

A THEORETICAL STUDY OF THE ELECTROKINETIC TRANSDUCER

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'1

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## LIST OF SYMBOLS

|   |           |                         |
|---|-----------|-------------------------|
| A, B, C, D, Constants                               | Cu        | Copper                  |
| $\lambda$ Wavelength in angstroms                   | K         | Potassium               |
| d Displacement                                      | Li        | Lithium                 |
| E Dielectric constant                               | Na        | Sodium                  |
| e Charge on electron                                | =         | Equals                  |
| ev Electron volt                                    | $\neq$    | Not equal to            |
| h Planck's constant and depth of potential box      | $\approx$ | Is of the order of      |
| k Constant  | $\sim$    | Equivalent              |
| m Mass  | $\alpha$  | Force or angle          |
| P Pressure  | $\Delta$  | Increment               |
| p Momentum  | $\ominus$ | Angle                   |
| q Displacement                                      | $\lambda$ | Wavelength              |
| r Radius  | $\nu$     | Frequency               |
| T Kinetic Energy                                    | $\pi$     | 3.1416                  |
| t Time  | $\rho$    | Density                 |
| $U_1, U_2$ Frequency                                | $\phi$    | Angle                   |
| V Potential energy                                  | $\Psi$    | Amplitude of wavelength |
| v Velocity  | $\psi$    | Amplitude of wave       |
| W Total energy                                      |           |                         |
| $W_1, W_2, W_3, \text{ or } W', W'',$ Energy levels |           |                         |
| x Displacement                                      |           |                         |
| $\dot{x}$ Derivative with respect to time           |           |                         |

## PREFACE

In submitting this thesis, one of the first to be submitted by the School of General Engineering, it is felt that some introductory remarks are in order. The subject chosen could easily fall into the field of Applied Chemistry, Applied Physics or Engineering. It is necessary to correlate these fields to some degree for the purpose of obtaining unity of thought. Let us think of Chemistry as that science which investigates the composition of substances, together with the various combinations and decompositions resulting from the action and influences of chemical forces as they act on the outer electrons surrounding the nucleus. On a similar basis Physics is that science which treats of the laws and properties of matter and the manifestations and transformations of energy when the nucleus and all accompanying electrons are considered. Similarly, then one should think of Engineering as that science which utilizes the findings of the physicist and chemist in the conception of, and reduction to, the design and construction of those material items required by society, in a manner that is efficient, economical, and safe for use.

This science of Engineering is divided into various specialties born of necessity to serve the demands of society. Recently in the development of the Institute of Technology, certain of the leaders have become convinced that there exist justifiable need for a combination of these special fields into a composite course in basic engineering. This curriculum has been termed General Engineering which adequately describes the undergraduate program.

The administration is of the opinion that the Graduate work, which requires one-third of the total credit hours in the field of physics and mathematics, is more fundamental than is the case with the special fields.

To be in keeping with the General Engineering curriculum, a thesis topic has been chosen which is fundamental or basic in nature, yet it is one which has potential application in all fields of Engineering. Since this work is based primarily on a specialized field of Physics and is presented by an engineer for engineering consumption, the author sincerely desires his friends in the field of physics to forgive the elementary nature of this presentation of their highly developed techniques and scientific methods. To those in Engineering being introduced to the new concepts to follow, it is the authors hope that they will not feel that this work has departed too far from the definition of Engineering previously given.

This presentation of an explanation of the phenomena arising from the use of a fritted tube and suitable electrodes in the generation of an electric potential has been made primarily by utilization of one of the newer branches of physics--quantum mechanics. There is little doubt that one sufficiently well versed in the field of Chemistry and Physical Chemistry could arrive at just as plausible an explanation. It so happens that the author's training and experience indicated that the quantum mechanics method was the most simple and direct.

Most of the theoretical explanation to follow was taken from Elementary Quantum Mechanics by Ronald W. Gurney, M. A., Ph. D., Research Associate in the University of Bristol. To those familiar with this work, you will find the text and diagrams identical with the work of Gurney in places, and differing in others since this work is confined to engineering application wherever possible.

## ACKNOWLEDGMENT

The author wishes to take this opportunity to express his gratitude to Doctor Clark A. Dunn for his very helpful suggestions concerning the organization of the work to follow, and for his cooperation in the preparation of the material. To Professors Fristoe and Betts of the Electrical Engineering Department, the author is indebted for many of the useful ideas and suggestions resulting from the discussions of common problems from divergent points of view. To Mr. Gordon Smith of the Research Apparatus Development Laboratory, the author is indebted for the success of most of the experiments because of his skill in the art of glass blowing and metal work. The author feels that it would be a serious omission not to express his appreciation to his wife J. Mildred Norton for her valuable aid in the proof reading and preparation of the original manuscript.

## CHAPTER I

### PRESENTATION OF PROBLEM AND REVIEW

#### OF THEORY OF OPERATION

The October 1948 issue of The Review of Scientific Instruments carried an article describing an electrokinetic transducer, by Milton Williams of the Humble Oil and Refining Company, Houston, Texas.<sup>1</sup> A brief review of the article was given as follows:

A description is given of a transducer which utilizes, for the transition of sonic to electrical energy, the electrokinetic potential development by the movement of a fluid through a porous solid. The construction and calibration of the transducer are described, and results of measurements of pressure fluctuations in oil pipe lines are presented.

The Division of Engineering Research with which the author is associated had been requested to purchase equipment similar to that described in the above article, but commercial equipment is of questionable accuracy and dependability. After surveying the constructional features of the transducer described, it was decided that one should be built for laboratory trials.

From this beginning a series of events followed which made it desirable to consider certain aspects of this project as a thesis topic. Trial runs using the above described transducer connected directly into a #208 DuMont Oscilloscope revealed some interesting results. As a pressure pickup instrument the results were highly satisfactory, especially so since the

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<sup>1</sup> Milton Williams, The Review of Scientific Instruments, Vol. 19, No. 10 (October, 1948), pp. 640-646.



electrode arrangement gives a wide degree of control over the transducer characteristics. The start of further investigations resulted from some unexplained results obtained while working with various electrode arrangements.

Referring to Fig. 1 for constructional details and arrangement of parts, it is interesting to note that from this cell a potential output of the order of 10 to 15 millivolts was obtainable. Furthermore this potential output was found to be polarized as was evident from the scope image of the generated voltage. It was also observed that a useful output was obtainable from the transducer without amplification when weights no larger than a few milligrams were dropped on the diaphragm. This indicated the extreme sensitivity which could be obtained from the transducer.

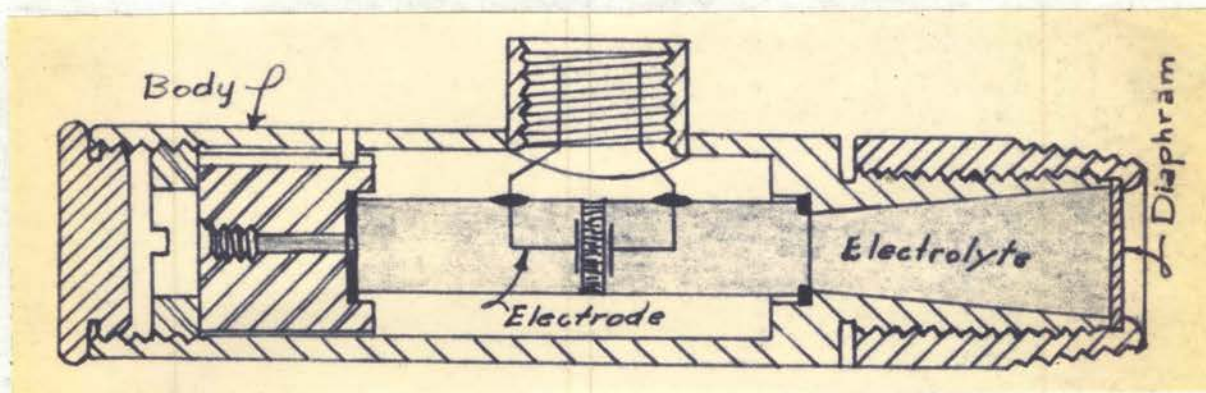


Fig. 1. Electrokinetic Transducer

Giving due consideration to these findings it was evident that the fritted tube when fitted with proper electrodes and charged with an electrolyte was capable of performing the duties of most of our common transducers such as the variable condenser, variable resistance, variable inductance and piezoelectric phenomena. While working with Professor H. T. Fristoe, the idea was conceived that this same fritted tube when properly fitted with electrodes

could possibly be used to perform in a manner similar to the diode and triode vacuum tube, i. e., to rectify, amplify, and oscillate. With these possibilities in mind, it was thought that the theory underlying such a potentially useful tool fulfilled the qualifications for theses in Engineering, particularly General Engineering.

The origin of the potential difference appearing between the electrodes as discussed in Mr. Williams article did not coincide with certain observed facts. The transducer was originally developed from considerations arising in electro-osmotic and accompanying phenomena. Various texts discuss electrokinetic phenomenon wherein the streaming potential accompanying the fall of solid particles through a fluid, or the flowing of a fluid past solid boundaries, is associated with the development of potential differences. The potential differences at the electrodes in the transducer were attributed to this streaming potential, arising from the flow of fluid through the porous diaphragm. Observation revealed that the output of the transducer when viewed on the scope did not necessarily follow the flow of the fluid through the diaphragm. Referring to Fig. 1 again, it is evident that for the fluid to flow through the fritted disc it must first be activated by a movement of the very stiff steel diaphragm. In the laboratory it was noticed that a fairly severe blow on the diaphragm with the plastic handle of a screw driver resulted in a relatively small deflection on the scope. Conversely light blows with the blade of the screwdriver resulted in a greatly increased deflection of the scope. This finding does not invalidate the use of the transducer as a pressure pickup due to what might appear to be a non-uniform relationship. It does serve to demonstrate that the potential does not appear to depend upon the flow of the fluid, but rather in this case seems to be activated by the shock wave traversing the sensitive element. Furthermore



with a modified version of the apparatus consisting of an all glass tube without the brass protecting body experiments were made using the transducer as a microphone wherein it was again observed that when the tube was orientated with it's axis parallel to the source of sound a minimum output was observed. With the axis oriented perpendicular to the source of sound an increased output was observed, which, if output were dependent upon fluid flow, should have resulted in a minimum output in this position. These observations led to a serious questioning of the origin of the potential difference developed. In order to question a proposed theory one must offer some substitute theory which represents a plausible explanation of the phenomenon, and which can be substantiated by experimental means. The value of a theory lies not only in its ability to account for the experimental facts, but also in its suggestiveness of new modes of attack. Therefore, if the theory to be suggested is of value, it should suggest other explanations of basic phenomenon.

Considerable time was spent checking into the possibilities of obtaining the change from electrophoretic phenomenon. A brief discussion of this phenomenon will be given using material developed in the text Electro-Chemistry, by Craighton and Kohler.<sup>2</sup> When two heterogeneous substances are brought into contact one with the other, the one possessing the higher dielectric constant will assume or take on a positive charge with respect to the other. ( $\epsilon$  water = 81;  $\epsilon$  pyrex glass = 7). The mechanism by which this charge takes place is not clear, two separate phenomena manifest themselves and it is not known with scientific certainty which occurs first. In this

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<sup>2</sup> H. Jermain Craighton, Principles and Applications of Electrochemistry Vol. 1, Principals, pp. 143-165.

case common water molecule is known to be non-symmetrical having 105 degrees between the two oxygen atoms, and we find on the surface of most materials in contact with water a double layer of oriented molecules. This double layer is practically immovable and is the so-called stationary film encountered in hydraulics, soil mechanics, heat transfer, etc. Since water generally assumes a positive charge with respect to the solid, we find the surface of the solid to be negative and the water molecules oriented with their positive charge next to the surface. Experiment and observation have shown that this effect does not end abruptly, but exerts it's influence to the surrounding medium diminishing according to Fig. 2.

