussion of $H$-matrix in detail, see Tiwari²].

Let $f \in D_\alpha$ and choose $b$ so that $0 < x < b < X$ and

\[
f_x = \begin{cases} 
\left( 1 - \frac{x}{X} \right) f, & x < X; \\
b, & \text{otherwise.}
\end{cases}
\]

Then

$f_x \in D_\alpha$

and

\[
\int_{\lambda_0}^\infty \lambda dJ_b(f_x, \lambda) \in D_b(f_x), \quad (\lambda, \text{ real}), \tag{5.3}
\]
where \( \lambda_0 \) (independent of \( b \)) is the lower bound of the spectrum and conditions of lemma 3.3 are satisfied. (Compare Titchmarsh\(^7\), pp. 95-96.)

Since
\[
| J(f, \lambda) - J(f_X, \lambda) | \leq | J(f, f - f_X, \lambda) | + | J(f_X, f - f_X, \lambda) |
\]
\[
\leq \| f \|_{0, \infty} \| f - f_X \|_{0, \infty}^{\frac{1}{\alpha}} + \| f_X \|_{0, \infty} \| f - f_X \|_{0, \infty}^{\frac{1}{\beta}},
\]
[by (5.1) with \( a = 0, \beta = \lambda \)], it follows that \( J(f_X, \lambda) \) tends to \( J(f, \lambda) \) uniformly with respect to \( \lambda \) as \( X \) tends to infinity.

By computing \( D_b(f_X) \) in a straightforward manner, making \( X \) tend to infinity first and then \( b \) tend to infinity, we obtain

\[ D_b(f_X) \text{ tends to } D(f), \text{ as } X, b \text{ tend to infinity.} \]

Therefore from (5.3), for any positive \( A > \lambda_0 \), we obtain

\[ \frac{1}{A} \int_{\lambda_0}^{A} \dot{d} J(f, \lambda) \leq D(f) \]

and since \( A \) is arbitrary,

\[ \int_{\lambda_0}^{\infty} \dot{d} J(f, \lambda) \leq D(f) \]

holds, where \( f \in \mathcal{D}_r \).

Let

\[ f(0) = 0, f \in \mathcal{D}_r, \ p, q, r \in \mathcal{M}, \]

then by (4.3) and (5.2) with \( g = f \), we have

\[ D(f) = \int_{-\infty}^{\infty} \dot{d} d J(f, \lambda). \]

6. Variation of the eigenvalues with \( p, q, r \).

**Definition:** The matrix \( P = \begin{pmatrix} p & q \\ q & r \end{pmatrix} \) is said to be *pseudo-monotonic* in \( I \), if \( p \geq 0 \), \( \det P \geq 0 \) in \( I \) and for \( j > k, j, k = 0, 1, 2, \ldots, p_j \geq p_k, \det (P_j - P_k) = \det (P_k - P_j) \geq 0 \), where \( p_j, q_j, r_j \) are the values of \( p, q, r \) at a point \( x_j \in I \) and \( P_j \) is the matrix \( P \) with \( p, q, r \) replaced by \( p_j, q_j, r_j \).

The matrix \( P \) may be called the *matrix* of the Dirichlet (Neumann) problem under consideration.
Let $\lambda_n$, $\mu_n$, $c_n$ and $N(\lambda, P_j)$ denote, respectively, the eigenvalue, the eigenvector, the Fourier co-efficient and the number of eigenvalues not exceeding $\lambda$ for the Dirichlet (Neumann) problem with matrix $P_j$ and $\mu_n$, $\chi_n$, $d_n$ and $N(\lambda, P_k)$ those for the same problem with matrix $P_k$.

We establish the following theorem.

**Theorem 6.1.** Let the matrix $P$ be Pseudo-monotonic. Then

$$\lambda_n < \mu_n \quad \text{and} \quad N(\lambda_n, P_k) > N(\lambda_n, P_j), \quad j > k, \quad j, k = 0, 1, 2, \ldots$$

**Case I. Interval finite:** Since $P$ is Pseudo-monotonic, therefore for $j > k, j, k = 0, 1, 2, \ldots$, $p_j \geq p_k > 0$, $\det P_j$, $\det P_k \geq 0$ and $\det (P_j - P_k) \geq 0$. Then by lemma 3.2 each eigenvalue $\lambda_n$ is positive.

Now

$$D_\delta (f, P_k) = \int_0^b (F, F, P_k) \, dt, \quad F = \begin{pmatrix} f_1 \\ f_2 \end{pmatrix} = \begin{pmatrix} f \\ f \end{pmatrix}$$

$$= \int_0^b (F, F, P_j) \, dt + \int_0^b (F, F, P_k - P_j) \, dt.$$ 

Since $(F, F, P_k - P_j)$ is positive definite, therefore $D_\delta (f, P_k) \geq D_\delta (f, P_j)$ (6.1) for any $f \in \mathcal{D}_0$.

Put

$$f = \chi_0 (x) = \{\chi_{10}, \chi_{20}\}.$$ 

Then

$$\| \chi_0 \|_0, b = 1 \quad \text{and we have}$$

$$\lambda_0 = \lambda_0 \| \chi_0 \|_0, b = \lambda_0 \sum_{n=0}^{\infty} c_n^2 \leq \sum_{n=0}^{\infty} \lambda_n c_n^2 \leq D_\delta (f, P_j) \leq D_\delta (f, P_k),$$

by (3.2) and (6.1).

Thus

$$\lambda_0 \leq \mu_0.$$ 

Put

$$f = \delta_0 \chi_0 (x) + \delta_1 \chi_1 (x),$$

where

$$\delta_0, \delta_1 \text{ are constants:}$$

$$\delta_0 = B (A^2 + B^2)^{-1/2}, \quad \delta_1 = -A (A^2 + B^2)^{-1/2}.$$
Thus by lemma 3.1,
\[ A = \langle X_0, \psi_6 \rangle_{0, b}, \quad B = \langle X_1, \psi_7 \rangle_{0, b}, \quad \delta_0^2 + \delta_1^2 = 1, \quad c_0 = A\delta_0 + B\delta_1 = 0. \]

Then
\[ \sum_{n=1}^{\infty} c_n^2 = \parallel \delta_0 X_0 + \delta_1 X_1 \parallel_{0, b} = \delta_0^2 + \delta_1^2 = 1. \]

Therefore
\[ \lambda_1 = \sum_{n=1}^{\infty} c_n^2 \leq \sum_{n=0}^{\infty} \lambda_n c_n^2 \leq D_b(f, P_j) \leq D_b(f, P_b), \quad f = \delta_0 X_0 + \delta_1 X_1. \]

Thus by lemma 3.1,
\[ \lambda_1 \leq \delta_0^2 \mu_0 + \delta_1^2 \mu_1 \leq (\delta_0^2 + \delta_1^2) \mu_1, \]
showing that
\[ \lambda_1 \leq \mu_1. \]

The general case \( \lambda_n \leq \mu_n \) follows in the same way as Titchmarsh (pp. 89–90). The second part of the problem is an immediate consequence of the first.

Case II. Interval infinite: When the interval \([0, b]\) is replaced by \([0, \infty)\), the theorem follows by exactly similar arguments as before by using the results of Art. 4.

Case III. Each spectrum possibly continuous but each has at its left hand end point a discrete eigenvalue \( \lambda_0 \) and \( \mu_0 \) respectively.

We have, if \( X_0 \) is the eigenvector corresponding to \( \mu_0 \),
\[ \lambda_0 = \lambda_0 \parallel X_0 \parallel_{0, \infty} = \lambda_0 \int_{\lambda_0}^{\infty} dJ(\lambda_0, P_4, \lambda) \leq \int_{\lambda_0}^{\infty} \lambda dJ(\lambda_0, P_4, \lambda) \leq D(\lambda_0, P_j) \leq D(\lambda_0, P_b) = \mu_0. \]

Hence as before the result can be extended to other discrete eigenvalues. The theorem is therefore completely established.

7. Variation of the eigenvalues with the interval: upper and lower bounds of the nth eigenvalue

In the following we assume \( p > 0 \) and \( \det P \geq 0 \).

Let \( N_X(\lambda) \) denote the number of eigenvalues not exceeding \( \lambda \) of the Dirichlet (Neumann) problem of the interval \([0, X]\). The following theorem holds.

Theorem 7.1. Let \( \lambda_n, \mu_n \) denote, respectively, the nth eigenvalue for the Dirichlet (Neumann) problem of the interval \([0, b]\) and \([0, B]\), where \( B > b \). Then
\[ \lambda_n \geq \mu_n \quad \text{and} \quad N_b(\lambda) \leq N_B(\lambda). \]
Let \( \psi_n \), \( c_n \) be the \( n \)th eigenvector and the Fourier co-efficient for the problem of the interval \([0, b]\) and \( \chi_n \), \( d_n \) those for the problem of the interval \([0, B]\).

Put

\[
\psi_n(x) = \begin{cases} \psi_n(x), & 0 \leq x < b; \\ 0, & b \leq x \leq B. \end{cases}
\]

Then by (3.2), it follows that \( D_B(f) \geq \sum_{n=0}^{\infty} \mu_n d_n^2 \) and therefore

\[
\lambda_n = D_B(\psi_n) = D_B(f) \geq \sum_{n=0}^{\infty} \mu_n d_n^2 > \mu_n \sum_{n=0}^{\infty} d_n^2 = \mu_n,
\]

showing that the result holds when \( n = 0 \). The case \( \lambda_n \geq \mu_n \) for all integral values of \( n \) follows as before. The second part of the theorem is an obvious consequence of the first.

To obtain the bounds of the \( n \)th eigenvalue of the problem under discussion, we subdivide the fundamental interval \([0, X]\) into a finite number of mutually disjoint sub-intervals \( I_s : [x_{s-1}, x_s] \), \( s = 1, 2, \ldots, m \), \( x_0 = 0 \), \( x_m = X \), and consider the Dirichlet and the Neumann problem for each sub-interval \( I_s \).

For our problem of the interval \([0, X]\), let \( \lambda_n, \psi_n, c_n \) denote, respectively, the eigenvalue, the eigenvector and the Fourier co-efficient, the corresponding entities for the Neumann problem of the interval \( I_s \), \( n = m_n, m_n \), \( d_n, d_n \), respectively. For the Dirichlet problem of the interval \( I_s \), let \( \lambda_n, \psi_n \) be the eigenvalue and \( \psi_n, \) the corresponding eigenvector.

Put

\[
\mu_n = \{ \mu_n, s = 1, 2, \ldots, m; n = 0, 1, 2, \ldots \}, \mu_0' \leq \mu_1' \leq \mu_2' \leq \ldots,
\]

\[
\lambda_n = \{ \lambda_n, s = 1, 2, \ldots, m; n = 0, 1, 2, \ldots \}, \lambda_0' \leq \lambda_1' \leq \lambda_2' \leq \ldots.
\]

Finally, suppose that

\( M_s(\lambda) \) denote the number of eigenvalues not exceeding \( \lambda \) of the Neumann problem of the interval \( I_s \);

\( M'_X(\lambda) \), the number of numbers \( \mu_n \) not exceeding \( \lambda \) in the fundamental interval \([0, X]\).

\( N_s(\lambda) \), the number of eigenvalues not exceeding \( \lambda \) of the Dirichlet problem of the interval \( I_s \);

and \( N'_X(\lambda) \), the number of numbers \( \lambda_n \) not exceeding \( \lambda \) in \([0, X]\).

The following theorem is now established.
Theorem 7.2. With notations explained as above,

(i) \( \mu_n' \leq \lambda_n \leq \lambda_n' \);

(ii) \( N'_X(\lambda) \equiv \sum_{i=1}^{m} N_X(\lambda) \leq M'_X(\lambda) \equiv \sum_{i=1}^{m} M_X(\lambda) \).

We prove (i). Then (ii) is an immediate consequence of (i).