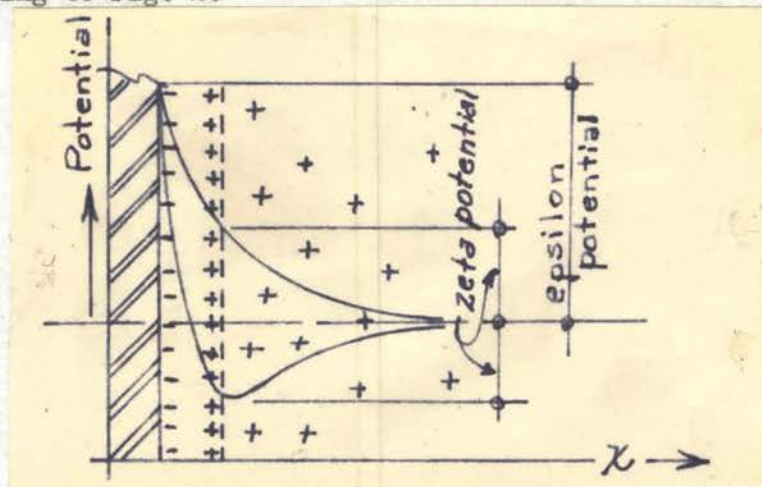


Fig. 2. Potential Distribution

The orientation of the molecules and the effect of the apparent charge either give rise to ionization of the molecules, or ionization of the molecules is the contributing factor in the orientation of the molecule and hence the origin of the charge. Ionization is the gain or loss of one or more of the loosely bound outer molecular electrons. (An atom or molecule being originally electrically neutral has it's electrical condition changed to positive when it loses an electron because of the loss of part of the negative charge



that contributed to the neutrality balance.)

Therefore, we have then either a double layer formed producing ionization or ionization takes place aiding in the formation of the double layer. Some support is found for the ionization preceding the double layer from the chemical reaction of the water and glass. This reaction is known to take place at a very slow rate, however if we concede this source of ionization we should expect the useful output from the transducer to increase with time until some optimum output is reached, and then to diminish due to increased conductance of the electrolyte. This has not been found to be the case, the cells have their greatest output immediately upon charging. This output seems to decline at a very slow rate; some cells have shown only negligible loss over periods as long as 18 months.

Of more common occurrence is the rapid formation of a double layer immediately upon contact of a fluid and solid and at the interface of fluid to fluid or fluid to solid contacts. Returning to the non-symmetrical water molecule it is conceivable that these molecules orientate themselves along the solid boundary due to polar conditions. Once a few molecules have oriented themselves at the surface boundary the surface begins to acquire a negative charge, thereby attracting more water molecules until the surface is entirely covered. In this manner without the benefit of external forces, the solid becomes negatively charged and the water positive. Necessarily then the strong positive charge in the fluid will extend its influence for some distance into the fluid. Determinations of the rate of potential decrease show that it follows some exponential function. For stationary water in contact with glass the thickness of the charged film that remains practically immovable is of the order of one to two molecular diameters; while the exponential region extends for several molecular diameters into the solution

before diminishing to negligible proportions. The exponential region begins to acquire mobility immediately after leaving the fixed boundary film. It is conceivable to contribute the charge in the transducer to the flow of fluid through the porous diaphragm which would sweep part of the charged particles out into the region surrounding the electrodes. However, if the potential output is attributed to this means, it should be possible to increase the output by increasing the number of charged ions available to be collected at the electrodes. Experiment has shown that the output of the cells follows the condition found to be most conducive to electro-osmosis. Instead of more and more ions giving additional effect, there is an optimum concentration of ions corresponding to optimum output. One is led to believe then that units which have remained practically unchanged for long periods must have some stabilizing condition which holds the ionic concentration at or near the optimum. It is hard to visualize what constitutes this stabilizing influence since as previously discussed the chemical reaction between the water and the glass is proceeding slowly all the time which adds to the ionic concentration.

Before arriving at a suitable place to propose the new theory of operation, considerable time should be spent in the development of quantum mechanics to provide a foundation for the proposal. It is not expected that the quantum mechanics presented will be complete, and all unnecessary mathematics has been omitted for the sake of simplicity.

## CHAPTER II

### INTRODUCTION TO THE IDEAS OF QUANTUM MECHANICS

We are all familiar with the spectrum of electromagnetic radiation ranging from the very low frequencies of a few cycles per second to the extreme frequencies accompanying radioactive disintegration or cosmic rays. (See Appendix A) We are also aware of the extremely small range of frequencies into which all visible light is confined. This causes us no inconvenience since the sun's radiation, our source of light, falls almost in the center of the optimum range of visibility to the human eye. Possibly in the scheme of development of the universe the controlling powers have caused the eye to be activated at the frequency of the radiations present for the purpose of allowing observations of limited portions of the universe. It also happens that the production of artificial radiations in the visible range are easy to produce; therefore, we are allowed to extend our efforts even when natural radiations cease, due to the systematic movements prescribed by the rules of universal motion. Great minds have expended unbelievable effort beginning long before the advent of the telescope by Galileo on this narrow range of light frequencies. The laws of optics have been developed and perfected over the centuries and represent today one of our most exacting as well as most informative scientific fields. Attesting the development of this branch of physics are the wonders of the two hundred inch telescope on Mount Palamore. Yet since our physical size on the scale of the universe, or better from the human point of view, we sometimes lose sight of the limitations of our physical laws because they hold true in such a large percentage



of the cases to which they are applied. Take for example the laws of optics which remain valid in the cases in which we apply them - yet should the dimensions of the universe remain unchanged and our size suddenly be reduced by one-thousand times, then optical instruments of the non-reflecting type constructed by our present laws of optics would no longer yield the same precise result. The laws of optics would fail because the dimensions of the lens itself would be approaching in thickness the length of a wavelength of light. This means that there would be no continuous wave or succession of light quanta for the lens to average the effect of the incident light; hence, the lens would be unable to cause the light to react in the manner in which it does on our present scale with the universe. The practice of taking measurements and writing laws on the statistical averages of the results of the action of millions and millions times millions of particles is the basis of our present laws of engineering. Take for example only a sufficient number of particles such that the removal (or addition) of ten or a hundred particles affects the total an appreciable percentage and the laws of engineering meet with the same lack of accuracy that the laws of optics did in the previous example. Pressures inside a closed system, for example, are attributed to the molecular activity of the fluid filling the system. Imagine a closed system having two compartments connected by an orifice one molecule in diameter; we say according to our present point of view that the pressure on each side of the diaphragm is equal. If the system could be reduced to one in which the fluid consists of only nine molecules and the length of the orifice connecting the two parts of the system is of negligible length, then we must at all times have an unbalanced pressure since we will have more molecules on one side than the other.

The recognition of discontinuities does not invalidate our present laws, but rather restricts their sphere of application. In all our engineering problems, we are dealing with matter composed of a sufficiently large number of particles so that the laws of statistical averages apply. It is interesting to note that, while we are not particularly hindered by this physical limitation in engineering and the same is true in the other sciences to greater or lesser degree, the same ideas apply to our social life as well. One of the best established laws of economics is the law of supply and demand. This law is dependent upon the operation of statistical averages for its enactment. Imagine, for instance, two suppliers and one consumer or vice-versa. Insurance rates are dependent upon the statistical averages holding for a certain percent of the population insured.

Without some preparation and forethought an announcement that Newton's law of gravitation held only in certain restricted limits would certainly be met with scorn by engineers. Yet this is exactly what happens. Newton's law was developed from an observation and will hold as is observe daily, because the point of observation is the same as that from which the law was founded. When a rock is thrown into the air, for instance, it is expected to return as far as possible to some lower state of potential energy in accordance with the law of gravitation. To how many particles was kinetic energy delivered? To count them would be an endless task. Hence with this great multitude of particles, we observe the law of gravitation being enacted as the statistical average of all these particles exchange energy and balance their motion so as to coincide with the law previously observed. If it were possible to observe each particle separately, does it seem practical that some of the particles would not obey Newton's law? Maybe not at this point,

but later it will be evident that while the particles appear to be solid and immovable from our point of view, there is a probability that an individual particle may be at a considerable distance even approaching infinity from the center of the mass at any instant.

The past few paragraphs have been included to show why quantum mechanics has been used to discuss the problem at hand, in this instance we have to deal with particles which no longer conform to classical mechanics. If we could again imagine ourselves becoming so small that from our point of view atoms appeared to be the size of base balls, then the classical laws of mechanics culminating with the great work of Hamilton would no longer hold because the basis of classical mechanics is statistical averages.

Let us consider our universe in its entirety as it is known today. Classical mechanics cannot accurately predict the happenings throughout interstellar space because the particles are too few, too large, and too far apart for their coordinated action to lend themselves to statistical average. This point of view is admirably shown by Einstein's theory of relativity. At first thought, one might conclude that at least three concepts and methods of calculation are required, one for the microscopic universe, one for the macroscopic universe and a third for the universe in its entirety consisting of ours and countless other galaxies, whose only law is constant change. However, this is not the case; the displacement of or relegation to its proper sphere of application of classical mechanics by N. Bohr in the early 1900s wherein matter and energy gained the concepts of quantization, and the evolution of the newer quantum mechanics in 1925-26 provides us with a tool that was developed to yield a result in agreement with observed measurements. While being developed for predicting the behavior of the microscopic



universe aside from the nucleus of atoms, it has been found to be applicable in the macroscopic universe when properly extended with aid from the theory of relativity. Therefore we see that the quantum mechanics is compatible with the classical mechanics, in fact there must be a one to one correspondence between the two when they are applicable to the same system.

### CHAPTER III

#### QUANTUM MECHANICS

In order to appreciate the significance of the proposed theory of operation of the electrokinetic transducer, certain fundamental concepts must be clearly understood. These concepts will be developed in the material to follow with particular attention being given to graphical presentation in order that a qualitative understanding may be had without recourse to undue mathematical derivations.

Briefly the points to be covered are as follows, first there is the concept that all particles in the universe have an allowed region or sphere of activity beyond which they are forbidden. Then the very useful idea of potential boxes defining the boundary between the allowed and unallowed regions and their extension to multiple boxes will be discussed. After developing the boxes it will be shown that the position of the particle can be given by a mathematical expression. This equation developed by the German physicist Schroedinger is invaluable in the solution of atomic problems. Finally the atom as proposed by Bohr will be discussed as well as the newer concepts of atomic structure.

##### a. Allowed and Unallowed Regions and Single Potential Boxes.

One of the first concepts to be developed is that regarding the position of all material particles which make up our universe. The forces of attraction and repulsion between material particles define certain restrictions on their relative positions, these restrictions are known to be a function of the energy

level of the particles. If we assign a region wherein a particle may reside, then that part of space beyond this region is forbidden or unallowed. As the energy of the particle increases or decreases the allowed and unallowed regions change their dimensions. From Newtonian mechanics we have learned that the division between the allowed and unallowed regions is very sharp and definite. In quantum mechanics it is found that the boundary takes on width, in fact, it becomes fuzzy giving rise to the probability of finding a particle outside the allowed region.

In dealing with these allowed and unallowed regions the concept of potential boxes or the path of the potential energy curve between the regions becomes important. The shape, size and significance of the potential box will be discussed and developed. After the boxes have been developed we will take up the  $\psi$  (psi) curves--or the paths followed by the particles as they traverse the allowed region between the potential boundaries.