Put

\[ f(x) = \psi_0(x), \quad 0 \leq x \leq X. \]

Then by (3.2),

\[ D_{s-1, t}(\psi_0) \geq \sum_{n=0}^{\infty} \mu_{n, t} \delta_{n, t}. \]

Hence

\[ \lambda_n = D_X(\psi_0) = \sum_{s=1}^{m} D_{s-1, t}(\psi_0) \geq \sum_{s=1}^{m} \sum_{n=0}^{m} \mu_{n, t} \delta_{n, t} = \mu'_0 \sum_{n=0}^{m} d_{n, t} (\text{by the Parseval theorem}) \]

Thus

\[ \lambda_n \geq \mu'_0 \| \psi_0 \|_{0, t} = \mu'_0. \]

Put

\[ f(x) = a_0 \psi_0(x) + a_1 \psi_1(x), \quad a_0^2 + a_1^2 = 1. \]

Then

\[ \bar{\lambda}_1 = \lambda_1 (a_0^2 + a_1^2) \geq \lambda_0 a_0^2 + \lambda_1 a_1^2 = D_X(a_0 \psi_0 + a_1 \psi_1) \]

\[ = \sum_{s=1}^{m} D_{s-1, t}(a_0 \psi_0 + a_1 \psi_1) \geq \sum_{s=1}^{m} \sum_{n=0}^{m} \mu_{n, t} \delta_{n, t}, \]

where we have chosen \( \mu_{n, t} = 0 \), by suitably choosing the constants \( a_0, a_1 \) as in theorem 6.1.

Thus

\[ \bar{\lambda}_1 \geq \mu'_0 \| a_0 \psi_0 + a_1 \psi_1 \|_{0, t} = \mu'_0. \]

The general case \( \lambda_n \geq \mu'_n \) now follows as in theorem 6.1. The first part of the inequality is thus proved.

To prove the second part of the inequality (i), put

\[ f(x) = \psi_{0, t}, \quad \text{in } x_{k-1} < x < x_k; \]

\[ = 0, \quad \text{otherwise}; \]
and
\[ \lambda'_k = \lambda_{0,k} \text{ for fixed } k, k = 1, 2, \ldots, n. \]

Then
\[ \lambda'_0 = \lambda_{0,k} \sum_{k=1}^{N_k} (\psi_{0,k}) = D_X(f) \geq \sum_{n=0}^{\infty} \lambda_n c_n^2, \text{ by (3.2)} \]
\[ = \lambda_0 \| \psi_{0,k} \|_{0,x} = \lambda_0. \]

Put
\[ \lambda'_j = \lambda_{1,k}, j = 0, 1; k, \text{ fixed.} \]

If \( j = 1, \) we put
\[ f(x) = a_0 \psi_{0,k}(x) + a_1 \psi_{1,k}(x), \quad x_{k-1} < x < x_k \]
\[ = 0, \quad \text{otherwise} \]
\[ a_0^2 + a_1^2 = 1. \]

If \( j = 0, \) we take
\[ f(x) = b \psi_{0,k}, \quad x_{k-1} < x < x_k \]
\[ = b, \quad \text{otherwise} \]
\[ a_0^2 + b^2 = 1. \]

The analysis now proceeds as in theorem 6.1 and Chaudhuri and Everitt¹, (pp. 196-197), so as to obtain \( \lambda'_2 \geq \lambda_2 \) and for any positive integral \( n, \lambda'_n \geq \lambda_n. \) The second part of the inequality (i) is thus proved. Hence the theorem follows.

Let \((p_1, q_1, r_1), (p_2, q_2, r_2)\) be the values of \((p, q, r)\) at the points \( x = x_{i-1} \) and \( x = x_i, \) respectively, of the sub-interval \( I_i: [x_{i-1}, x_i]. \) Also, let \( P \) reduce to \( P_1, \) at \( x = x_{i-1} \) and to \( P_2 \) at \( x = x_i. \)

Let
\[ N_{1X}(\lambda) = N_{2X}(\lambda, p_0, P_2), \quad i = 1, 2; \]
\[ N_2(\lambda, s), \] the number of eigenvalues not exceeding \( \lambda \) of the Dirichlet problem of the interval \( I_i \) with matrix \( P_2; \)

and
\[ M_1(\lambda, s), \] the number of eigenvalues not exceeding \( \lambda \) of the Neumann problem of the interval \( I_i \) with matrix \( P_1. \)

We establish the following theorem.

**Theorem 7.3.** Let the matrix \( P \) be Pseudo-monotonic. Then with notations explained above
\[ \sum_{i=1}^{n} N_2(\lambda, s) \leq N_{1X}(\lambda) \leq \sum_{s=1}^{n} M_1(\lambda, s), \] for fixed \( n, \)
where \( X > Y, \) \( Y \) being a root of \( \det (P - \lambda E) = 0, \) for fixed \( \lambda. \)
Now, for two positive quadratic forms \( \sum c_{ik} x_i x_k, \) \( \sum d_{ik} x_i x_k, \) the inequality
\[
\big| c_{ik} \big|^{1/n} \leq \big| d_{ik} \big|^{1/n} \leq \big| c_{ik} + d_{ik} \big|^{1/n}
\]
holds, where \( \big| c_{ik} \big| \) are determinants of the co-efficients, \( n \) positive integer (Hardy Littlewood, Polya, p. 35, Formula 2.13.8).

Since
\[
P_2 - \lambda E = (P - \lambda E) + (P_1 - P_2)
\]
it follows from (7.1), since \( P \) is pseudo-monotonic, that
\[
det (P_2 - \lambda E), \ det (P_1 - \lambda E) > 0, \ if \ det (P - \lambda E) > 0.
\]
By theorem 6.1 it follows that
\[
N_2(\lambda) < N_X(\lambda) < N_1(\lambda).
\]
Also by theorem 7.2,
\[
\sum_{i=1}^{n} N_2(\lambda, s) \leq N_X(\lambda), \ \sum_{i=1}^{n} M_1(\lambda, s) \geq N_1(\lambda).
\]
From (7.3) and (7.4),
\[
\sum_{i=1}^{n} N_2(\lambda, s) \leq N_X(\lambda) \leq \sum_{i=1}^{n} M_1(\lambda, s).
\]
Let us choose \( \lambda \) so that \( p_1 > \lambda, \ det (P_1 - \lambda E) > 0, \) which, by (7.2) holds if \( p > \lambda \), \( det (P - \lambda E) > 0. \) Then by lemma 3.2, there are no eigenvalues less than \( \lambda \) with this choice of \( \lambda \) and therefore
\[
M_1(\lambda, s) = 0 \ and \ N_2(\lambda, s) = 0,
\]
whenever \( p > \lambda, \ det (P - \lambda E) > 0. \)

Let \( Y \) be determined as the root of \( det \ (P(Y) - \lambda E) = 0, \) where \( \lambda \) is a given real number. Since \( P \) is increasing, it is possible to choose \( x > Y \) so that \( p > \lambda \) holds. For all such \( x, \) since \( P \) is pseudo-monotonic, \( det (P(x) - P(Y)) > 0 \) and therefore \( P(x) - \lambda E = P(Y) - \lambda E + P(x) - P(Y), \) by (7.1) leads to
\[
det (P(x) - \lambda E) > 0.
\]
Let the interval \([0, X], X > Y, \) be chosen large enough so that for a point of subdivision \( x_m, \) say, for some \( n < m, x_m = Y \) holds. Then (7.6) holds for all \( s > n, \) and the theorem follows.
Since \( \lambda \) is given, \( Y \) is fixed and therefore \( n \) is fixed. It follows therefore from the above theorem that \( N_X(\lambda) \) is bounded independently of \( X \). Since by theorem 7.1, \( N_X(\lambda) \) increases with \( X \), therefore

\[
\lim_{X \to \infty} N_X(\lambda) = N(\lambda),
\]

where, as will be evident from discussion in Art. 8 next, \( N(\lambda) (\ll \infty) \), represents the number of eigenvalues not less than \( \lambda \) in the singular case.

8. A criterion for the discreteness of the spectrum

The following theorem provides a criterion for the discreteness of the spectrum of the boundary value problem under consideration.

**Theorem 8.1.** Let (i) \( p, q, r \) satisfy the conditions laid down in Art. 1, the matrix \( P \) being pseudo-monotonic. If (ii) \( p > a > 0 \), then the determinant \( \det (P - aE) \geq 0 \), then the spectrum is discrete over the range \((a, \infty)\).

Let \( \lambda_{nX}, \lambda_{nX'} \) denote the eigenvalues for the problems of the intervals \([0, X]\) and \([0, X']\) respectively. Then by theorem 7.1, for \( X \leq X' \), \( \lambda_{nX} \geq \lambda_{nX'} \), showing that \( \{\lambda_{nX}\} \) is steadily decreasing. Now by condition (ii) \( \lambda_{nX} \geq a \). Thus \( \{\lambda_{nX}\} \) tends to a limit \( \lambda_n \), say, as \( X \) tends to infinity. Hence the sequence \( \{\lambda_{jX}\}, j = 0, 1, \ldots, h \), of eigenvalues lying in \((a, \beta)\) tend to \( \{\lambda_j\}, j = 0, \ldots, h \), (not necessarily all different), as \( X \) tends to infinity.

Let \( \lambda_n < \lambda_n \). Since the Green’s matrix \( G(X, x, \xi, \lambda) \), \( \lambda = \mu + iv \), is regular except for simple poles at \( \lambda_{nX} \), therefore \( G(X, x, \xi, \lambda) \) is regular if \( \lambda_n + \delta \leq \mu < \lambda_n - \delta, \) where \( \delta = 1/4 (\lambda_n - \lambda) \) and \( X \) large enough. (Compare Titchmarsh', p. 149).

We introduce the matrix \( H(x, y) \) which is not a Green’s matrix but has the same discontinuity property as the Green’s matrix for the ‘\( X \)-Case’, substitute

\[
G_{ij}(X, x, \xi, \lambda) = G_{ij}(X, x, \xi, \lambda) - H_{ij}(x, \xi),
\]

\( G_{ij}, H_{ij} \) elements of \( G \) and \( H \) respectively,

and argue as in Chakravarty’s (pp. 401-402), so as to obtain

\[
|G_{ij}(X, x, \xi, \lambda)| \leq (v^2 + 1)^{1/2} K(x, \xi, \delta, |\lambda|),
\]

where \( K \) is a constant depending on the arguments shown.

Thus

\[
|G_{ij}(X, x, \xi, \lambda)| \leq M |v|^{-1}
\]

for given

\( x, \xi, x \neq \xi, \lambda_n + \delta \leq \mu \leq \lambda_n - \delta, \quad -\delta \leq v \leq \delta. \)
Then by arguments similar to those in Titchmarsh (p. 149), it follows that the Green's matrix $G(x, \xi, \lambda)$ in the singular case $[0, \infty)$ is regular except at the points $\lambda_n$ and that $\lambda_n$ is at most a simple pole of $G(x, \xi, \lambda)$. Hence the spectrum is discrete over $(\alpha, \beta)$.

Again, from above it follows that $G(x, \xi, \lambda)$ is a meromorphic function of $\lambda$ and therefore the matrix $(m_\alpha(\lambda))$ is also meromorphic (vide, Art. 1). Hence also the spectrum is discrete over $(\alpha, \beta)$.

Finally, defining $f(x)$ by

$$f(x) = \psi_\alpha(x), \quad 0 < x < X,$$

$$= 0, \quad \text{otherwise,}$$

and following Titchmarsh (p. 150), by using (5.3), it can be shown that $\lambda_0$ is actually an eigenvalue. In the general case, $\lambda_n$ is an eigenvalue for the boundary value problem in the singular case $[0, \infty)$.

$$N(\lambda) = \lim_{x \to \infty} N_x(\lambda)$$

is thus the number of eigenvalues not less than $\lambda$ in the singular case $[0, \infty)$.

In particular, if $\rho, q, r$ satisfy the conditions of Art. 1 and the matrix $P$ is Pseudomonotonic, the spectrum is discrete over $(0, \beta)$.

9. Distribution of the eigenvalues

Put

$$\varphi = \alpha + \gamma + \{(\gamma - \alpha)^2 + 4\beta^2\}^{1/2}$$

and

$$\eta = \alpha - \gamma - \{(\gamma - \alpha)^2 + 4\beta^2\}^{1/2}$$

where $\alpha, \beta, \gamma$ are real numbers and $\lambda$ is a real number, $\lambda \geq 1/2 \max (\varphi, \eta)$.