In using the quantum mechanics approach to atomic problems and relationships it is convenient to first draw or visualize an energy diagram. As we progress to more difficult engineering problems, this method of approach is widely used; therefore, little of the material to follow will be new, only the point of view or position of observation will have to be altered. Eventually, we will work with and examine the Schroedinger wave equation, one of the fundamental equations of quantum mechanics. Since in the above equation in all of its various forms, the potential energy of the system always appears as a function of the coordinates, particular attention will be paid to the potential energy as we progress.

Some thought has been given to the problem of throwing a particle into the air - now let us investigate the energy relationships accompanying the particle as it ascends and descends.

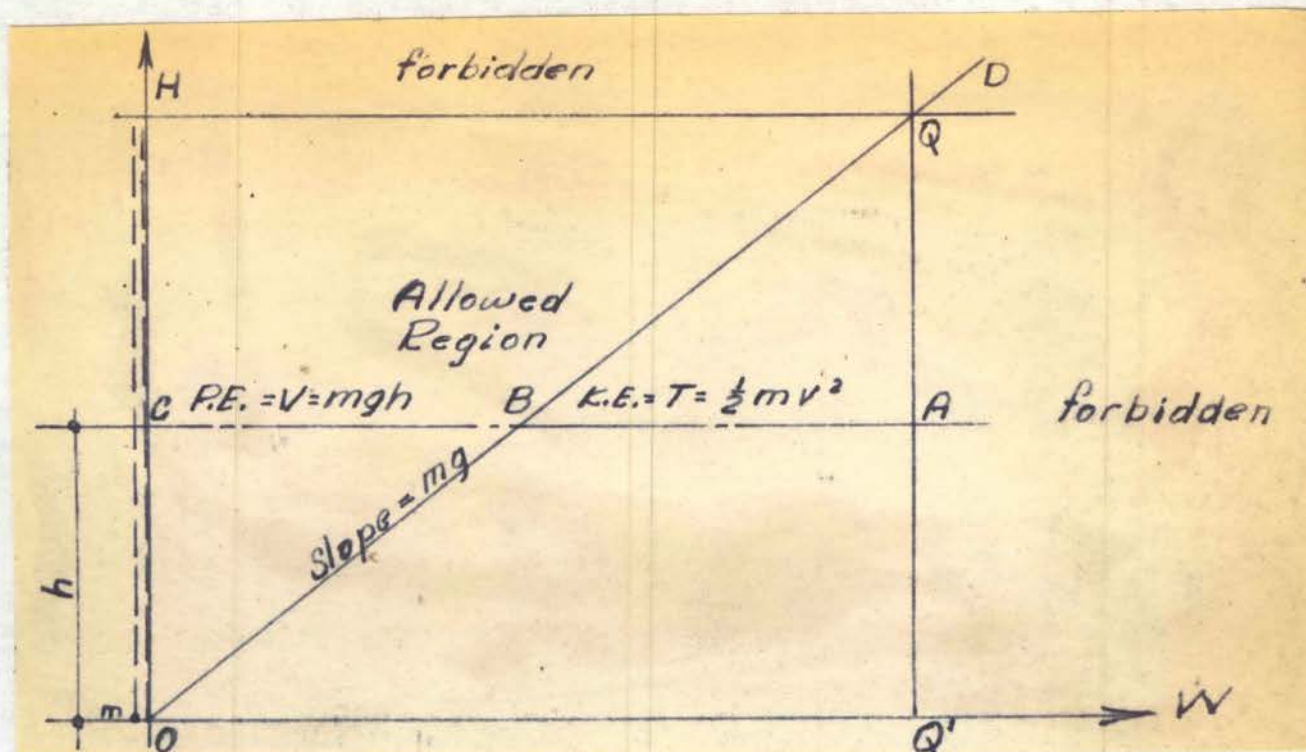


Fig. 3. Allowed and Forbidden Regions

Referring to Fig. 3, if the mass  $m$  is thrown vertically upward with a given initial velocity it will rise to a height  $H$  equal to  $v^2/2g$ . We know from classical mechanics, that neglecting air-resistance the total energy of the system will remain constant. In the above figure, the line  $Q - Q'$  represents the total energy. As the body rises it acquires potential energy  $V$  equal to  $mgh$  at any height  $h$ , and loses kinetic energy  $T = W - V = m/2(v^2 + 2gh) - mgh = \frac{1}{2}(mv^2)$ . Thus lines parallel to the  $W$  axis and divided by the diagonal  $O - Q$  gives the kinetic and potential energy at any height  $h$ . Hence, the potential energy  $V$  increases until it equals the total energy  $W$  at height  $H$ . According to classical mechanics, the particle will now return from the maximum height  $H$  to the starting point. To suggest that the particle might rise to a height above  $H$  is absurd, because to do so it's potential energy would need to be negative - and therefore meaningless. We say then



from classical mechanics that the region below  $H$  is allowed and that above or beyond  $H$  is forbidden. The forbidden region necessarily applies only to particles with a given total energy  $W$ , some other particle with greater total energy can enter this region only to find itself confronted with a similar equalization of energies and forbidden region. This same exchange of energies forms the basis of the equilibrium of the universe.

If  $W = \text{total energy}$

$V = \text{potential energy}$

then when  $W > V$  we are in an allowed region

$W = V$  we are at the boundary

$W < V$  we are in a forbidden region

Let us extend this conception of allowed and forbidden regions associated with given energy levels to the atoms in a solid such as a piece of iron or steel. We know from everyday reasoning that the allowed region of the individual atoms must be small, else over a period of time the detail of fine engravings would become blurred or thin electro-plates of rare metals would be absorbed into the parent metal. It is supposed that the atoms do possess some degree of freedom and that the distance of their travel at room temperatures is of the same order as atomic dimensions. We conclude then that each atom of a solid has a little allowed region and the whole remainder of the solid represents the unallowed region. Therefore, irregardless of the direction in which the atom moves, it's potential energy must rapidly increase and the kinetic energy must decrease, else the atom would leave it's allowed region which is impossible unless there is a change in the total energy of the atom. An atom in a piece of iron at equilibrium conditions will then possess a total energy greater than the



potential energy or  $W > V$ . The atom then must oscillate in boundary conditions in the form of a sphere whose circumference has an energy level  $W = V$  and hence as the atom proceeds to the boundary, it will fall back or be reflected in the manner of the stone thrown into the air. Pictorially this condition can be represented by a section of a sphere, the surface of the sphere representing the boundary where the interchange of energies causes the total energy to equal the potential energy. Necessarily, the radius of the sphere must increase or decrease in accordance with the change in total energy. For use in quantum mechanics, a slightly different picture represents this condition more clearly however. Referring to Fig. 4, there is plotted along the vertical axis the energy of two distinct states,  $W_1$  and  $W_2$ . The horizontal axis represents the displacement amplitude  $q$  or the distance from the position of minimum potential energy.

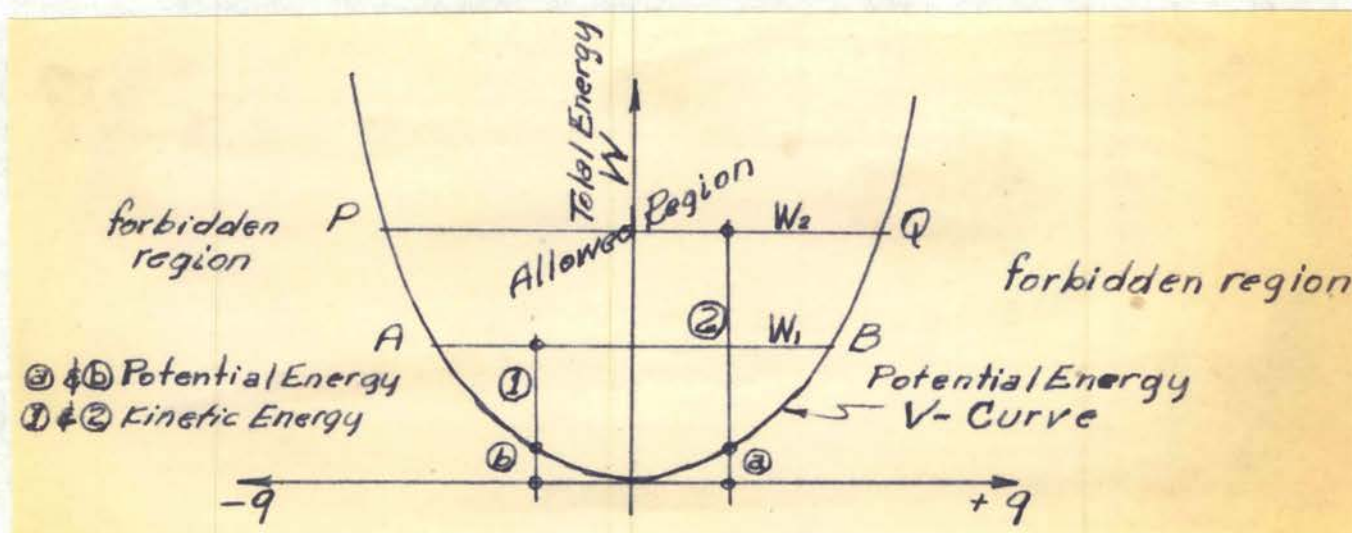


Fig. 4. Parabolic Potential Box

According to Gurney, in this case the atom is trapped or confined in a kind of potential bowl or box. At the boundary A, B, P, Q the value of  $W$  is

equal to  $V$ ; therefore, the atom is reflected and oscillates from side to side. At the vertical axis, the kinetic energy is a maximum as is determined by the distance from the  $W$  level vertically to the  $v$  curve at any radius. Evidently, energy level  $W_2$  represents an energy level higher than  $W_1$  because the Kinetic energy 2 is greater at all points than 1. We say then, that an atom or particle represented by state 2 is in an excited state or higher energy level.

Later we will find that if the potential box is on the surface of a solid and opens outward the atom or electron bound in the box can escape from the solid if its energy is raised to a sufficiently high level. In fact, it is evident that as soon as the energy level exceeds the depth of the confining box then the particle is no longer bound but drifts off as a free electron.

The same reasoning applies to the atoms comprising a diatomic or polyatomic molecule. Each atom remains attached to the others so long as its total energy  $W$  is less than the potential energy  $V$  provided by the combined molecules. Ordinary chemical reactions illustrate this point in that we invariably find an exchange of atoms taking place. From the amount of heat released one concludes that in chemical reactions the forces between the atoms must be small indeed when compared to that required to cause an exchange of atomic particles. If an atom acquires energy such that  $W - V$  is greater than the depth of the molecular potential box, then the atom escapes from the molecule and the molecule is said to dissociate.