We seek for solutions of the equation

$$\begin{cases}
  u''(x) - \beta v'(x) + (\lambda - \alpha) u(x) = 0 \\
  v''(x) - \beta u'(x) + (\lambda - \gamma) v(x) = 0
\end{cases} \quad (9.1)$$

where $\{u, v\}$ satisfy the Dirichlet-form of boundary conditions, viz.,

$$u(0) = 0 = v(0); \quad u(X) = 0 = v(X). \quad (9.2)$$

Solving (9.1) for $u, v$ and making $\{u, v\}$ satisfy the boundary conditions (9.2), we derive after some easy steps

$$\sin \xi X \sin \xi X = 0 \quad (9.3)$$
Therefore, if $N_X(\lambda, a, \beta, \gamma)$ be the number of eigenvalues not exceeding $\lambda$ in the interval $(0, X)$, we have

$$N_X(\lambda, a, \beta, \gamma) \geq \frac{X}{\pi} \left[ \left( \lambda - \frac{1}{2} \triangle \right)^{1/2} + \left( \lambda - \frac{1}{2} \eta \right)^{1/2} \right] + 2.$$  \hspace{1cm} (9.4)

Similarly, if $M_X(\lambda, a, \beta, \gamma)$ be the number of eigenvalues not exceeding $\lambda$ in the interval $(0, X)$ of (9.1) with boundary conditions in Neumann’s form, viz.,

$$u'(0) = 0 = u'(0); \quad u'(X) = 0 = u'(X)$$  \hspace{1cm} (9.5)

we have

$$M_X(\lambda, a, \beta, \gamma) \leq \frac{X}{\pi} \left[ \left( \lambda - \frac{1}{2} \triangle \right)^{1/2} + \left( \lambda - \frac{1}{2} \eta \right)^{1/2} \right] + 2.$$  \hspace{1cm} (9.6)

**Lemma 9.1.** Let (i) $p > r$, (ii) $p, q$ monotone increasing and (iii) $(p - r) r' - 2qq' \geq 0$.

Then

$$\triangle(x) = p + r + \{(p - r)^2 + 4q^2\}^{1/2}$$

and

$$\eta(x) = p + r - \{(p - r)^2 + 4q^2\}^{1/2}$$

are both monotone increasing.

Since

$$(p - r)^2 + 4q^2 \geq 4q^2,$$

it follows that $\{(p - r)^2 + 4q^2\}^{1/2}$ is monotone increasing. Therefore

$$(p - r) (p' - r') + 4qq' \geq 0$$

and

$$\frac{d\eta(x)}{dx} \geq 0;$$

so that $\eta(x)$ is monotone increasing. Again, since $\{(p - r)^2 + 4q^2\}^{1/2} \geq p - r$, it follows that $\triangle(x) \geq 2p$. Therefore $\triangle(x)$ is monotone increasing.
The lemma remains true if \( p - r \) is assumed monotone increasing instead of \( q \).

We establish the following theorems on the distribution of the eigenvalues of the boundary value problem under consideration.

**Theorem 9.1.** Let the matrix \( P \) be Pseudo-monotonic and \( p, q, r \) satisfy the conditions of lemma 9.1. Then \( N(\lambda) \), the number of eigenvalues not exceeding \( \lambda \) in the singular case of the problem under consideration, is given by

\[
N(\lambda) = \frac{1}{\pi} \int_0^\infty \left[ \left\{ \lambda - \frac{1}{2} \Delta(x) \right\}^{1/2} + \left\{ \lambda - \frac{1}{2} \eta(x) \right\}^{1/2} \right] dx + O(X^{1/2} \lambda^{1/4}), \quad \lambda \to \infty,
\]

where \( X \) is determined by \( \det (P(X) - \lambda E) = 0 \).

It follows from theorem 7.3, with notations explained there, that

\[
\sum_{s=1}^n N_1(\lambda, s) \leq N(\lambda) \leq \sum_{s=1}^n M_1(\lambda, s),
\]

where \( X' \geq X \) and \( X \) is given by \( \det (P(X) - \lambda E) = 0 \).

Making \( X' \) tend to infinity through certain sequence, we then obtain

\[
\sum_{s=1}^n N_2(\lambda, s) \leq N(\lambda) \leq \sum_{s=1}^n M_2(\lambda, s). \tag{9.7}
\]

For the interval \( I_s : (x_{s-1}, x_s) \), let \( \Delta_s(x), \eta_s(x), j = 1, 2 \), stand for \( \Delta(x) \) and \( \eta(x) \) respectively when the matrix \( P \) is replaced by \( P_1 \) at \( x = x_{s-1} \) and by \( P_2 \) at \( x = x_s \).

Then it follows from (9.4), (9.6) and (9.7) that

\[
\sum_{s=1}^n \left[ \left\{ \lambda - \frac{1}{2} \Delta_{s+1}(x) \right\}^{1/2} + \left\{ \lambda - \frac{1}{2} \eta_{s+1}(x) \right\}^{1/2} \right] \frac{\delta_s}{\pi} - 2n \leq N(\lambda)
\]

\[
\leq \sum_{s=1}^n \left[ \left\{ \lambda - \frac{1}{2} \Delta_{s+1}(x) \right\}^{1/2} + \left\{ \lambda - \frac{1}{2} \eta_{s+1}(x) \right\}^{1/2} \right] \frac{\delta_s}{\pi} - 2n \tag{9.7}
\]

where \( \delta_s \) is the length of the interval \( I_s \).

Noting that

\[
F(x) = \{\lambda - \frac{1}{2} \Delta(x)\}^{1/2} + \{\lambda - \frac{1}{2} \eta(x)\}^{1/2}
\]
by lemma 9.1, steadily decreases from \( F_0 = F(0) \) to \( F_X = F(X) \) as \( x \) increases from 0 to \( X \), it is possible to choose the points of sub-division \( x \) of the interval \((0, X)\) in such a manner that the oscillation of \( F(x) \) in each \( I_i \) is equal to

\[
\frac{F_0 - F_X}{n}.
\]

(Compare Chaudhuri and Evrriott, p. 206 and De Wet and Mandl, pp. 572-580.)

Thus in \( I_i \),

\[
\left[ \left\{ \lambda - \frac{1}{2} \Delta \Delta (x) \right\} \right]^{1/2} + \left\{ \lambda - \frac{1}{2} \eta \right\}^{1/2} - \left[ \left\{ \lambda - \frac{1}{2} \Delta \Delta (x) \right\} \right]^{1/2} + \left\{ \lambda - \frac{1}{2} \eta \right\}^{1/2} = \frac{F_0 - F_X}{n}.
\]

This leads to

\[
\sum_{i=1}^{n} \left[ \left\{ \lambda - \frac{1}{2} \Delta \Delta (x) \right\} \right]^{1/2} + \left\{ \lambda - \frac{1}{2} \eta \right\}^{1/2} \delta_i \leq I(\lambda) + \frac{X(F_0 - F_X)}{n \pi}
\]

where

\[
I(\lambda) = \frac{1}{\pi} \int_0^x \left[ \left\{ \lambda - \frac{1}{2} \Delta \Delta (x) \right\} \right]^{1/2} + \left\{ \lambda - \frac{1}{2} \eta \right\}^{1/2} \right] \right] dx.
\]

Similarly,

\[
\sum_{i=1}^{n} \left[ \left\{ \lambda - \frac{1}{2} \Delta \Delta (x) \right\} \right]^{1/2} + \left\{ \lambda - \frac{1}{2} \eta \right\}^{1/2} \delta_i \geq I(\lambda) - \frac{X(F_0 - F_X)}{n \pi}
\]

Hence from (9.7'), (9.8) and (9.9),

\[
| N(\lambda) - I(\lambda) | \leq \frac{X(F_0 - F_X)}{n \pi} + 2n.
\]

Choose \( n \) so that the right hand side of (9.10) is minimum. This gives

\[
n^* = \frac{X(F_0 - F_X)}{2 \pi}.
\]

Therefore from (9.10),

\[
N(\lambda) = I(\lambda) + O \left( X^{1/2} (F_0 - F_X)^{1/2} \right).
\]
The theorem follows from (9.11), since \(|F_0 - F_\epsilon| \leq |F(0)| \leq K \lambda^1\), \(K\), const.

The following theorem is next established.

**Theorem 9.2.** If the conditions of theorem 9.1 are satisfied and if (i) either \(p\) or (ii) \(r\) or (iii) \(p - r\) or (iv) \(p + q < r\), \((q(0) \geq 0)\), be convex downwards, then

\[
N(\lambda) \sim \frac{1}{\pi} \int_0^X \left[ \left( \lambda - \frac{1}{2} \lambda(x) \right)^{1/2} + \left( \lambda - \frac{1}{2} \eta(x) \right)^{1/2} \right] \, dx, \text{ as } \lambda \text{ tends to infinity.}
\]

We give details of the proof when \((p + r)\) is convex downwards with outlines in other cases.

Since \(p(x) + r(x)\) is convex downwards, we have

\[
p(u) + r(u) \leq p(0) + r(0) + \frac{p(X) + r(X) - p(0) - r(0)}{X} u,
\]

\(0 < u < X, \ p'_x(0), > 0, \ r(0) \geq 0, \)

since \(p > 0\). det \(P \geq 0\) for \(x\) in \(I\).

This leads to

\[
\lambda - \frac{1}{2} \eta(u) \geq \lambda - \frac{1}{2} \{p(u) + r(u)\} \geq \lambda - \frac{1}{2} \{p(X) + r(X)\} \frac{u}{X},
\]

so that

\[
I(\lambda) = \frac{1}{\pi} \int_0^X \left[ \left( \lambda - \frac{1}{2} \lambda(x) \right)^{1/2} + \left( \lambda - \frac{1}{2} \eta(x) \right)^{1/2} \right] \, dx
\]

\[
\geq \frac{1}{\pi} \int_0^X \left[ \lambda - \frac{1}{2} \{p(X) + r(X)\} \frac{u}{X} \right] \, dx
\]

\[
\geq \frac{1}{\pi} X \lambda^{1/2} \left( 1 - \frac{Q(X)}{2X} \right)^{1/2}, \text{ where } Q(X) = p(X) + r(X).
\] (9.12)

Therefore from theorem 9.1 and the inequality (9.12), it follows that

\[
|N(\lambda) - I(\lambda)| \leq K \pi X^{-1/2} \lambda^{-1/4} \left( 1 - \frac{Q(X)}{2X} \right)^{-1/2} I(\lambda) = \epsilon I(\lambda), \text{ say, where}
\]

\(\epsilon\) tends to zero as \(\lambda\) tends to infinity, \(X\) being determined by

\[
\text{det } (P(X) - \lambda E) = 0.
\]
Thus the theorem is proved when \((p + r)\) is convex downwards.

Again, since
\[
(p - r)^2 + 4q^2 \leq (p + r)^2 + 4q^2 \leq (p + r + 2q)^2,
\]
therefore
\[
\lambda - \frac{1}{2} \triangle (u) \geq \lambda - (p + q + r) \geq \lambda - \{p(X) + q(X) + r(X)\} \frac{u}{X},
\]
since \(p + q + r, \ (q(0) \geq 0)\), is convex downwards: \(0 < u < X\).

Finally,
since
\[
\{(p - r)^2 + 4q^2\}^{1/2} \geq p - r, \ r - p,
\]
it follows that
\[
\lambda - \frac{1}{2} \eta (u) \geq \lambda - p (u), \ \lambda - r (u).
\]
Therefore
\[
\lambda - \frac{1}{2} \eta (u) \geq \lambda - p (X) \frac{u}{X}, \ 0 < u < X,
\]
if \(p\) is convex downwards,

and
\[
\lambda - \frac{1}{2} \eta (u) \geq \lambda - r (X) \frac{u}{X}, \ 0 < u < X,
\]
if \(r\) is convex downwards.

In any case the analysis therefore follows as before.

10. Acknowledgements

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Short Communication

Exact solution for the unsteady motion of a viscous fluid in a porous annulus

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Abstract

In this note, the problem of unsteady motion in a porous annulus has been studied. Using finite Hankel transform, closed form solution is obtained for the axial velocity component under the restriction that the ratio of suction and injection at the walls are same.

Key words: Unsteady, Viscous, Porous, Annulus, Suction, Injection.

Introduction

The geometry of porous layers is of great importance in the problems of pulmonary physiology, where there is a need for measuring the blood volume in the lungs.

The purpose of this note is to present the exact solution for the time dependent motion of a viscous fluid in an annulus with porous walls. It is assumed that the rate of suction at one wall is equal to the rate of injection at the other. Finite Hankel transform is applied and closed form solution for the axial velocity is obtained. The average axial velocity profiles are depicted graphically.

Basic equations

We consider the flow to take place in a porous annulus bounded by two infinite cylinders with radii a and b (b > a). A cylindrical polar coordinate system (r, θ, x) is chosen with axis of annulus as x axis, and v, u the radial and axial velocity components respectively. The governing equations are
Continuity equation:

\[ \rho \left[ \frac{\partial v}{\partial t} + v \frac{\partial v}{\partial r} + u \frac{\partial v}{\partial x} \right] = -\frac{\partial p}{\partial r} \]
\[ + \mu \left[ \frac{1}{r} \frac{\partial v}{\partial r} + \frac{\partial^2 v}{\partial r^2} - \frac{v}{r^2} \right] \]  

(1)

\[ \rho \left[ \frac{\partial u}{\partial t} + v \frac{\partial u}{\partial r} + u \frac{\partial u}{\partial x} \right] = -\frac{\partial p}{\partial x} + \mu \left[ \frac{\partial^2 u}{\partial x^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \frac{\partial^2 u}{\partial r^2} \right] \]

(2)

The boundary conditions are:

At \( t = 0 \), \( u = 0 \) for \( a \leq r \leq b \)
At \( r = a \), \( b \), \( u = 0 \) for all \( t \)
At \( r = a \), \( v = V_a \) and \( r = b \), \( v = V_b \)

(4)

The condition that suction and injection rates are equal implies

\[ aV_a = bV_b \]

(5)

This restriction makes the axial velocity independent of \( x \).

Integrating (3) and (1), we get

\[ v = \frac{aV_a}{r} \]

(6)

and

\[ p = -\frac{\rho V_a^2}{2r^2} + A \]

(7)

where \( A \) is independent of \( r \).

Introducing the following non-dimensional variables

\[ \lambda = \frac{r}{a}, \quad \phi = \frac{u}{\left(\frac{p_0 - p_L}{\rho \mu L}\right) a^2}, \quad \tau = \frac{\mu t}{\rho a^2} \]

(8)

where \( L \) is the characteristic length, and \( (p_0 - p_L) \) is the pressure difference, we obtain from (3) the equation for \( \phi \) as

\[ \frac{\partial \phi}{\partial \tau} = 1 + \frac{\partial^2 \phi}{\partial \lambda^2} + \left( \frac{1 - \phi}{\lambda} \right) \frac{\partial \phi}{\partial \lambda} \]

(9)
where \( \alpha = \rho V_s \), \( a/\mu = \) Cross Reynold’s number of suction parameter. The boundary conditions (4) become

At \( \tau = 0, \phi = 0 \) for \( 1 \leq \lambda \leq b/a = \sigma \)

At \( \lambda = 1, \phi = 0 \) for all \( \tau \). \hspace{1cm} (10)

In obtaining this equation, we have tacitly assumed a non-zero axial pressure gradient which is necessary for setting up an unsteady flow. This in turn implies that \( A \) is a linear function of \( x \). We can write the solution (9) as the sum of a steady part, and an unsteady part in the form

\[
\phi (\lambda, \tau) = \phi_\infty (\lambda) - \phi_T (\lambda, \tau)
\] \hspace{1cm} (11)

From (9), by taking the steady part only, we get the equation for \( \phi_\infty \) as

\[
1 + \frac{\partial^2 \phi_\infty}{\partial \lambda^2} + \left( \frac{1 - a}{\lambda} \right) \frac{\partial \phi_\infty}{\partial \lambda} = 0
\] \hspace{1cm} (12)

with boundary conditions

\( \phi_\infty = 0 \) at \( \lambda = 1, \sigma \).

The solution of (12) is

\[
\phi_\infty = A + B\lambda^a - C\lambda^2 \text{ for } a \neq 2
\] \hspace{1cm} (13)

where

\[
A = \frac{\sigma^2 - \sigma^a}{2(2 - a)(1 - \sigma^a)}, \quad B = \frac{1 - \sigma^2}{2(2 - a)(1 - \sigma^a)}, \quad C = \frac{1}{4 - 2a}
\]

and

\[
\phi_\infty = A_1 (1 - \lambda^2) - \frac{\lambda^a \ln \lambda}{2} \text{ for } a = 2
\] \hspace{1cm} (14)

where

\[
A_1 = \frac{\sigma^2 \ln \sigma}{2(1 - \sigma^a)}
\]

The equation for \( \phi_T \) is

\[
\frac{\partial^2 \phi_T}{\partial \lambda^2} + \left( \frac{1 - a}{\lambda} \right) \frac{\partial \phi_T}{\partial \lambda} = \frac{\partial \phi_T}{\partial \tau}
\] \hspace{1cm} (15)
with boundary conditions

At $\tau = 0$, $\phi = \phi_0$

At $\lambda = 1$, $\sigma, \phi_\tau = 0$

As $\tau \to \infty$, $\phi_\tau \to 0$.

By substituting $\phi_\tau = \lambda^{(a/2)} \psi_\tau$, (15) is simplified to

$$\frac{\partial^2 \psi}{\partial \lambda^2} + \frac{1}{\lambda} \frac{\partial \psi}{\partial \lambda} - \left(\frac{a}{2\lambda}\right)^2 \psi = \frac{\partial \psi}{\partial \tau}$$

(16)

Now, we define (Sneddon\textsuperscript{3}) the Hankel transform as

$$\tilde{\psi}(s, \tau) = \int_0^a \lambda \psi(\lambda, \tau) \left[ J_k(s\lambda) Y_k(s\lambda) - J_k(s\sigma) Y_k(s) \right] d\lambda$$

where $k = a/2$, $s$ is a root of the equation (Abromowitz and Stegun\textsuperscript{3})

$$J_k(s) Y_k(s\sigma) - J_k(s\sigma) Y_k(s) = 0$$

(17)

where $J_k$ and $Y_k$ are Bessel functions of first and second kind respectively. The inverse transform is

$$\psi(\lambda, \tau) = \frac{\pi^2}{2} \sum_k \frac{s^2 (J_k^2(s))}{J_k(s) - J_k(s\sigma)} \left[ J_k(s\lambda) Y_k(s) - J_k(s\sigma) Y_k(s) \right]$$

(18)

where summation is taken over the positive roots of (17). Applying the above transform in (16) and its inverse, we obtain the solution for axial velocity in dimensionless form as

$$\phi = \phi_0 - \lambda^{(a/2)} \frac{\pi^2}{2} \sum_k \frac{e^{-s^2 \tau} s^2 J_k^2(s\lambda)}{J_k(s) - J_k(s\sigma)} \left[ J_k(s\lambda) Y_k(s) - J_k(s\sigma) Y_k(s) \right]$$

(19)

where $\phi_0$ is given by (13) and (14), and $\tilde{\psi}$ is the transform of $\psi$. The series on the right side is convergent. It can be seen that as $\tau \to \infty$, we obtain solution for steady case as given by Berman\textsuperscript{4}. It should be remarked that Verma and Gaur\textsuperscript{5} have obtained a similar solution using Laplace transform, but it was commented that further analysis was not possible. However, in this note, the solution is more elegant and graphical representation is provided.

Figure 1 gives the average axial velocity profiles for various suction parameters. It can be seen that the suction parameter increases, the point of maximum velocity shifts towards the other boundary. Fig. 2 depicts the axial velocity and shows how the unsteady part dies out with passage of time. In Fig. 3, the average axial velocity is represented as a function of $\sigma$. 
FIG. 1. Average axial velocity profiles for different suction parameters at $\tau = \pi$. 
Fig. 2: Axial velocity field at different times when $\alpha = 4$, $\phi = 5$. 

\[ \lambda \rightarrow \]

\[ \phi \]

\[ \tau = \frac{\pi}{4} \]
\[ \tau = \frac{\pi}{2} \]
\[ \tau = \pi \]
Fig. 3: Average axial velocity field for different values of $\sigma$ when $\tau = \pi$ and $\alpha = 4$.

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References

Short Communication

A note on the nonlinear vibrations of rectangular plates with parabolically varying thickness

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Abstract

An analysis of the large amplitude vibrations of rectangular plates of parabolically varying thickness is presented. The method is based on Berger's assumption of neglecting the second invariant of the middle surface strain in the expression corresponding to the total potential energy of the system, in conjunction with a Galerkin procedure.

Key words: Parabolically varying thickness, large amplitude, frequency, taper constant.

1. Introduction

Investigations relating to nonlinear vibration are few in comparison with those for linear cases. This is, probably, due to the difficulties involved in solving the nonlinear differential equations. Berger\(^1\), however, has proposed an approximate method to solve such problems which is simple and accurate for all practical purposes. Nash and Modeer\(^2\) extended this technique offered by Berger to a dynamic case which was subsequently followed by different authors\(^3-6\).

The work presented in this paper is to study the large amplitude vibrations of rectangular plates with parabolically varying thickness by means of Berger's method in combination with a Galerkin procedure.

2. Basic equations and their solutions

Let a flat rectangular plate with parabolically varying thickness and of length \(2a\) and of breadth \(2b\) be subjected to a normal load \(q\). The origin of the cartesian
coordinate system is located at the centre of the plate. The governing differential
equations for the deflection function \( w \) of the plate exhibiting large deflection may be
put in the following forms:

\[
\nabla^2 (D \nabla^2 w) - (1 - \nu) \left[ \frac{\partial^2 D}{\partial x^2} \frac{\partial^2 w}{\partial y^2} - 2 \frac{\partial^2 D}{\partial x \partial y} \frac{\partial^2 w}{\partial x \partial y} + \frac{\partial^2 D}{\partial y^2} \frac{\partial^2 w}{\partial x^2} \right] \\
- \frac{12CE}{1 - \nu^2} f(t) \Phi^2 w - q = 0
\]

(1)

where \( D = \frac{Eh^3}{12} (1 - \nu^2) \) is the flexural rigidity of the plate, \( E \) is the Young’s modulus,
\( e \) is the first invariant, \( u, v \) are the inplane displacements along \( x \)- and \( y \)-directions,
respectively; \( h = h(x, y) \) is the thickness of the plate at a point \( (x, y) \) from the origin,
and \( \nu = \) Poisson’s ratio and \( p \) is the density of the plate material and \( \Gamma \) is a constant
of integration \( f(t) \) being an unknown function of time to be determined.

Let the law of thickness variation be \( h = h_0 (1 + \beta x^2 / a^2) \).

If the problem be restricted to the finding of the fundamental mode of frequency only
one can set the expression for \( w \) compatible with the boundary conditions for a plate
with hinged immovable edges as

\[
W = \cos \frac{\pi X}{2} \cos \frac{\pi Y}{2} F(t)
\]

(3)

where \( F(t) \) is an unknown function of time and \( X = x/a, Y = y/b \) and \( W = w/h \)
have been introduced in their nondimensional forms. The actual analysis for obtaining
the time differential equation as well as the evaluation of the coupling constant \( \Gamma \)
may be omitted for brevity (actual analysis is given in Ref. 6). The time
differential equation may, thus, be put straight forward in the following form

\[
\ddot{F}(t) + AF(t) + BF^2(t) = Q.
\]

(4)

3. Deductions

Free linear vibration

The frequency parameter \( \Omega \) appears to be

\[
\Omega^2 = 12 (1 - \nu^2) \rho a^4 \omega^2 / Eh^3 = (\pi/2)^2 \gamma / (1 + 0.1306 \beta)
\]

(5)

where \( \omega \) is the circular frequency of the plate. The values of the frequency parameter
have been computed and are displayed in Table I for different values of the taper
constant \( \beta \).
Table I

Values of the frequency parameter $\Omega^2$ for different values of $\beta$ and aspect ratio $(a/b)$
Rectangular plate with hinged immovable edges

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<th>$-0.5$</th>
<th>$-0.4$</th>
<th>$-0.3$</th>
<th>$-0.1$</th>
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<table>
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<td>16.0775</td>
<td>18.2971</td>
<td>19.9523</td>
</tr>
</tbody>
</table>

Nonlinear static case

If the inertia term in eqn. (4) is rejected the static behaviour of the plate can be obtained from the following equation

$$AF + BF^3 = Q.$$  \hspace{1cm} (6)

The nonlinear static behaviour has been shown in Fig. 1.