Up to this point we have considered the energy relationships of a large number of particles and to some extent the energies of an atom bound in a solid. In the field of electricity, particularly in the field of electrostatics, we deal with the action of electrons. Let us investigate the motion



and energy of an electrically charged particle in an electrostatic field. Referring to Fig. 5, let A and B be two parallel condenser plates which are respectively positive and negative. If ultraviolet light is allowed to fall on the plate A at the point x we expect a photon or photoelectron to be ejected from the metallic surface. Let us examine one of the photons that leaves the plate at right

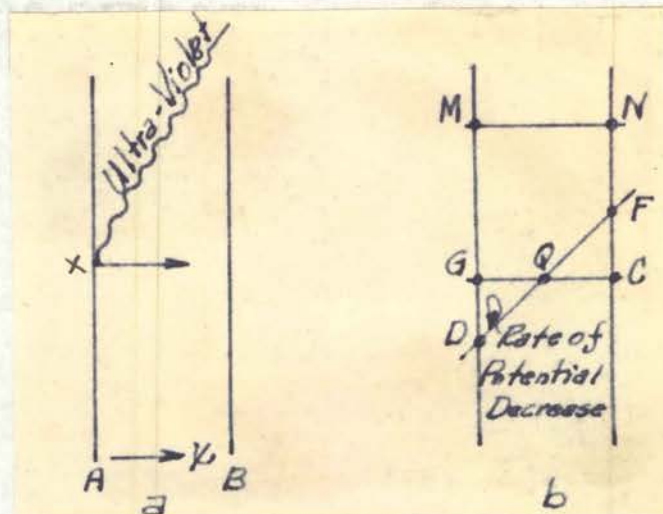


Fig. 5. Photoelectron in a Condenser

angles as indicated by the arrow. Once the electron has escaped from the surface its negative charge will cause it to be repelled by the negative plate tending to retard its travel and cause it to return to the plate from which it came. The potential energy as the electron travels across the condenser is represented by the line D-F in Fig. 5 b. The particle may or may not reach plate B. If  $W$  or the total energy is such as to be represented by line M-N it will arrive at plate B with residual energy equal to F-N. If on the other hand, the total energy  $W$  is properly expressed by the level G-C, the particle will advance to point Q then return to plate A.

In the above discussion, we have assumed that the ultra-violet light was sufficient to overcome the forces holding the electron on the surface of the plate and hence cause its escape. Let's examine the phenomenon of escape by drawing a comparison with the more familiar phenomena of the evaporation of a liquid into a gas. Suppose we have a container partially filled with liquid. Above the liquid we produce a vacuum so that for a



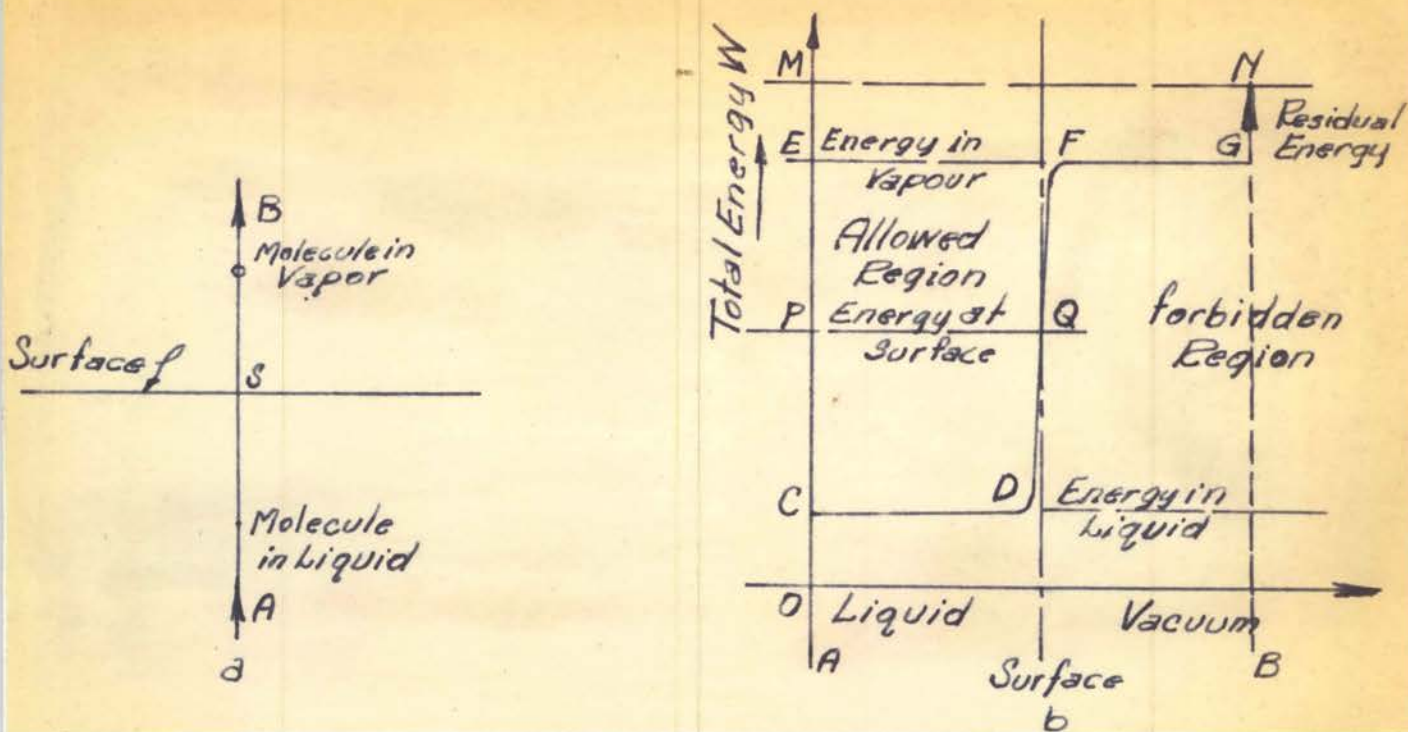


Fig. 6. Liquid to Vapor Potential Box

small volume of the liquid we have the condition depicted by Fig. 6, a.

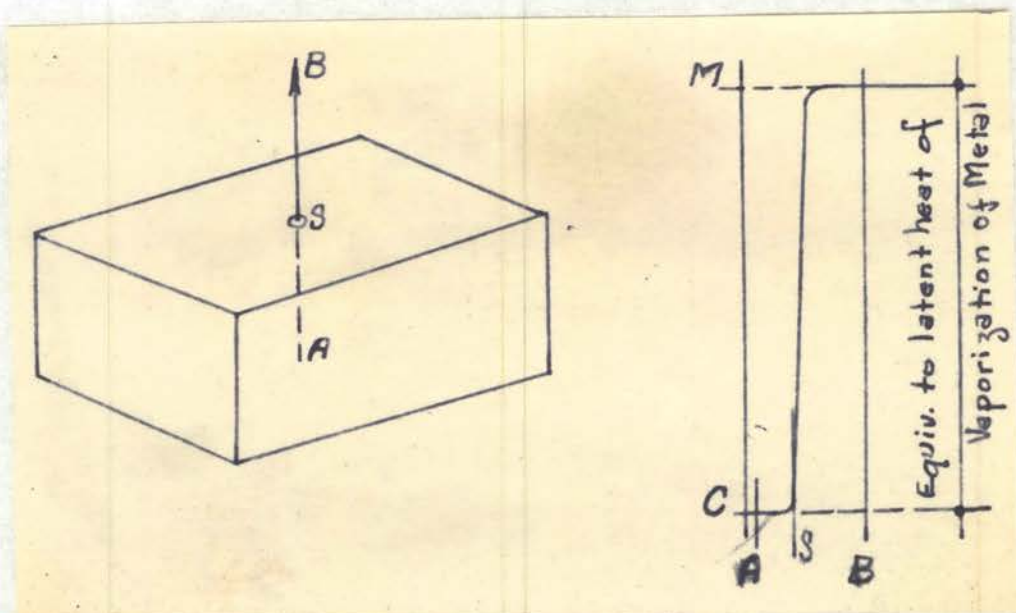
The straight line A-B drawn perpendicular to the surface will represent the path of a molecule moving up to the surface and out into the vacuum.

Fig. 6, b shows the energy changes accompanying the molecule along its path. Let the abscissa be the height  $h$  along line A-B and let S be the point where A-B cuts the surface. To the left of S, we have liquid and to the right, vapor or vacuum. A molecule at rest in the vapor possesses more energy than one in the liquid; therefore, an increase in energy is represented by the ordinates to the curve. If C-E represents the difference in energy in the liquid and in the vapor, then F-G represents the potential energy outside the surface and C-D that within the liquid. Then the potential energy of a molecule along line A-B will be given by the curve similar to C-D-F-G.

We know that as a molecule approaches the surface it must acquire an

energy greater than a certain critical energy before it can escape. If it does escape the energy will follow a path somewhat like the path C-D-F-G-N of Fig. 6, but C-M will represent the kinetic energy with G-N being the excess or residual energy. Only exceptional molecules will have sufficient energy to escape and the average kinetic energy will be represented by some line P-Q. For this average molecule the region beyond Q is in classical mechanics forbidden so that the molecule is turned back at the boundary. It is interesting to note that if P-Q is chosen so that C-P and G-N are the average values of the kinetic energy in the liquid and the vapor respectively then P-M is equal to the latent heat of vaporization at the temperature considered.

Returning to the problem of the extraction of an electron from the surface of a metallic solid - we have a similar energy graph to that of extracting a molecule from the surface of the liquid.

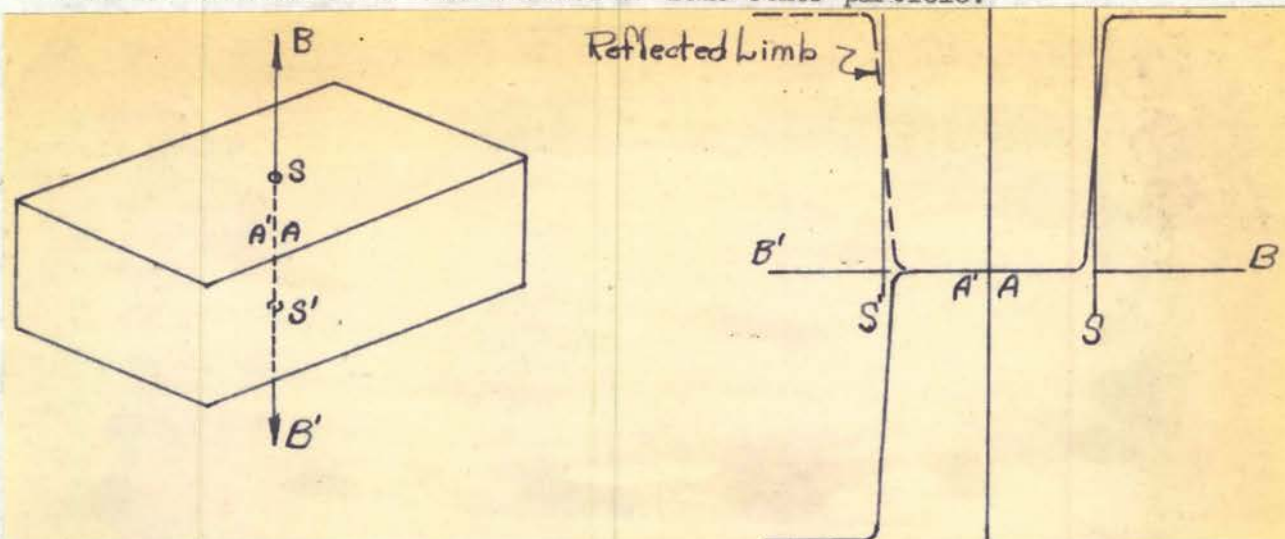


The escape of an electron from the surface of a metallic solid is relatively infrequent due to the extremely high latent heat of vaporization.

(See Appendix B) As the electron escapes it will be free to wander at will



until it collides with some surface or some other particle.



From the work of Gurney if we consider both sides of the small metallic sample we will get a potential energy curve as shown above. For convenience in use the left hand limb is usually reflected upward so that an allowed region is established in the form of a box. The potential box is usually represented in the form shown below. See Fig. 7.