Nonlinear free and forced vibrations

To avoid repetition one may be referred to Ref. 6 for the analysis of free and forced vibrations. The relative time periods of free linear and nonlinear vibrations ($T/T^*$) have been presented graphically (Fig. 2) against relative amplitude ($A_0/h_0$).

4. Numerical results and discussion

The values of the frequency parameter have been computed for different values of taper constant $\beta$ and aspect ratio $a/b$. Table I shows that the frequency increases with the increase of $\beta$ while for the same value of $\beta$ the frequency decreases with the increasing value $(a/b)$. 

Figure 2 depicts the relative period of vibrations in terms of the relative amplitude $(A_0/h_0)$ for $a/b = \frac{1}{2}$. In all calculations $v$ has been taken to be 0.3 and the values of $\beta$ ranges from -0.5 to +0.5. It is evident from Fig. 2 that the general trend is to decrease the period of nonlinear vibration with the increase of amplitude. Further, this decreasing tendency of $T^*$ is faster when $\beta$ decreases through negative values than when it does so through positive values. It has been further observed that the decreasing value of $(a/b)$ further accelerates this trend.

In conclusion, it appears that the nonlinear effects are stronger when $\beta < 0$ than the case when $\beta > 0$. This can be explained in the light of the fact that in the first case $\beta < 0$ the mass concentration near the supports decreases and the overall plate stiffness is decreased whereas in the latter case, as $\beta$ increases through positive value, the overall plate thickness is increased because of the increased thickness near the
boundary. In the first case the effect is to increase the frequency and the opposite holds when $\beta > 0$.

5. **Acknowledgement**

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I.I.Sc.—8
Contributions to the chemistry of phosphazenes

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Abstract

Our significant findings on the aminolysis reactions of halogenocyclophosphazenes are summarised with emphasis on the synthesis and characterisation of novel bicyclic phosphazenes and spirocyclic phosphazenes. The use of chromatographic techniques for the separation of cyclophosphazene derivatives and elucidation of their structures by NMR and IR spectroscopy are also reviewed.

Key words: Halogenocyclophosphazenes, aminolysis reactions, bicyclic phosphazenes, spirocyclic phosphazenes, chromatography, NMR and IR spectroscopy.

1. Introduction

Phosphazenes are inorganic hetero atom compounds with alternate phosphorus and nitrogen atoms in a valence unsaturated skeleton. They can be cyclic or linear and some typical examples are shown below.

I. $X = \text{Cl}$
   CYCLIC TRIMER

IV. $X = \text{Br}$
   CYCLIC TETRAMER

II

III

\[ n \approx 15,000 \]
There has been considerable progress in the chemistry of these compounds during the last two decades from both fundamental and technological points of view\textsuperscript{3-4}. The fundamental studies are mainly concerned with (a) the chemical reactions of the hexachloride(I), (b) spectroscopic and crystallographic studies to elucidate the structural chemistry of phosphazenes and (c) synthesis and characterization of linear phosphazene polymers. The development of ‘speciality’ phosphazene polymers has proceeded rapidly\textsuperscript{4} and one material (PNF 200) is now produced commercially\textsuperscript{5}. This material is the first rubber to combine the four qualities of oil resistance, durability, resistance to heat and flexibility at low temperature. The development of flame retardant textiles is clearly a ‘growth’ industry in view of legislative enactments in this connection in many countries. The use of alkoxy (aryloxy) phosphazenes for this purpose is well documented\textsuperscript{1-2}. Other potential applications of phosphazene derivatives include the use of (a) aziridinocyclophosphazenes as chemosterilants\textsuperscript{5,9}, (b) platinum chloride complexes of (methylamino) phosphazenes as anti-tumour agents\textsuperscript{5,6} and (c) ammmono cyclophosphazenes as sources of plant nutrients\textsuperscript{5,8}.

We have carried out some extensive investigations of the chemistry of cyclocphosphazenes under a binational project on “Phosphazenes—A group of Phosphorus-Nitrogen Compounds” between the Indian Institute of Science and Birkbeck College. This project is designed to train young scientists in research methodology and is sponsored by the University Grants Commission, New Delhi, and the Overseas Development Ministry, London. Our research interest in phosphorus-nitrogen chemistry has been primarily concerned with the fundamental aspects of the subject. The topic provides an interesting and challenging field of research and has aroused a great deal of international interest. A larger number of papers on this subject have been presented at major Conferences\textsuperscript{*} devoted both to phosphorus chemistry and to the chemistry of inorganic heterocyclic compounds. A consolidated account of the results of our investigations during 1973-77 is presented in this review.

2. Aminolysis reactions of $N_4P_4Cl_6$ (II)

Although the substitution reactions of the hexachloride, $N_6P_6Cl_6$ (I), have been investigated in great detail, similar reactions of $N_4P_4Cl_6$ (II) have received much less attention. This lack of information may well reflect the considerable difficulties encountered in separating complex mixtures of products and in assigning unambiguous structures to the pure isomers\textsuperscript{8}. Fig. 1 shows the positional and geometric isomers that can occur in the tetramer system. Replacement of the chlorine atoms of $N_4P_4Cl_6$ (II) by a substituent group (R) can take place by the geminal or the non-geminal route, i.e., attack at a

---

Fig. 1. Possible substitution products from \( \text{N}_4\text{P}_4\text{Cl}_4 \) (II). The phosphorus atoms are represented by the corners of the squares and the full and broken lines represent orientation of the substituents above and below the \( \text{N}_4\text{P}_4 \) ring plane respectively. Chlorine and ring nitrogen atoms are not shown.
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≡ PCl\(_R\) or \(≡ \text{PCl}_2\) site. Our objectives in a detailed study of the nucleophilic replacement reactions of the octachloride(II) were (a) to determine the replacement patterns, (b) to compare the results with those for the analogous reactions of \(\text{N}_3\text{P}_4\text{Cl}_6\) (I), and (c) to ascertain if the mechanisms postulated for the reactions of \(\text{N}_3\text{P}_4\text{Cl}_6\) (I) would also be valid for those of the octachloride(II).

The reaction of \(\text{N}-\text{methylaniline}\) with \(\text{N}_3\text{P}_4\text{Cl}_6\) (II) was reported in 1960–61 and only two compounds were isolated\(^{15,8}\). Our reinvestigation of this reaction has revealed its great complexity and we have obtained ten derivatives, \(\text{N}_3\text{P}_4\text{Cl}_6-n (\text{NMePh})_n\) \([n = 1, 2\) (two isomers), 3, 4 (five isomers) and 6]. The replacement of chlorine atoms beyond the tetrakis stage is difficult and attempts to prepare the octakis (N-methylanilino) derivative, \(\text{N}_3\text{P}_4 (\text{NMePh})_8\), have not been successful. Structures have been assigned to the chloro-N-methylanilino derivatives on the basis of \(^1\text{H}\) NMR data (in some cases aided by \(^{31}\text{P}\) NMR spectra) and chemical evidence. The methoxy derivatives, \(\text{N}_3\text{P}_4 (\text{OMe})_8-n (\text{NMePh})_n\) \([n = 2\) (two isomers), 4 (two isomers) and 6] have been prepared to further confirm the structural assignments\(^{15,29}\). The chlorine replacement pattern by N-methylanilino groups is predominantly nongeminal as found also for the reaction of \(\text{N}_3\text{P}_4\text{Cl}_6\) (II) with dimethylaniline\(^{11}\). However, in contrast to the dimethylaniline reaction where only one bis-derivative, \(2\text{-trans-6-}\text{N}_3\text{P}_4 (\text{NMePh})_2\text{Cl}_6\) is formed\(^{21}\), the reaction of \(\text{N}_3\text{P}_4\text{Cl}_6\) (II) with \(\text{N}-\text{methylaniline}\) (a much less reactive amine) gives two bis-isomers, m.p. 145° C and 105° C, in comparable yields\(^{16,13}\). X-ray crystallography establishes 2-trans-6 and 2-trans-4 structures respectively for these two isomers\(^{15,14}\). The isolation of only one tris (N-methylanilino) derivative and the apparent absence of pentakis-derivatives, compared with the isolation of three tris- and two pentakis-chlorodimethylamino-cyclotetraphosphazenes, suggests that there is tendency for chloro-(N-methylanilino) cyclotetraphosphazenes containing an odd number of chlorine atoms to react further to give derivatives with an even number of chlorine atoms.

We have also recently completed the first systematic studies of the reaction of \(\text{N}_3\text{P}_4\text{Cl}_6\) (II) with primary amines\(^{12,15-17}\). The ethylamino- and \(\text{t}-\text{butylamino-cyclotetraphosphazenes}\) isolated in these reactions have nongeminal structures and are listed in

\[
\text{N}_3\text{P}_4\text{Cl}_6 + 2n \text{RNH}_2 \rightarrow \text{N}_3\text{P}_4\text{Cl}_6-n (\text{NHR})_n + n \text{RNH}_2, \text{HCl} (R = \text{Et, Bu})
\] (1)

Table I. Compounds containing both \(≡ \text{PCl(NHR)}\) and \(≡ \text{P(NHR)}_2\) groups have not been obtained. After the tris-stage of replacement of chlorine atoms in the \(\text{t}-\text{butylamino}\) system (and after the tetrakis-stage in the ethylamino-system), resinous materials are formed predominantly. However, the octakis (amino)-derivatives, \(\text{N}_3\text{P}_4 (\text{NHR})_8\) could be easily prepared by using a two-three fold excess of the amine. These observations have been rationalised by postulating a common "metaphosphorimidate" intermediate (formed by elimination of hydrogen chloride from \(\text{PCl(NHR)}\) groups) for the formation of resins and the octakis (amino) derivative\(^{19}\).

The hexachloride (I) reacts with \(\text{t}-\text{butylamine}\) only by the geminal mode of replacement; both geminal and non-geminal products are obtained in the analogous
Contributions to the Chemistry of Phosphazenes

Table I

Ethylamino and t-butylamino derivatives of $N_4P_4Cl_8$ (II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>MP (°C)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_4P_4Cl_7$ (NHEt)</td>
<td>liq.</td>
<td></td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHEt)$_2$</td>
<td>116</td>
<td>2, 4, 4, 6, 8, 8 : 2-trans-6</td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHEt)$_3$</td>
<td>124</td>
<td>Nongeminal</td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHEt)$_4$</td>
<td>68-70</td>
<td>2, 4, 6, 8, 8 : 2-cis-4-trans-6</td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHEt)$_5$</td>
<td>96</td>
<td>2, 4, 6, 8, 8 : 2-cis-4-trans-8</td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHEt)$_6$</td>
<td>158</td>
<td>2, 4, 6, 8, 8 : 2-cis-4-cis-6-trans-8</td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHEt)$_7$</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHBu')</td>
<td>51-52</td>
<td></td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHBu')$_2$</td>
<td>171</td>
<td>2, 4, 4, 6, 8, 8 : 2-trans-6</td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHBu')$_3$</td>
<td>127</td>
<td>2, 4, 6, 6, 8, 8 : 2, 4</td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHBu')$_4$</td>
<td>163-165</td>
<td>2, 4, 6, 8, 8 : 2, 4, 6</td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHBu')$_5$</td>
<td>180-200 (d)</td>
<td></td>
</tr>
<tr>
<td>$N_4P_4Cl_6$ (NHBu')$_6$, HCl</td>
<td>190-195 (d)</td>
<td></td>
</tr>
</tbody>
</table>

The exclusive nongeminal replacement pattern observed for $N_4P_4Cl_8$ (II) with both these primary amines is probably due to the greater reactivity of the octachloride (II). An $S_n 2 (P)$ mechanism is compatible with the observations.

Chlorocyclotetraphosphazenes containing both ethylamino and t-butylamino groups have also been prepared in order to assess the role of the substituent and the nucleophile in determining the structures of the products. Reactions of the mono-derivatives, $N_4P_4Cl_7$ (NHEt) and $N_4P_4Cl_7$ (NHBu') with two equivalents of ethylamine and t-butylamine are summarized in Fig 2. These results suggest that the nucleophile determines the course of these aminolysis reactions and not the substituent already present. A similar conclusion has been drawn from the aminolysis reactions of $N_4P_4Cl_8$ (I)1-3.

The most significant highlight of our studies on the aminolysis reactions of the octachloride (II) and its primary amino-derivatives is the isolation and characterization of novel bicyclic phosphazenes (Fig. 3)15,18-20. The expected fully aminolysed cyclotetraphosphazenes are also obtained in these reactions. The relative yield of the two types of product is strongly influenced by the reaction solvent. Bicyclic phosphazenes are formed in highest yield (ca. 40-60%) in chloroform or methylene chloride. In diethyl
Fig. 2. The effect of the nucleophile in the aminolysis reactions of (amino) chlorocyclotetraphosphazenes.

ether or carbon tetrachloride, formation of bicyclic phosphazenes \( \text{N}_4\text{P}_4\text{Cl}_6(\text{NMe})_2 \) (NR) has not been observed: only the fully substituted cyclotetraphosphazene derivatives are obtained (ca. 75–80\%). A proton abstraction mechanism has been proposed for the intramolecular, transannular nucleophilic substitution leading to the formation of bicyclic phosphazenes\(^{18,20}\). Crystallographic studies of two bicyclic phosphazenes, \( \text{N}_4\text{P}_4(\text{NHMe})_6 \) (NMe)\(^{21}\) and \( \text{N}_4\text{P}_4(\text{NMe})_6(\text{NHEt})(\text{NEt})^{22} \), show that the original 8-membered ring
Fig. 3. Formation of bicyclic phosphazenes. The substituents pointing towards the bridgehead nitrogen atom are shown by shaded lines.
retains its phosphazene character (P–N distances 1.58–1.61 Å) but the bridgehead P–N bond lengths (1.71–1.76 Å) are significantly longer and phosphazene-like.

Our preliminary conclusions on the aminolysis reactions of \( \text{N}_4\text{P}_4\text{Cl}_8(\text{II}) \) can be summarised briefly. After the replacement of the first chlorine atom, electron release by the amino substituent at P(2) into the phosphorus-nitrogen ring would preferentially deactivate the adjacent phosphorus atoms, P(4) and P(8) and thereby favour nucleophilic attack at the distant phosphorus atom, P(6). Hence, a reactive amine should give a 2, 6-product almost exclusively as observed for ethylamine and dimethylamine. Both 2, 6- and 2, 4-bis isomers are obtained in the reaction of \( \text{N}_4\text{P}_4\text{Cl}_8(\text{II}) \) with less reactive amines, N-methylaniline, dibenzylamine, t-butyramine and benzylamine. The ratio of these bis isomers varies markedly with the reaction solvent. As yet, we have no clear rationalisation for these observations although the preferential deactivation at P(4) is likely to diminish with a weaker electron-releasing amino-substituent at P(2) and hence promote substitution at both P(4) and P(6). The step-wise replacement of chlorine atoms continues in secondary amine reactions and compounds with all the possible stages of replacement \( (n = 3–8) \) are formed, although not necessarily for
all amines. The reactions of the primary amines are more complex. In addition to the step-wise replacement of chlorine atoms to yield chloro (amino)-cyclotetraphosphazenes, intermolecular condensation (resins) and intramolecular displacement (bicyclic phosphazenes) occur. The latter pathway is also found for the reaction of bis (primary amino) cyclotetraphosphazene derivatives with a secondary amine (Me₂NH)²⁸. The three pathways discussed above are illustrated in Fig. 4.

![Diagram](image_url)

Fig. 4. The three possible pathways in the reactions of N₄P₄Cl₄ (II) or N₄P₄(NHR)₂Cl₂ (VIII) with amines,
3. Reactions of \( \text{N}_3\text{P}_3\text{Cl}_6 \) (I) and \( \text{N}_3\text{P}_3\text{Br}_6 \) (IV)

We have also studied the reaction of N-methylaniline with the hexachloride(1)\(^{18}\) and isolated the derivatives \( \text{N}_3\text{P}_3\text{Cl}_{6-n} \) (NMePh)_n \( [n = 1, 2 \text{ (two isomers)}, 3 \text{ (two isomers)} \) and 6]. In addition, a dealkylated product, \( \text{gem-N}_3\text{P}_3\text{Cl}_6 \) (NMePh) (NHPhe) has been obtained from a reaction carried out in boiling xylene. The nongeminal bis isomers are obtained in comparable amounts. The tris-isomers have geminal and cis- nongeminal structures. The former is the major product formed in all reactions with stoichiometries of 1:6 \( \text{N}_3\text{P}_3\text{Cl}_6 \) (I): PhNHMe and above, even in polar solvents such as methyl cyanide. In contrast, the reaction of \( \text{N}_3\text{P}_3\text{Cl}_6 \) (I) with six equivalents of a more reactive secondary amine (dimethylamine, diethylamine and piperidine) leads to the predominant formation of the trans- tris-derivative, \( \text{N}_3\text{P}_3\text{Cl}_6 \) (I), particularly in methyl cyanide). The relative proportion of the geminal tris-isomer in these reactions can be enhanced in aromatic reaction media\(^{24}\). The reasons for the divergent behaviour of N-methylaniline are uncertain but it is likely that its aromatic and weak basic character are contributing factors.

The preparation of the bromocyclophosphazenes \( (\text{NPBr}_3)_n \) from phosphorus tribromide, bromine and ammonium bromide is particularly tedious and time-consuming and these factors have undoubtedly contributed to the lack of interest in the chemistry of these compounds. We chose to study the reaction of the hexabromide, \( \text{N}_3\text{P}_3\text{Br}_6 \) (IV), with ethylamine in order to compare the reactivity of P-Br and P-Cl bonds towards a nucleophilic reagent of this type. The reaction was carried out in diethyl ether at \(-30\) to \(-50^\circ \text{C}\) and the ethylamino-derivatives, \( \text{N}_3\text{P}_3\text{Br}_{6-n} \) (NHEt)_n \( [n = 1, 2 \text{ (two isomers)}, 4 \) and 6] and the hydrogen bromide adducts, \( \text{N}_3\text{P}_3\text{Br}_6 \) (NHEt)_4, HBr and \( \text{N}_3\text{P}_3 \) (NHEt)_6, HBr were isolated\(^{35}\). Our study of this reaction and a previous report of the dimethylamine reaction\(^{26}\) suggest that the replacement of the halogen atoms of \( \text{N}_3\text{P}_3\text{Cl}_6 \) (I) and \( \text{N}_3\text{P}_3\text{Br}_6 \) (IV) by amino groups is very similar. However, two points of difference are that (a) bromo-derivatives are hydrolytically less stable and consequently much more difficult to purify and (b) the formation of resins in the reactions of \( \text{N}_3\text{P}_3\text{Br}_6 \) (IV) with the primary amine is considerably enhanced.

In 1963, the reactions of \( \text{N}_3\text{P}_3\text{Cl}_6 \) (I) with the diamines, \( \text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_{2(n=2,3} \) or 4), were reported to give compounds with an \( \text{ansa-structure}^{27} \). The following year, a short paper was published by Italian workers\(^{18}\) on the \( ^{31}\text{P} \) NMR spectrum of the propylendiaminodervative, \( \text{N}_3\text{P}_3\text{Cl}_4 \) [NH(\text{CH}_2)_3NH]CH, which clearly indicated that this compound had a spiro- and not an \( \text{ansa-structure} \) (Fig. 5). This anomaly in the literature apparently escaped the attention of workers in the field of phosphorus-nitrogen chemistry. We have reinvestigated the reaction of \( \text{N}_3\text{P}_3\text{Cl}_6 \) (I) with ethylendiamine and obtained the derivative \( \text{N}_3\text{P}_3\text{Cl}_4 \) [NH(\text{CH}_2)_3NH] (m.p. 198$^\circ \text{C}$) described previously. We have also synthesised a new \( t\)-butylamino (ethylenediamino) cyclophosphazene derivative by two different routes (Eqn. 2).
A small quantity of $\text{N}_3\text{P}_3\text{Cl}_4(\text{NHBu})_2$ has also been obtained. This compound appears to be the first geminal cyclotriphosphazene derivative.

---

\[ \text{gem-}N_3P_3Cl_4(\text{NHBu})_2 \xrightarrow{H_2N(CH_2)_3NH_2} N_3P_3Cl_4(\text{NHBu})_2[NH(CH_2)_3NH] \xrightarrow{\text{Bu}^+\text{NH}_2} \]

FIG. 5. The possible products of a reaction between $N_3P_3Cl_4(\text{I})$ and a bifunctional reagent $HXYH$ ($X$ and $Y$ need not be directly bonded).
containing three chlorine atoms and three primary alkylamino-substituents. Chemical
and NMR spectroscopic evidence show that these ethylenediamino derivatives have
spirocyclic structures\textsuperscript{26,29}. A recent X-ray structure of the dimethylamino derivative
\(N_3P\) \((NMe_2)_4[NH(CH_2)_6NH]\) has confirmed this conclusion\textsuperscript{26}.

The reactions of chlorocyclotriphosphazenes with ethanolamine, \(NH_2(CH_2)_3OH\),
are very similar to those with ethylenediamine and again spirocyclic products are formed.
In addition to the mono(ethanolamino) derivative, \(N_3P_2Cl_4[NH(CH_2)_6O]\), small quantities
of two bis-derivatives, \(N_3P_2Cl_3[NH(CH_2)_6O]_2\), have been obtained. Analogous
bis (ethylenediamino) cyclotriphosphazenes could not be prepared. After two chlorine
atoms of \(N_3P_2Cl_4(I)\) have been replaced by ethylenediamino- or ethanolamino-
group further replacement of chlorine atoms gives cross-linked products almost exclusively
(Fig. 5)\textsuperscript{26}.

4. Chromatographic techniques

Aminolysis reactions of halogenocyclophosphazenes invariably give a mixture of products
with different degrees of halogen replacement which may also include geometric
positional isomers. In addition, some unreacted starting material can be present. The amine
hydrochloride formed in the reaction can also hinder the purification of the derivatives owing to its considerable solubility in many reaction solvents. A further complication in reactions involving primary amines is the formation of resinous materials as a result of side reactions. Hence, the separation of pure cyclophosphazene derivatives from such complex reaction mixtures is very difficult. The "classical" methods of separation—fractional crystallisation and extraction (based on differences in solubility) and fractional distillation and sublimation (differences of volatility)—are often of limited utility. However, the introduction of column, thin-layer and gas-liquid chromatographic techniques has greatly simplified this difficult task\textsuperscript{31}.

We have used thin-layer chromatography (silica gel adsorbent) for monitoring the course
and extent of aminolysis reactions and to identify the components of various fractions collected during column chromatographic separations. TLC can also be used for semi-
quantitative estimates of relative yields by visual estimation of the size and intensity of
the "spots". The isolation of compounds by preparative TLC is possible but the tediousness of the method and the small quantities of pure compounds obtained are serious limitations. Table II gives the TLC \(R_f\) values for some representative aminocyclophosphazenes.