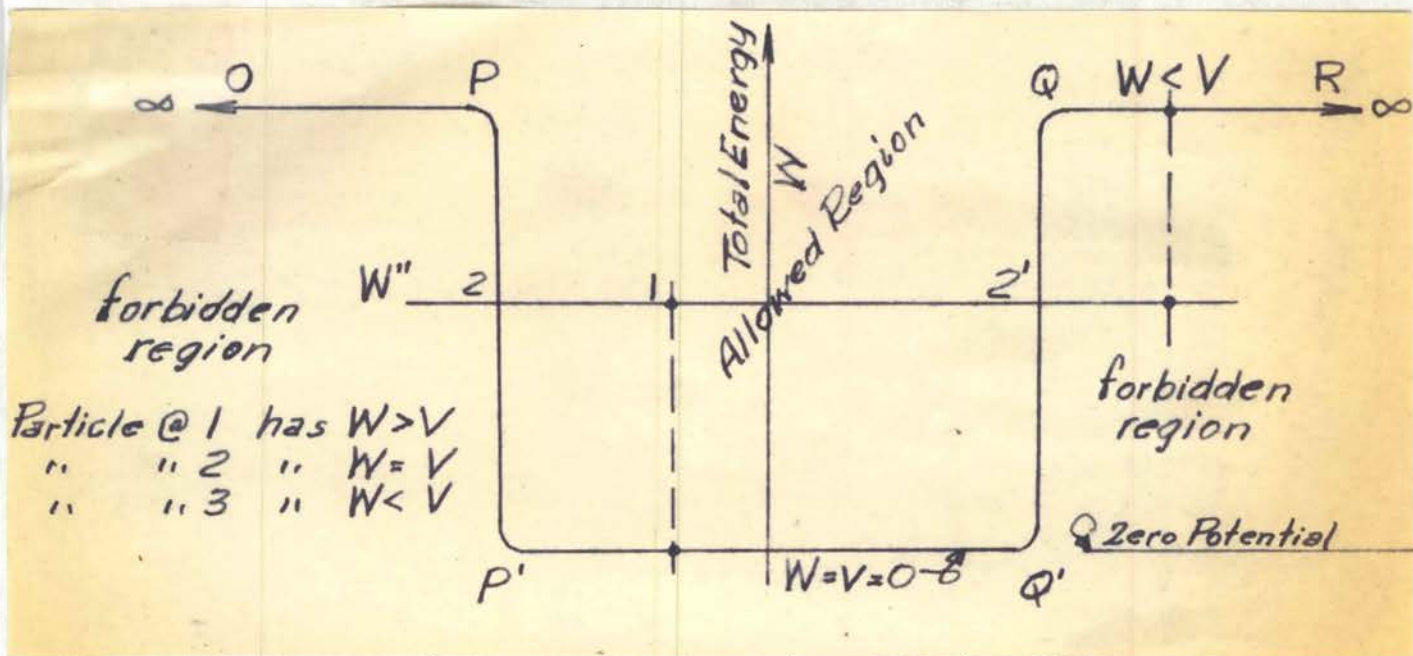


Fig. 7. Ideal Potential Box  $W - V = \text{Constant}$

According to previous reasoning we conclude that a solid body or a

fluid forms a box presenting potential boundaries to the escape of particles. The nucleus of atoms in like manner forms a potential box for the electrons. Referring to Fig. 7, we see that a particle in position 1 has potential energy equal to zero; therefore, it's total energy is greater than it's potential energy and the particle is in an allowed region. If the particle is in position 2 or 2' it's total energy is equal to it's potential energy; therefore, it is reflected from the boundary. A particle in position 3 has potential energy greater than the total energy; hence, it is an unallowed region and cannot exist. Therefore, the box holds the particle between p' 2 2' Q'. Due to reflection at the boundary and the sudden change in the potential energy, the particle pulsates or vibrates between 2 and 2' with potential energy equal to  $v$  at 2 and 2' and zero in between.

The potential box takes on a modified shape when we make the transition from macroscopic to microscopic or atomic particles. Thus, for microscopic or atomic particles or electrons it is usual to represent the potential curve as shown in Fig. 8. Here we have an electron in motion with average kinetic

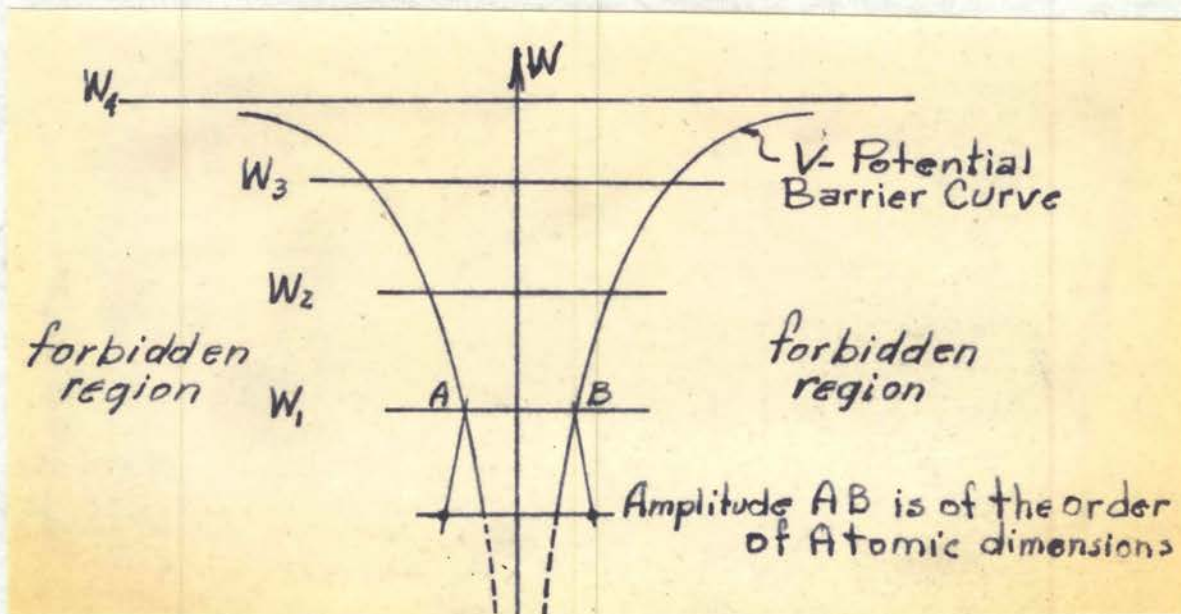



Fig. 8. Potential Box for Atomic Particles



energy  $T$  equal to  $(W - V)$  and confined to a small allowed region of little more than atomic amplitude. For a single electron with a positive nucleus we have  a V curve in one dimension as given above. In Fig. 8 if the energy of the electron is  $W_1$  the electron will occupy an energy level equal to  $W_1$  above and will have a vibrational amplitude as shown by A-B. The same is true for  $W_2$  and  $W_3$ ; however, if the total energy  $W$  happens to be equal to  $W_4$  the particle will not be bound by the potential box and can escape. These potential boxes are useful in forming a mental picture of energy levels, but the picture is not entirely correct. The sketch below shows a top view or plan, and edge view of the electron path as it traverses the potential box. This sketch shows the path of the particle in



two dimensions. Actually the path forms a washer and oscillates from inner to outer boundary. If we project all these motions on a single axis of the washer such as A-B plane then this represents the path along an energy level from A to B in the previous figures. When the washer is rotated we have a three dimensional shell which is known as the electron shell. This then is the picture of an electron in one of the excited states as given by quantum mechanics.

b. Probability and the Heisenberg "Uncertainty Principle."

As has been previously stated in quantum mechanics a particle always has a finite possibility of being found at some distance outside the allowed area. This necessitates a new method of measurement and calculation for evidently the same mechanics used to predict the position of a particle confined to definite boundaries can give little information about a particle that can

make occasional excursions outside these boundaries. To account for these trips outside the allowed region, use is made of probability values obtained from the square of the amplitude of the  $\psi$  pattern of the particle. Follow the development of the potential boxes and probability values Heisenberg proposed his "Uncertainty Principle." Briefly this principle states that the product of a change in the position and a change in the momentum of a particle are equal to a constant. This means that if the particle is confined to a particular position its momentum must vary, or if its momentum is fixed at a given value little information can be obtained as to its position.

In the study of quantum mechanics we have to be guided by experiment. Necessarily when experiments are run use must be made of instruments for measuring and recording results. Of the five senses we possess we utilize our sight almost exclusively in the determination of measured quantities. Measurements made in this manner are termed coincidence measurements or c values because we determine a measured value by observing a pointer come into coincidence with some position on a graduated scale.

Statistical values tend to average about some mean value and gives a graph somewhat as follows.

For some time before the event



of quantum mechanics and the uncertainty principle it was thought that the spread in readings were due to errors in the measuring instruments and varying conditions of the experiment. Therefore, use was made of the familiar error curve shown in Fig. 9, a.

As Gurney states today the physicist uses the distribution curve shown in Fig. 9, b. It was formerly assumed that atomic particles obeyed the laws



of classical mechanics. Review of the data gathered by thousands of experimental physicist offered conclusive evidence that spectra lines on photographic plates depend upon swarms of particles and that these particles did not define a sharp line. Spectra lines always have some spread, therefore what was previously thought to be errors in measurements was in reality the natural spread of the lines. Admitting then that atomic particles will not obey the laws of classical mechanics we must substitute some form of measurement for the maximum value of the error curve. This does not mean that we cannot define a system, but we must substitute a pattern of values for the one unambiguous result previously sought. Once the shape of the pattern has been determined we know all that needs to be known about the system.

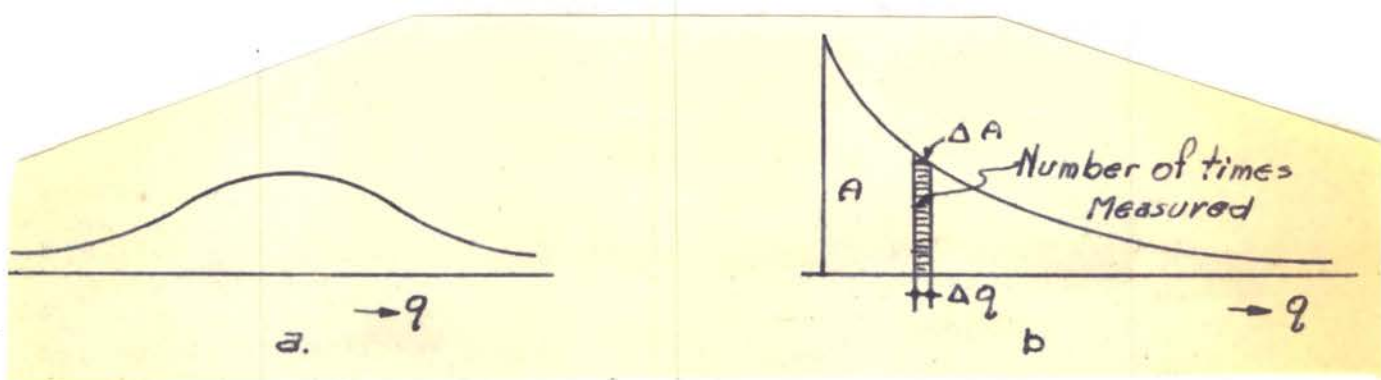


Fig. 9. Error and Distribution Curves

Suppose we have already made a number of readings on an experimental phenomena, and that Fig. 9, a gives the smoothed curve embodying the results of a very large number of measurements of the quantity  $q$ . Instead of using the maximum value as the correct result we determine a distribution curve as in Fig. 9, b. In the distribution curve if we take a small range of values  $\Delta q$  the area of this strip is  $N(q)\Delta q$  and gives the number of observations

whose results fall in the  $\Delta q$  range. The same is true of any other vertical strip so the total area under the curve is equal to the total number of observations that have been made. If at some time later after the distribution curve has been made we decide to make  $n$  additional observations, we can find the probability of any of the  $n$  observations falling in a given  $\Delta q$  range. To do this we must alter the scale of ordinates until the total area under the curve is equal to  $n$ . If the area under the curve is made equal to unity, then the area of any strip would give us the probability  $P(q)\Delta q$ , that the result of any one observation will lie between  $q$  and  $q + \Delta q$ .

The probability has a value which varies inversely with the velocity. An examination of a simple swinging pendulum will illustrate this point. If a pendulum swings between two walls or boundaries without friction and high speed motion pictures are made of the pendulum, examination of the resulting negatives will reveal that most of the frames show the pendulum in the neighborhood of the walls. This is because the velocity of the pendulum is the least at the walls and hence the probability of it being photographed is the greatest when it's velocity is the least. Fig. 10 shows graphically in a the probability curve as it varies with  $q$  or it's amplitude from the center position.

For a macroscopic pendulum  $A + \Delta q$  is not allowed because the classical boundary is highly effective against the passage of the pendulum. The probability of finding the pendulum at

$$q < A = \text{very large}$$

$$q > A + \Delta q = 0 \quad (\text{cannot be greater than } A)$$

The above is what we have been taught to expect from classical mechanics.



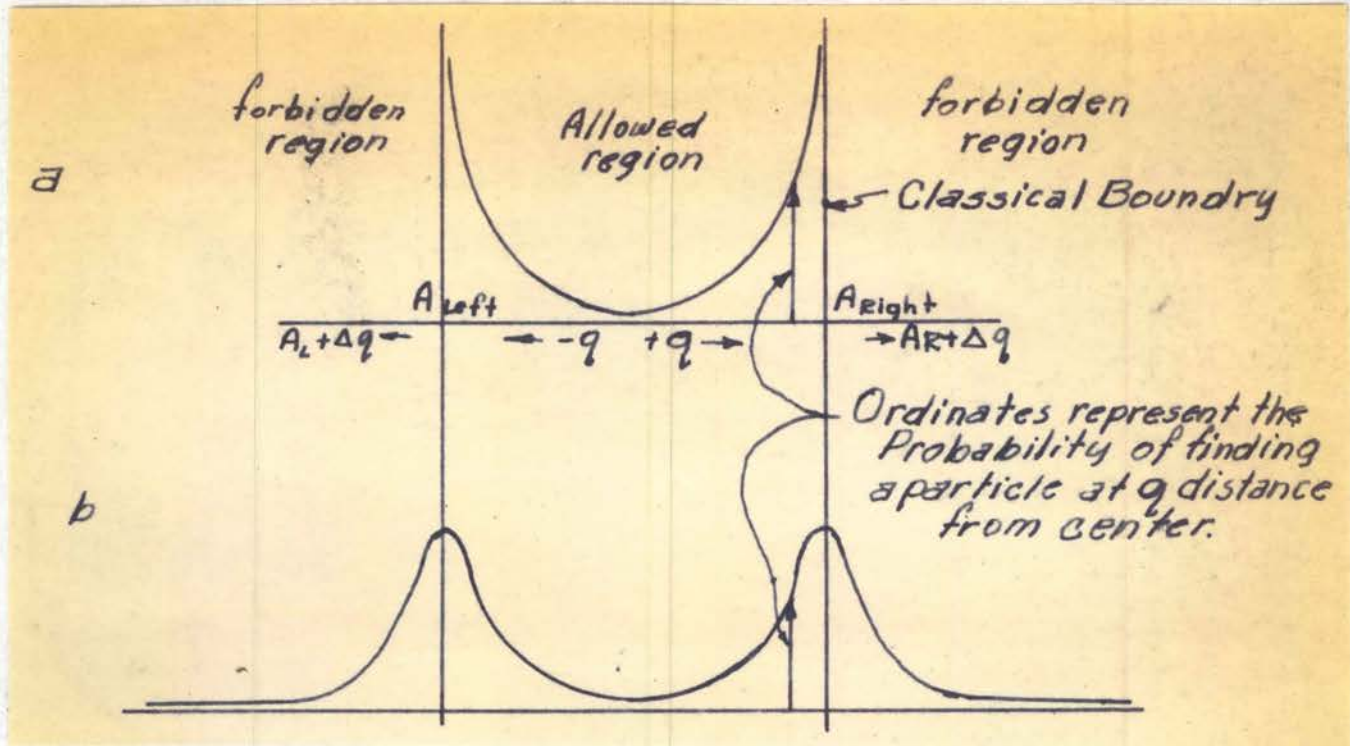


Fig. 10. Probability Curves

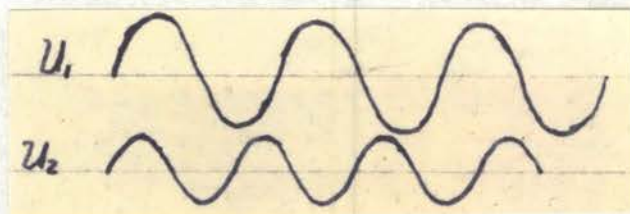
For microscopic pendulums or particles in motion we get the probability pattern of Fig. 10, b. This pattern tells us that there is a finite chance of finding the particle outside the region of the classical boundary of its confining potential.

If  $P$  is the probability of finding the microscopic pendulum or atomic particle at a point it has been found that  $P$  is equal to the square of  $\psi$  of  $(\psi)^2$ .  $\psi$  is the amplitude of the curve in Fig. 10, b. The use of the square roots of the amplitude of the  $\psi$  pattern for the determination of the probability is based on the particle velocity. From the equation

$$v = \frac{1}{2} at^2, \quad t^2 = \frac{2v}{a}$$

which is proportional to the probability of a particle being at a certain place at time  $t$ . In the development of quantum mechanics from experimental data the answers to many problems were known, hence quantum mechanics came into use as the result of the need of a method

of calculating from fundamental data. The use of square roots of amplitudes have analogies in various places in physics; in all kinds of wave motion, sound waves, light waves, electrical and mechanical waves, etc., it is the square root of the intensity that we use, i.e. the amplitude of the wave. Therefore, an equation which gives us a  $\psi$  pattern (called a psi pattern) is called a wave equation. The amplitude of this wave (absolute value) squared gives the probability of the particle being at a particular point on the wave at a given instant. If we draw upon our knowledge of light for a comparison we know that two light waves of slightly different frequencies can interfere one with the other.



To find the energy we measure the amplitude of the waves independently and add them vectorially. This resultant combined amplitude squared is proportional to the energy or intensity of the combined waves. We find by means of coincidence measurements certain numbers which give us the frequency and amplitudes. To get the probability amplitude it is then only necessary to square this measured or calculated amplitude.

Quantum mechanics introduced the idea of purely theoretical quantities based on the patterns obtained from spectrum analysis and electron diffraction experiments. These theoretical quantities depend only upon the shape of the universe or the manner in which particles react in the universal fields, and not on the particular apparatus at hand or the conditions of the experiment.

The "Uncertainty Principle" of Heisenberg is perhaps one of the most



important observations in the scheme of the development of quantum mechanics. One of the events leading up to the development of the Uncertainty Principle was the fact that we cannot observe an atomic structure or system without disturbing it. For instance, measurements made with a beam of light offer as little disturbance to the atomic structure as any means of measurement in use. When an atomic structure is examined with a light beam the result is a diffraction pattern such that if the wave length of the light is reduced by  $1/10$  our pattern progresses from one to two in the sketch below. In one the pattern covers considerable area, however, its intensity will give considerable knowledge of the energy or momentum of the particle. In two we are able to observe that the particle is at a specific point but little information is to be gained about it's energy. Since light disturbs the atoms the image below represents only a blurred substitute of the



incident light beam. Before 1925 the maximum value was used, since that time use has been made of patterns with spread and fringe areas. Later we will return to the Uncertainty Principle in connection with two potential boxes.

Atomic particles will never obey classical laws and the patterns must be studied by use of quantum mechanics. The shape and size of the pattern is extremely important in determining the intensity.

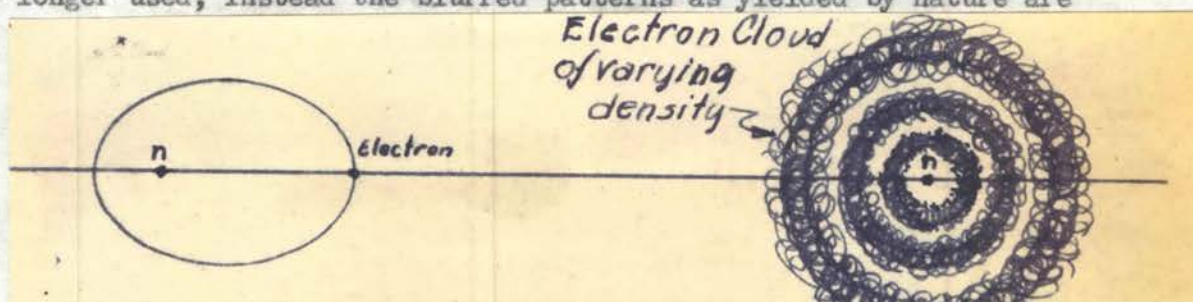
c. The Bohr Atom, De Broglie Equation and the Schroedinger Wave Equation.

The atom as postulated by Bohr was based upon a minature solar system. Good agreement was had between this model and experimental results in general. Certain discrepancies were evident however; for instance the Bohr

model could not account for the ground state of the electron. The reason being that in this state the electron resides on the nucleus and not in a shell or orbit.

A French Physicist De Broglie proposed a fundamental equation of nature relating the wave length of particles to their momentum. Shortly thereafter Schroedinger postulated his wave equation for determining the position of atomic particles and suggested it's validity in the unallowed as well as in the allowed range, when the solutions were made in terms of the De Broglie wave length.

In the study of atomic problems today the orbits as postulated by Bohr are no longer used, instead the blurred patterns as yielded by nature are used.

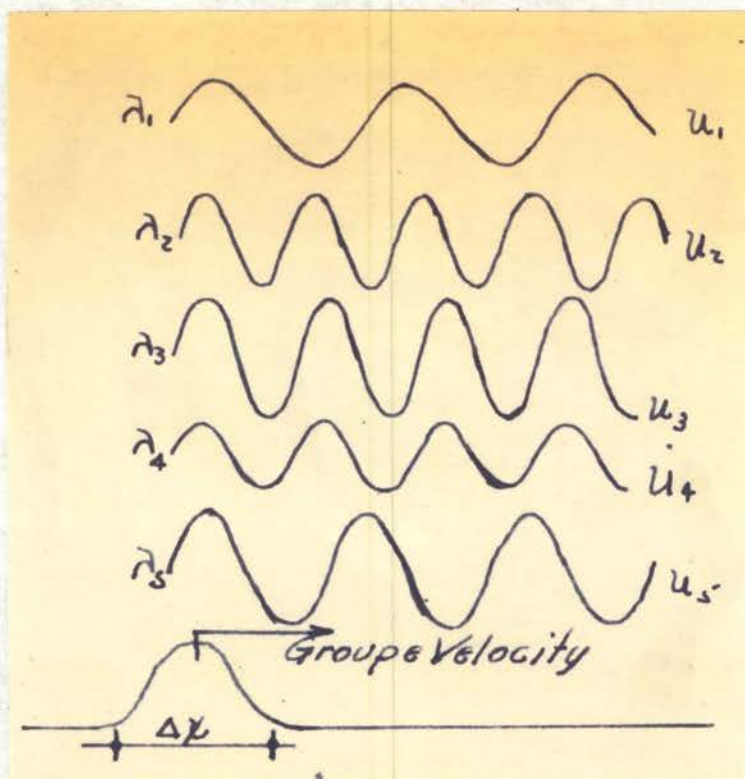


In 1924-25 De Broglie proposed the idea that particles and waves were synonymous and therefore particles should have a wave length. As one Englishman has put it "we should adopt a more general viewpoint and compromise on wavicles." Up until this time light had been treated by wave theory. Shortly after De Broglie's announcement a beam of light was shown to exert a pressure on a small mirror thereby proving that light must have mass and exist in some discrete quanta.