The formation of novel bicyclic phosphazenes, \(N_4P_4(NMe_2)_8(NHR)(NR)\), from the
reaction of \(N_3P_2Cl_6(NHR)_2\) with an excess of dimethylamine in chloroform has been
described above. The bicyclic phosphazene has a lower TLC \(R_f\) value than the related
octakis(amo) cyclotetraphosphazene derivative, \(N_4P_4(NMe_2)_8(NHR)_2\) (also formed
in the same reaction), thus permitting a ready distinction between the two types of
derivatives\textsuperscript{26}.
## Table II

**TLC $R_f$ values of selected cyclophosphazene derivatives**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R_f$</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.85&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 2, 4, 6: 4-trans-6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.81&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 2, 4, 6: 4-cis-6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.79&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6: 2-cis-4-cis-6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePa$)</td>
<td>0.73&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 2, 4: 4, 6, 6</td>
</tr>
<tr>
<td>$N_5P_2$ ($NMeP$)</td>
<td>0.66&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ (NHP&lt;sub&gt;Ph&lt;/sub&gt;) ($NMeP$)&lt;sub&gt;Ph&lt;/sub&gt;</td>
<td>0.28&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 2: 4: 4, 6, 6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.96&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.93&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 4, 6, 8, 8: 2-trans-6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.93&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 6, 8, 8: 2-trans-4</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.84&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 8, 8: 2-trans-4-cis-6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.80&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 2, 6, 6: 4, 4, 8, 8</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.75&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 2, 6, 8: 4, 4, 6-trans-8</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.70&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 8: 2-cis-4-trans-6-trans-8</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.56&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 8: 2-trans-4-cis-6-trans-8</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.66&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 8: 2-cis-4-cis-6-trans-8</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.68&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2-trans-6: 2, 4, 4, 6, 8, 8</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMePh$)</td>
<td>0.71&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMeEt$)</td>
<td>0.58&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 8, 8: 2-trans-6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMeEt$)</td>
<td>0.53&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Nongeminal</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMeEt$)</td>
<td>0.18&lt;sup&gt;a&lt;/sup&gt;, 0.74&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 8, 8: 2-cis-4-trans-8</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMeEt$)</td>
<td>0.65&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 8: 2-cis-4-trans-6-trans-8</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ ($NMeEt$)</td>
<td>0.58&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 8: 2-cis-4-cis-6-trans-8</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ (NHBu&lt;sub&gt;t&lt;/sub&gt;)</td>
<td>0.87&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ (NHBu&lt;sub&gt;t&lt;/sub&gt;)</td>
<td>0.74&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 4, 6, 8, 8: 2, 6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ (NHBu&lt;sub&gt;t&lt;/sub&gt;)</td>
<td>0.65&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 4, 6, 8, 8: 2, 6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ (NHBu&lt;sub&gt;t&lt;/sub&gt;)</td>
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<td>2, 4, 6, 6, 8, 8: 2, 4, 6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ (NHBu&lt;sub&gt;t&lt;/sub&gt; ($NMeEt$)</td>
<td>0.72&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 4, 6, 8, 8: 2: 6</td>
</tr>
<tr>
<td>$N_5P_2Cl_6$ (NHBu&lt;sub&gt;t&lt;/sub&gt;) ($NMeEt$)</td>
<td>0.55&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2, 4, 6, 6, 8, 8: 2: 4</td>
</tr>
</tbody>
</table>

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*a* Data from Refs. 9, 16, 17 and 23.

*b* Adsorbent: silica gel.

*c* Eluent: benzene.

*d* Eluent: benzene-petrol (60-80°) (1: 1).

*e* Eluent: benzene-petrol (40-60°) (1:1).

*f* Eluent: benzene-ethyl acetate (9: 1).
Column chromatography over silica gel is essential to obtain many of the chloro (N-methylanilino)-cyclophosphazene derivatives formed in the reactions of N-methylaniline with \( \text{N}_2\text{P}_3\text{Cl}_6 \) (I)\(^{18} \) and \( \text{N}_4\text{P}_4\text{Cl}_8 \) (II)\(^9 \). In some cases, fractional crystallisation of the reaction mixtures affords crystalline crops enriched in a particular derivative. After further purification by fractional crystallisation, the residual mixture is chromatographed.

The usefulness of column chromatography for the separation of chloro(primary amino) cyclotetraphosphazenes is limited because of considerable loss of material owing to irreversible adsorption or decomposition on the column. This problem is accentuated with increasing number of primary amino groups. For example, the tetrakis(ethylamino) isomers of \( \text{N}_4\text{P}_4(\text{NHEt})_4 \text{Cl}_4 \) cannot be eluted from the column even with very polar solvents (ethyl acetate)\(^{15} \).

Gas-liquid chromatography (GLC) is often much more efficient than column or thin-layer chromatographic technique for the separation of (amino) chlorocyclophosphazenes besides serving as a powerful analytical tool for estimating the relative yields of products. The separation of the two bis (N-methylanilino) tetrachlorocyclophosphazene isomers, \( \text{N}_4\text{P}_4(\text{NMePh})_4 \text{Cl}_4 \) has been achieved by GLC\(^{28} \). The cis-isomer has a larger retention time than the trans-analogue. The relative yields of the N-methylanilino derivatives in many reactions have been determined by this technique. Fig. 6. shows the GLC trace of a typical reaction mixture.

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**Fig. 6.** The GLC trace of the mixture obtained in the reaction of \( \text{N}_4\text{P}_4\text{Cl}_4 \) (I) with N-methylaniline (mol ratio 1:6) in boiling methyl cyanide (10 h) using a steel column (15' x 1/8") containing 7% Dexsil 300 GC liquid phase in chromosil W–HP at 265°C. The percentages refer to relative yield of the chloro (N-methylanilino) derivatives (A) 2-trans-4-\( \text{N}_3\text{P}_3(\text{NMePh})_4 \text{Cl}_4 \), (B) 2-cis-4-\( \text{N}_3\text{P}_3(\text{NMePh})_4 \text{Cl}_4 \), (C) 2, 2, 4-\( \text{N}_3\text{P}_3(\text{NMePh})_4 \text{Cl}_4 \) and (D) 2-cis-4-cis-6-\( \text{N}_3\text{P}_3(\text{NMePh})_4 \text{Cl}_4 \). The retention times are also shown.
The reaction of \( \text{N}_3\text{P}, \text{Cl},(\text{I}) \) with isopropylamine was reported in 1966 and one bis(iso-propylamino) derivative, \( \text{N}_3\text{P}, \text{Cl},(\text{NHPr})_2 \), was isolated\(^3\). We have reinvestigated this reaction and obtained an oily substance by column chromatography. The oil shows a single spot on TLC and its mass spectrum has a parent ion corresponding to the formula, \( \text{N}_3\text{P}, \text{Cl},(\text{NHPr})_2 \). Attempts to crystallize the oil were unsuccessful. GLG examination of the oil revealed the presence of all three \( \text{N}_3\text{P}, \text{Cl},(\text{NHPr})_2 \) isomers. These isomers have been separated by preparative scale GLC and characterized by NMR spectroscopy. The GLC retention times follow the trend \( \text{gem} < \text{trans} < \text{cis} \)\(^3\).

5. Proton magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy has proved extremely useful for determining the disposition of substituents in many cyclophosphazene derivatives. Three criteria are of general use for this purpose: (a) the number of proton environments, (b) the value of \( ^3J^*(\text{P-H}) \) and (c) the relative chemical shifts (geminal/nongeminal and cis/trans). However, unambiguous assignments are not always possible (particularly for cyclo-traphosphazenes) as it is often possible to interpret the data on the basis of more than one isomeric configuration. In many cases, the different proton environments are poorly resolved but some simplification is possible by recording the spectrum at higher field strength (i.e., 220 MHz)\(^3\). Fig. 7 illustrates the \(-\text{NCH}_3\) region of the 220 MHz spectrum of the tris-ethylamino derivative, \( \text{N}_4\text{P}_4\text{Cl}_4(\text{NHEt})_3 \). Each methylene group is coupled to the neighbouring methyl protons and also to the adjacent phosphorus nucleus. The multiplicity of the signals clearly indicates that there are three \(-\text{NCH}_3\) environments in this molecule. The magnitude of \( ^3J^*(\text{P-H}) \) (14.0 Hz) indicates a nongeminal structure\(^3\). Three such structures are possible (Fig. 8) but only one of them can give rise to three distinct \(-\text{NCH}_3\) environments [Fig. 8 (a)].

The assignment of structures to the chloro (N-methyl-anilino) cyclotri-\(^4\) and cyclo-tetra-\(^4\) phosphazenes is largely based on their proton NMR spectra. The \(^1\)H NMR data for the five tetrakis (N-methylanilino) cyclotetraphosphazene isomers of \( \text{N}_4\text{P}_4\text{Cl}_4(\text{NMePh})_4 \), along with their spectra and structures are shown in Fig. 9. The spectra provide good examples of the three criteria mentioned above. For example, the magnitude of \( ^3J^*(\text{P-H}) \) for \( \equiv \text{PCI}(\text{NMePh}) \) groups are \( \sim 4-5 \) Hz higher than that for \( \equiv \text{P}(\text{NMePh})_2 \) groups. Another notable feature of the spectra is the appearance of additional lines or broad humps among the sharp doublets expected from first-order considerations. This phenomenon is referred to as "virtual coupling". The presence (or absence) of "virtual coupling" can sometimes be useful for assigning structures to isomeric derivatives. The 2, 2, 6, 6-structure of \( \text{N}_4\text{P}_4\text{Cl}_4(\text{NMePh})_4 \), m.p. 162°C, follows from the absence of "virtual coupling" in its proton NMR spectrum [Fig. 9 (a)]. We have also distinguished the geminal 2, 2, 6, 6- and 2, 2, 4, 4- \( \text{N}_4\text{P}_4\text{Ph}_4(\text{NMe})_4 \) isomers as the spectrum of the latter contains a dimethylamino doublet with pronounced "virtual coupling"\(^3\). The strength of "virtual coupling" is closely related to the differences in chemical shifts of the phosphorus nuclei involved. Consequently, in some cases the above criterion is
The $^1$H NMR spectrum (220 MHz, CDCl$_3$) of N$_2$P$_2$Cl$_6$(NHEt)$_3$ (the $\text{--NCH}_2$ region only) is not useful for differentiating isomers [e.g., the proton spectra (NMe signals) of both 2-trans-4 and 2-trans-6-N$_2$P$_2$Cl$_6$(NMePh)$_2$ exhibit "virtual coupling"][7].
The 100 MHz $^1$H NMR spectra of bicyclic phosphazenes are generally too complex to yield structural information. However, the spectra are considerably simplified when they are recorded at higher field strength (220 MHz)$^{19,20}$. Complete analysis of the spectrum is then possible in most cases and confirms the bicyclic structure. A typical spectrum is shown in Fig. 10 along with the assignments. The protons of the groups attached to the junction phosphorus atoms, P (2) and P (6) are considerably deshielded. The two amino substituents at P (4) [or P (8)] are non-equivalent. An analysis of the shifts observed on the addition of Eu(fod)$_3$ indicates that the protons of the group pointing to the bridgehead nitrogen atom resonate at a higher field$^{19}$.

6. $^{31}$P NMR Spectroscopy

The commercial availability of Fourier Transform (FT) NMR spectrometers and the application of broad-band proton decoupling have improved the quality of phosphorus NMR spectra dramatically in recent years and good spectra can now be obtained with relatively small quantities of samples. Phosphorus NMR spectroscopy often confirms the structure assigned by an interpretation of proton NMR data. In some cases, it can provide independent evidence where proton NMR spectra may be uninformative. Many cyclophosphazene derivatives provide examples of multi-spin systems and their $^{31}$P spectra cannot usually be analysed by a first order approach.

Our studies of the reactions of $\text{N}_3\text{P}_3\text{Cl}_6$ (I) with ethanolamine and ethylenediamine have greatly benefited from phosphorus NMR data$^{21}$. The technique conclusively demonstrates that these reagents react by the spirocyclic route (see section 2). The spirocyclic derivatives, $\text{N}_3\text{P}_3\text{Cl}_6$($\text{NHCH}_2\text{CH}_2\text{X}$) ($\text{X} = \text{O}$ or $\text{NH}$; $\text{R} = \text{Ph}$ or $\text{NHBu}^+$) each, contain three chemically different phosphorus nuclei. The $^{31}$P $^1$H$^1$ spectra of these compounds are of the ABX type and a typical example is shown in Fig. 11. Such spectra are exceedingly rare in cyclotriphosphazene chemistry.
The $^{1}H$ NMR spectra (NMe region only) of five isomers of N$_4$P$_4$Cl$_4$(NMePh)$_4$ along with their structures. The values shown are the chemical shifts of N-methyl protons with $^3J(P\text{-}H)$ in parentheses. Spectrum (e) was measured in C$_6$D$_6$ at 220 MHz; the other spectra were recorded at 100 MHz in CDCl$_3$. 
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Fig. 10. The -NCH₂ and -NCH₃ region of the ¹H NMR (220 MHz, CDCl₃) spectrum of the bicyclic phosphazene, N₄P₄(NMe₂)₆(NHEt)(NEt) with assignments.