For a train of waves of slightly different frequency we are able by previously discussed means to add these waves and obtain a resultant. This resultant is called a groupe, and each group is recurring in nature or producing the well known beat phenomena.

Following De Broglie's postulation it was found that the groups





associated with the addition of the wave train was also associated with matter. If the phase velocity  $U$  is greater than the velocity of light, it interferes, and if the phase velocity  $U$  is less than that of light it identifies a particle.

In nature non-material particles approach or obtain infinite velocity therefore a solid or material object is being constantly bombarded by non-material particles. They bombard at a velocity of infinity hence as they hit this sheet of paper they immediately go to infinity and return in zero time therefore the net result of their bombardment is zero and we have no movement. The de Broglie equation states that a particle of mass moving with uniform velocity  $v$  (such that its kinetic energy  $= \frac{1}{2}mv^2 = W - V$ ) has a wavelength  $\lambda$  (De Broglie wave length).

We know that the momentum of a particle  $p = mv$  and the kinetic energy

$$T = \frac{1}{2}mv^2 = W - V$$

$$\text{then } \frac{m}{m} \left( \frac{mv^2}{2} \right) = W - V \quad \text{or} \quad \frac{m^2 v^2}{2} = m(W - V)$$

$$\text{but } m^2 v^2 = p^2$$

$$\text{therefore } p^2 = 2m(W - V) \quad \text{or} \quad p = \sqrt{2m(W - V)}$$

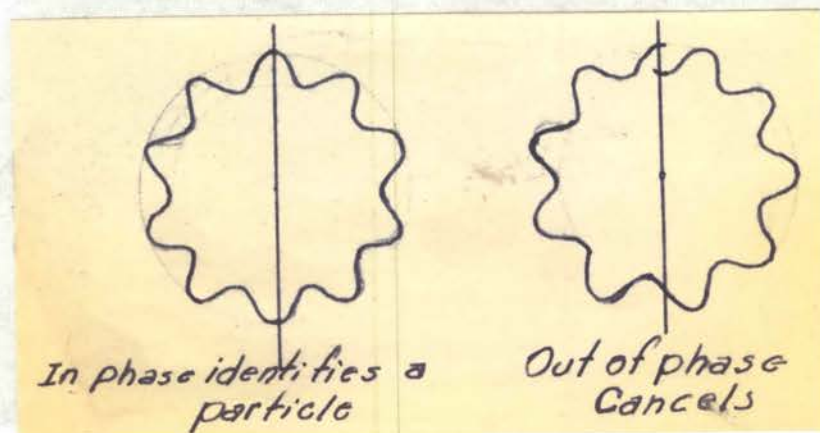
$$\text{and } \lambda = \frac{h}{\sqrt{2m(W - V)}} \quad \text{Equation 1}$$

De Broglie's equation implies that all particles having mass and moving at uniform velocity has an identifying wavelength. As we can see from the data below as the particle becomes heavier this wavelength becomes very short and for macroscopic particles is almost non-existent at ordinary velocities.

| particle           | velocity cm/sec             | wavelength             |                |
|--------------------|-----------------------------|------------------------|----------------|
|                    |                             | cm                     | Å <sup>o</sup> |
| electron           | 1                           | 7.27                   |                |
| electron           | $5.94 \times 10^7$ (1 volt) | $1.22 \times 10^{-7}$  |                |
| electron           | $7.2 \times 10^8$           | $1 \times 10^{-8}$     | 1.             |
| electron           | $1.24 \times 10^{10}$       | $5 \times 10^{-10}$    | .05            |
| alpha particle     | $1.5 \times 10^9$           | $6.56 \times 10^{-13}$ |                |
| golf ball (45 gr.) | $2.5 \times 10^3$           | $5.71 \times 10^{-22}$ |                |

Other physical significance can be attached to the De Broglie equation.

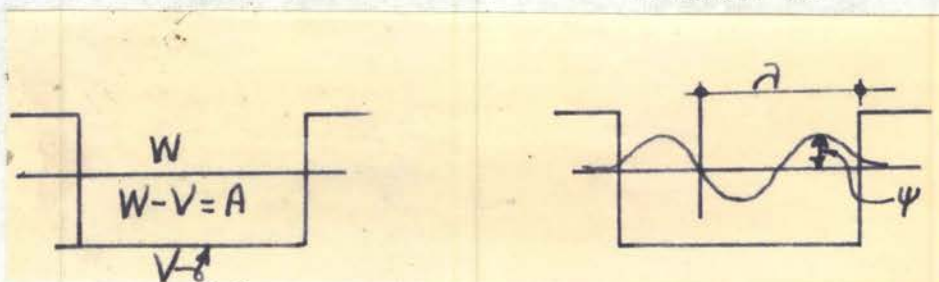
When  $\lambda$  is taken as the wave length or distance along an action train of waves we get the following picture.





It is interesting to note that another scientist Bragg also worked out the basic data leading to the De Broglie equation, but failed to see the significance of the relationship. The De Broglie equation is also derivable directly from the Schroedinger wave equation (see appendix C), but this equation and the work of Heisenberg followed the work of De Broglie. Therefore, De Broglie's equation was more of a postulation or suggestion that proved to be correct.

Use is made of the De Broglie wavelengths applied to atomic particles in a potential box such as Fig. 8, where  $W-V$  is constant. The resulting pattern will be sine or cosine curve with  $\lambda = \frac{h}{\sqrt{2m(W-V)}}$ , and amplitude  $\psi$ .



In these patterns  $\psi$  will take on positive and negative values but like the power from A.C., lines  $\psi^2$  is positive at all points thereby giving a positive value to the probability, finding the particle somewhere in all time space.

Referring again to Fig. 8 if  $W-V$  is constant then we would find the pattern expressed as a sine or cosine curve. Where  $W$  inside the box or well is  $> V$  and outside the box  $W$  is  $< V$ . We have the representation of a microscopic particle by means of waves whose wavelength is given by De Broglie's equation.

As has been previously mentioned the particle suffers reflection at the potential boundary and rebounds explosively off the blurred potential curve. This is analogous to the swing of the pendulum where the velocity



varies with  $q$  or the displacement from the center position. Examination of these phenomena in the light of De Broglie's equation, however, brings to light a discrepancy in the sine and cosine  $\psi$  patterns above.

Considering a given particle as the velocity increases,  $\lambda$  the wavelength decreases, and conversely as the velocity decreases,  $\lambda$  increases and we have the following relations from which we conclude that short wavelengths



Low Velocity - Long Wavelength      High Velocity - Short Wavelength  
are associated with high velocity and high energy particles. If the particle explodes off the boundary it accelerates as does the pendulum as it leaves the boundary of the well. This acceleration carries it to the opposite

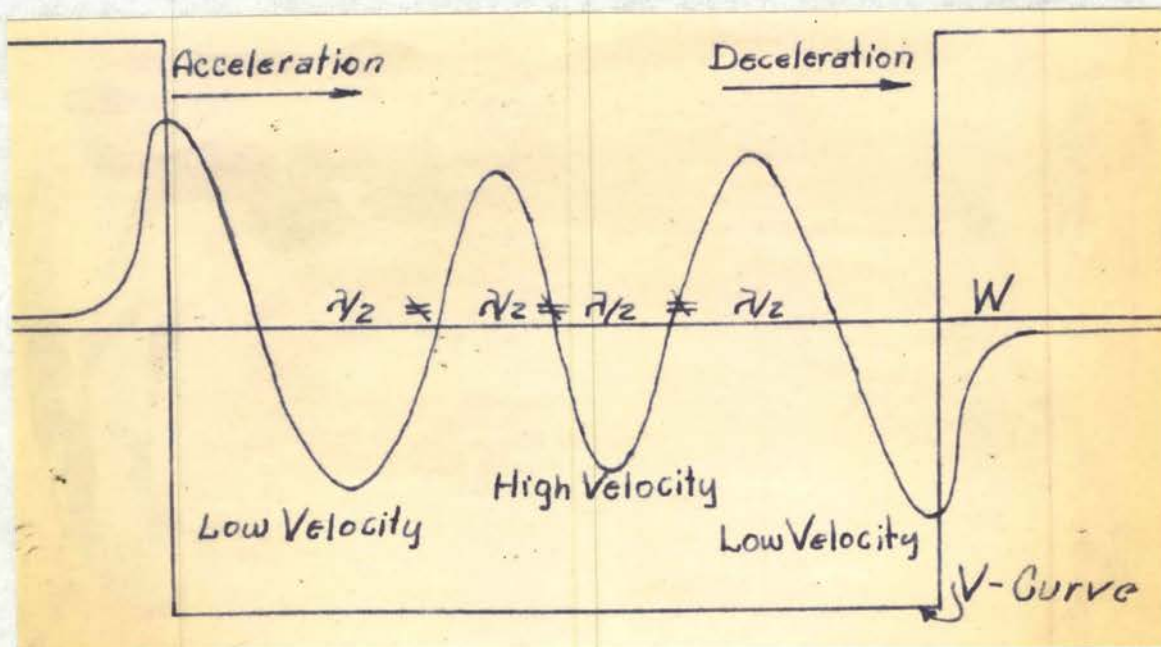


Fig. 11. Variable Momentum

boundary where the process is repeated and we have established an energy level containing a particle whose  $\psi$  pattern is represented by Fig. 11.

The  $\psi$  pattern then changes continually throughout the box, for which the change in velocity and wavelength requires a continual change in the momentum from point to point. It is these  $\psi$  patterns in the allowed region where  $W > V$  that keeps the particles in atoms and the atoms in molecules, as well as the universe in it's condition of equilibrium, except as the second law of thermodynamics demands a gradual unperturbed change.

Experimental evidence dictates, as has been previously discussed, that in quantum mechanics sharp or well defined rigid boundaries are not indicated but rather a blurred or somewhat ill defined barrier region in the approximate position of the classical boundary.

In seeking a mathematical interpretation of this blurred boundary the eminent German physicist Schroedinger proposed the idea that a differential equation whose solutions are in terms of De Broglie waves in the region where  $W > V$  might also be expected to apply where  $W < V$ . This was found to be the case, and the resulting equation is given below. In retrospect it is clear that the effect upon our understanding of nature made possible by this equation is more far reaching and fundamental than Newton's equations of motion and gravitation.

For the region where  $W > V$  Schroedinger's equation is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(W-V)\psi = 0 \quad \text{Equation 2}$$

In this equation when  $(W - V)$  is positive the equation correlates with a region in which the particle is allowed. With either constant values or slowly changing values with respect to  $x$  of the quantity  $(W - V)$  gives rise to the following solution.



$$\psi = A \cos 2\pi \frac{x}{\lambda} + B \sin 2\pi \frac{x}{\lambda} \quad \text{Equation 3}$$

After testing this solution and proving it's validity Schroedinger postulated that it should also hold for rapidly changing values of  $(W - V)$  with respect to  $x$  and for varying energies. Further inspection has shown that the equation holds in all cases where  $(W - V)$  is positive or negative and irregardless of the rate of change. This is to be expected however from the work of Heisenberg who previous to Schroedinger developed a form of matrix algebra to solve atomic problems. The work of Schroedinger is more easily applied and analyzed so that through the intervening years it has become the more popular.