The geminal structure of the bis (isopropylamino) derivative, N₆P₃Cl₄(NHPr)₂ m.p. 114°, is deduced from its ³¹P ¹H NMR spectrum which consists of a doublet (19.8 δ) and a triplet (6.2 δ) (relative intensities 2:1). The ³¹P NMR spectra of the non-geminal isomers are of the AB₂ type (trans: δ₁ 21.3, δ₂ 19.1; cis: δ₁ 21.9, δ₂ 19.0).¹³

The ³¹P ¹H NMR spectra of cyclotetraphosphazenes with different substituents and bicyclic phosphazenes are particularly interesting as they can provide examples of different types of a four spin system. Derivatives of the general formula, N₄P₄Cl₄(NRR')₂ with amino groups in 2, 4 or 2, 6 positions can be distinguished by their AA' BB' and A₂B₂ ³¹P spectra respectively. The analysis of A₂B₂ spectra is usually straightforward but that of AA' BB' spectra requires computer simulation.²⁶ The spectra of the bicyclic phosphazenes, N₄P₄(NHR)₆(R) (R = Me or Et) [Fig. 3(a)] are also of the A₂B₂ type. Unsymmetrically substituted bicyclic phosphazenes [Fig. 3(b)] provide examples
of an $A_2BC$ spin system. The $^{31}$P chemical shifts of bicyclic phosphazenes lie in the region 15-22 \( \delta \) which is well separated from the region characteristic of fully-aminolysed cyclotetraphosphazenes (4-10 \( \delta \)). Phosphorus NMR spectroscopy can thus be used as an analytical tool to estimate the yields of bicyclic phosphazenes and fully aminolysed cyclotetraphosphazenes formed in the same reaction$^{10}$ (Section 2). The spectrum of one such mixture is illustrated in Fig. 12.
Fig. 12. The $^{31}$P [$^1$H] FT NMR spectrum (36.4 MHz, CDCl$_3$) of a mixture of (a) $N_4P_4(NMe_3)_4$ (NHE)$_2$(NE) and (b) $N_4P_4(NMe_{6a})$ (NHE)$_2$. 
7. Infrared spectroscopy

The infrared spectra of cyclophosphazenes are valuable for "finger-printing" and thereby ascertaining the identity and purity of products in synthetic reactions. The spectra are characterised by a dominant vibration at 1150–1350 cm\(^{-1}\) which is attributed to a ring stretching frequency, \(\nu(P=N)\). For (amino)cyclophosphazenes, the above vibration occurs at 1210–1175 cm\(^{-1}\) whereas for (amino)cyclophosphazenes, this band is observed at 1300–1250 cm\(^{-1}\). The \((P=N)\) band is usually broad and often split. A precise measurement of \(\nu(P=N)\) is hampered by bands arising from the vibrations of the exocyclic amino substituents which also occur in this region\(^3\).

Infrared spectroscopy is particularly useful to distinguish hydrochloride adducts of (amino)cyclophosphazenes from their free bases. It also indicates that protonation occurs at a ring nitrogen atom. The ring stretching vibration, \(\nu(P=N)\) undergoes an upward shift of ca. 40–60 cm\(^{-1}\) in the adduct. New absorption bands are observed at 915–930 and 2400–2650 cm\(^{-1}\) attributable to \(-P-N(H)-P-\) linkage. The infrared spectra of the new bicyclic phosphazenes discovered by us have distinctive features compared to those of their related fully aminolysed cyclotetraphosphazene derivatives. The \((P=N)\) stretching frequency appears at 1185–1200 cm\(^{-1}\). A new band at 820–830 cm\(^{-1}\) is observed which has been assigned to the bridgehead \(P-N-P\) unit—the phosphazene part of the bicyclic skeleton. Fig. 13 shows some typical spectra which illustrate the above points\(^2\).

8. Other studies

The Faraday effect of some (amino)chloro cyclophosphazenes\(^5\) and nuclear quadrupole resonance of chloro- and bromo- cyclophosphazenes have been studied\(^7\). The crystal structures of triphenylphosphazenyln(NPPPh) \(\text{N}_2\text{P}_3\text{Cl}_3(\text{NPPPh})\) substituted cyclophosphazenes, \(\text{N}_2\text{P}_3\text{Cl}_3(\text{NPPPh})\) \(\text{N}_2\text{P}_3\text{Cl}_3(\text{NPPPh})\) \(\text{N}_2\text{P}_3\text{Cl}_3(\text{NPPPh})\) \(\text{N}_2\text{P}_3\text{Cl}_3(\text{NPPPh})\) \(\text{N}_2\text{P}_3\text{Cl}_3(\text{NPPPh})\) \(\text{N}_2\text{P}_3\text{Cl}_3(\text{NPPPh})\) \(\text{N}_2\text{P}_3\text{Cl}_3(\text{NPPPh})\) have been determined. The observed changes in the conformations of the phosphazene side chain with respect to the local ring NPN segment are correlated with the conclusions drawn from basicity measurements\(^4\).

Pot culture studies on the use of \(-\text{hexaammonocyclotriphosphazene}, \text{N}_2\text{P}_3(\text{NH}_4)_6,\) as a fertilizer for \(\text{Pumna Ragi}\) crop have been carried out in collaboration with the University of Agricultural Sciences, Bangalore. Enhanced yields of grain compared to control experiments (no fertilizer) are obtained. The yields are almost the same as those obtained with conventional treatments (ammonium sulphate + superphosphate or urea + superphosphate) on equal nutrient (N and P) basis at the recommended levels\(^1\). On a weight to weight basis, the quantities of the phosphazene compound required to produce the same effect as the two conventional treatments are ten- and six-fold less respectively.

9. Concluding remarks

In this review we have attempted to summarise the significant results of our fundamental investigations on (a) the replacement reactions of the octachloride, \(\text{N}_2\text{P}_4\text{Cl}_6(\text{II}),\) with
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Fig. 13. Infrared spectra of (a) \( \text{N}_4\text{P}_4(\text{NMe}_3)_6(\text{NHEt})_2 \), (b) \( \text{N}_4\text{P}_4(\text{NMe}_3)_6(\text{NHEt})_2 \), 2HCl and (c) \( \text{N}_4\text{P}_4(\text{NMe}_3)_6(\text{NHEt})_2(\text{NEt})_4 \).

various amines, (b) the isolation and characterization of bicyclic phosphazenes, a novel class of phosphorus-nitrogen compounds and (c) the formation of spirocyclic phosphazenes. We are now expanding our studies to other areas, viz., (a) alcoholysis reactions of chlorocyclophosphazenes, (b) thermal rearrangement reactions of alkoxy cyclophosphazenes, (c) tautomeric forms of hydroxycyclophosphazenes, (d) reactions of phosphazeny1 substituted cyclophosphazene derivatives, (e) kinetic studies and (f) metal complexes of phosphazenes. Our approach to these topics will again reflect our belief that many aspects of modern science require resources that are not always available in a particular laboratory. By complementing the resources of our respective laboratories, we are able to investigate a larger range of problems in greater detail and thereby make a more substantial contribution to the subject. We hope that this article will demonstrate how successful collaboration can help the participants to pursue their scientific interests to their mutual benefit.

10. Acknowledgement

We are greatly indebted to the University Grants Commission, New Delhi, and the Overseas Development Ministry, London, for their generous support. We also thank
the British Council for their valuable assistance. We are pleased to acknowledge the enthusiastic help and collaboration of scientists in Bangalore, U.K. and elsewhere for their participation in solving specific problems related to our work. In particular, we should like to mention Professors H. Manohar and K. Venkatesan (I.I.Sc., Bangalore—X-ray studies), Professor T. S. Cameron (Dalhousie University, Nova Scotia—X-ray studies), Dr. R. Keat (University of Glasgow—$^{31}$P NMR studies) and Dr. J. Ramakrishna (I.I.Sc., Bangalore—NQR studies). Our thanks are also due to the research scholars, Drs. A. C. Sau, M. N. Sudheendra Rao and K. Ramachandran for their valuable contributions to the project.

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BOOK REVIEWS


This is a good book which satisfies the objectives of the authors, namely, to provide an introductory course in electronic circuitry for the University students (equivalent to final year B.Sc. or first year M.Sc.). The physics students require an acquaintance with the physical processes in semiconductor materials and devices, taught in the Solid State Physics course, and with the basic ideas of electronic circuitry. It is the latter need which is tackled by the present authors with considerable success.

A quick look at the material presented in the book gives an idea of the way in which the authors have systematically developed their theme. Chapter 1 gives a brief introduction to the physical principles of semiconductors and the working of p–n junctions, at a simplified but adequate level. This chapter is followed by the use of diodes, not only as rectifiers but also in wave shaping, AM|FM demodulation and even in phase sensitive detection. The third chapter gives the basic principles and construction of transistors, followed by a chapter on the equivalent circuits for small signals. The stage is set for the next two chapters on single and multi-stage transistor amplifiers. Chapter 7 discusses the various types of feedbacks and their diverse applications. Then one goes to switching circuits, essentially the various types of multivibrators, with the digital circuits forming chapter 9. The next chapter deals with the problems of d.c. amplification.

All the above have been concerned with bipolar transistors. The next chapter deals briefly with unipolar field effect transistors and thermionic valves viewed as voltage-driven devices. Chapter 12 is a brief account of the negative resistance devices, opto-electronic devices and integrated circuits. After dealing with all the building blocks in the 12 chapters, there is a short chapter on small systems like regulated power supplies or decade counters. The next chapter contains a description of the laboratory exercises useful in teaching the subject. Chapter 15 gives some comments and solutions to the laboratory exercises. The book ends with three appendices on a variety of mathematical accessories.

The above description merely conveys the quantity of the coverage in the book. The quality of the material is equally worthy of comment. The material is logically developed and the book makes pleasant reading. In a vast subject like electronics, every author has his or her own bias and room exists for differing points of view. What one should check is whether the authors are successful with the point of view chosen by them. The answer is clearly positive in this case. The paper-back edition is a good buy for the money.

E. S. R. Gopal

I.I.Sc.—12

The science of motion, or mechanics, has been a basic subject for nearly four centuries now, starting with Galileo and Newton in the early days and coming to Einstein in recent times. The adjective classical is used to describe that part of the mechanics which deals largely with macroscopic sized objects, to differentiate it from the quantum description suited to microscopic elementary particles. Thus classical mechanics becomes a jumping board from where one starts a discussion of quantum phenomena or electrodynamics or celestial mechanics. Every serious student of physics or mathematics has to be acquainted with the basic principles of the subject and has a choice of many good text books from which the subject can be learnt.

In a sense, the present book follows a traditional path, starting with the mechanics of single particles and systems of particles. It then goes on to discuss the motion in central fields, small oscillations, Lagrangean formulation, Hamiltonian mechanics, canonical transformation and ends with the mechanics in the framework of the special theory of relativity. There is an appendix on the different coordinate systems. Indeed the first two chapters on vector algebra and on vector analysis would normally be treated as appendices in most books on mechanics. The authors are quite correct in their statement that the book could be used, with a suitable choice of the topics, at the B.Sc. level or at the M.Sc. level of most Indian universities. When judged by the goal set in this fashion, the book has undoubtedly fulfilled the objectives.

Because of this appeal to a wide class of students, the book is likely to be well received. In addition, the book is also well written and bears the mark of being tested on many batches of students, for instance, in the manner in which examples are worked out. Each chapter has a set of concept-based short questions as well as a collection of more detailed problems. This is also an attraction of the book. The preparation of the book has been assisted by a UGC programme and the printing has been subsidized by the National Book Trust. Thus the book is priced Rs. 18, which makes it a good value for the money spent.

Because of these plus points, the book is likely to go in for a reprinting soon. This likelihood makes one suggest a few items for the authors to ponder about. They have noted in time many typographical slips and have inserted an errata sheet. They should also consider whether a short chapter on the elements of solid and liquid mechanics (elasticity and hydrodynamics) would give a sense of completeness. They could also consider the possibility of providing answers to a few of the problems at the end of each chapter, in order to allow the students to check their progress. In the bibliography at the end of the book, one expects to find the book of Sudarshan and Mukunda "Classical Dynamics : A Modern Perspective" (Wiley - Interscience, New York, 1974). Although the book is beyond the level of our general M.Sc. students, it has become a classic in interpreting classical mechanics in a modern framework. The section on Compton effect seems out of place in a chapter dealing with relativistic mechanics. It could be
accepted in a place dealing with collision phenomena. In a chapter on relativistic mechanics, one may find some developments of the invariance properties of Thomas precession or other specific effects of special relativity. As mentioned earlier these suggestions are for future considerations.

The book leaves a pleasing impact and can certainly be recommended for our students.

E. S. R. Gopal