The solution 3 above gives the equation of the pattern whose absolute value of  $\psi$  squared is proportional to the probability  $P_x$  of finding a particle at  $x$  displacement from the center of the well as in Fig. 8.

For a physical interpretation of equation 2 applied to the box of Fig. 8 let us suppose that we know how the index of refraction of a medium varies for light of any frequency in the  $x, y, z$ , direction. A physicist will be able to tell by inspection the approximate nature of the wave form for any frequency. By solving the equation of wave propagation a mathematician will be able to calculate the precise wave form. In any atomic problem we are given or can determine the forces of attraction and repulsion between the particles, with which there is associated a certain potential energy  $V$ . When we know the potential field character in terms of  $x, y, z$ , this is equivalent to knowing the index of refraction of the medium at all points. By solving the Schroedinger equation the mathematician can calculate the precise values of  $\psi$  at all points. Use is made of  $\hbar$  numbers in the determination of the total energy  $W$  therefore  $W$  represents a quantity determined by



Newtonian methods.

The physicist or chemist must be able to tell by inspection, the rough form  $\psi$  will take and hence gain an idea of how the system will behave. In this sense the author, as an Engineer, has endeavored to inspect the Schroedinger equation and postulate the manner in which a physical phenomena takes place and use this theory of operation to design and use certain pieces of engineering equipment.

Returning to the Schroedinger equation, the region where  $W - V$  is negative or  $V$  is greater than  $W$ , equation 2 has the following solution.

$$\psi_k = C e^{-kx} + D e^{kx} \quad \text{Equation 4}$$

$$\text{from which } \frac{\partial^2 \psi}{\partial x^2} = k^2 C e^{-kx} + k^2 D e^{kx} = k^2 \psi$$

$$\text{Subst. in 2. } k^2 \psi + \frac{8\pi^2 m}{h^2} (W - V) \psi = 0$$

from which the second term in the equation above must be equivalent to the second term of equation 2

$$\text{so that } k^2 \psi - k^2 \psi = 0$$

$$\text{then } k^2 \psi = \frac{8\pi^2 m}{h^2} (W - V) \psi$$

$$\text{or } k^2 = \frac{8\pi^2 m}{h^2} (W - V)$$

It has been found that the value of  $\psi$  to give a solution is

$$k = \frac{2\pi}{h} \sqrt{2m(V - W)} \quad \text{Equation 5}$$

where  $W - V$  is equal to  $T$  or the kinetic energy but is negative and hence equivalent to  $V - W$  or imaginary kinetic energy. Since  $k$  must have the value

given by equation 5 as we enter the forbidden region--the solution is then

$$\psi_k = C e^{-\frac{2\pi}{h} \sqrt{2m(V-W)} x} + D e^{\frac{2\pi}{h} \sqrt{2m(V-W)} x}$$

Use must be made of three graphs to depict the proper patterns to fit the potential boxes of quantum mechanics. These are the modified sine or cosine patterns within the box and two exponential tails as above. If  $k$  in the equation of the tails is sufficiently large the pattern outside the barrier drops off or diminishes rapidly. This is what happens as the mass of the particle increases, and in these instances the boundary assimilates the classical boundary. This roughly gives the correspondence principle which states that for limiting cases the laws of quantum theory converge toward and finally become identical with the laws of classical mechanics. The limiting cases therefore show a one to one correspondence between quantum mechanics and classical mechanics hence the name Correspondence Principle.

The following figures give a picture of the complete pattern compared with the classical boundary.

When the area under the  $\psi$  curve is normalized by dividing by some factor, not including time, so as to make the total area under the curve to one (1), the result is a photograph of all time space for this particle and will give the probability of finding the particle in this particular photograph. Then  $|\psi|^2 dx$  is the probability of finding a particle in  $dx$  space range or the probability is  $P_{dx} = [x, x + \Delta x]$ .

In Fig. 12 the exponential tails approach the  $W$  axis asymptotically and soon become too close to allow particles to go to infinity, but there is no limit as to how far it may occasionally go before returning. Therefore, we have substituted for the complete wall of classical mechanics a

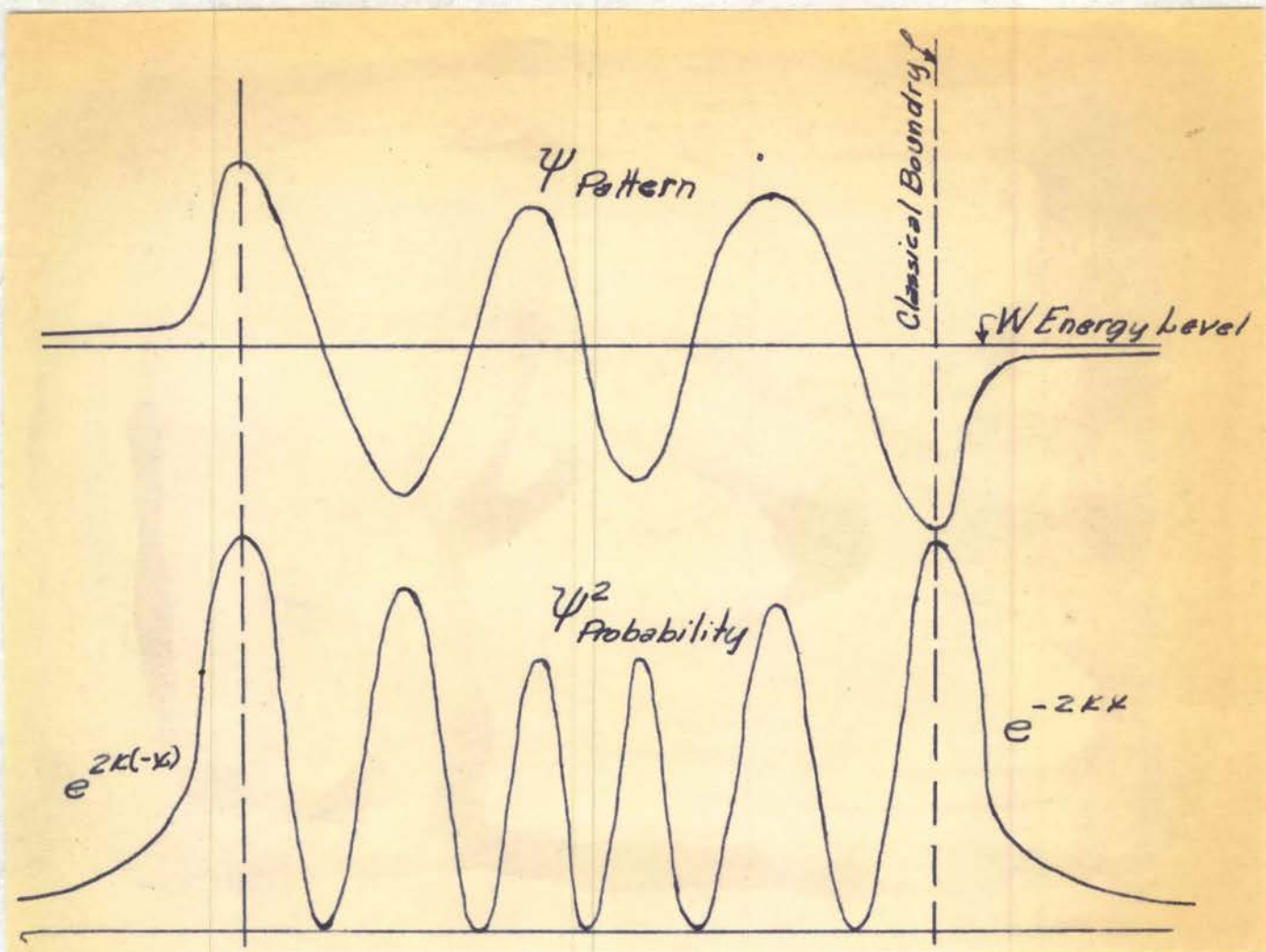


Fig. 12. Pattern and Probability Curve  
Compared with Classical Boundary

blurred boundary in which the rate of decrease of the forbidden area is given by  $e^{-2\kappa x}$ . This means that the solid objects of classical mechanics do not have the absolute surface we ordinarily associate with them, because the surface particles being bound by the surface atoms forming potential boxes are no longer classically restrained, but possess a positive probability of taking long excursions from the surface. Again we are confronted with the idea of the point of view, were we able to view the surface from a microscopic point of view we would find the surface to be extremely fuzzy



like that of a boiling water surface.

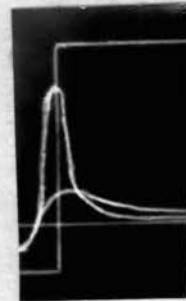
Looking at the effectiveness of the boundary we must evaluate the  $2kx$  which is  $3 \times 10^{13} \sqrt{m(V-W)}$ . For an electron we have  $m = 9.0 \times 10^{-28}$  gm., for a proton  $m = 1.6 \times 10^{-24}$  gm., and one electron volt =  $1.6 \times 10^{-12}$  ergs.<sup>1</sup>

If we set  $(V - W) = 1$  electron volt and calculate the value of  $e^{-2kx}$  at a distance of  $2A^0$  units beyond the boundary we find

$$\text{for the electron } e^{-2kx} = e^{-1.8} = .1$$

$$\text{for the proton } e^{-2kx} = e^{-76} = 10^{-43}$$

The sketch at the right shows pictorially the character of the tails as they traverse the boundary. Thus, we see that the boundary provided by the potential box offers about 42 times as much resistance to the passage



of the proton. Hence the electron has a fairly good chance of flowing out of the box with relative ease, while the proton due to its mass (1870 times the mass of the electron) finds the potential boundary to be fairly effective. Larger or heavier atoms or macroscopic particles find the boundary almost as rigid as the classical wall to the swinging pendulum. At the same time we make the transition to larger particles the De Broglie wavelength vanishes or becomes increasingly insignificant. (It is interesting to note that values exceeding approximately  $10^{28}$  or  $1/10^{28}$  become negligible to present day tools for measuring.) When the De Broglie wavelength tends to vanish the mechanics of Hamilton comes into being and can predict the position of a particle under the influence of any set of forces. It is for this reason that the inadequacy of classical mechanics was not discovered earlier.

<sup>1</sup> Ronald Wiefriid Gurney, Elementary Quantum Mechanics, pp. 18-19.

It should be noted that the charge on the particles does not enter into equation 2 directly. It enters indirectly through the potential energy  $V$ , since in any field  $V$  will depend upon the value and sign of the charge carried. The result then of a charged particle or applied field is to change the size (width or depth) of the potential box. These charges also determine the allowed energy levels since the level to which a particular pattern will sink in the potential box will depend upon its configuration.

The small probability of a proton or heavy particle being outside the classical boundary should not be neglected, for the present however, we are much more interested in the high probability the electrons have of penetrating the boundary.

If  $V = Cx$  or the potential is linear with  $x$  then  $(W - Cx)$  gives a solution to equation 2 of  $e^{+qx}$  and  $e^{-qx}$ .

For the right side of the box the proper exponential tail must be chosen.  $e^{+qx}$  gives a  $\psi$  pattern tending away from the  $W$  axis which means the particle would not return to the potential box, but might possibly go to some other system or disintegrate and transfer its energy to this or some associated system. If we use  $e^{-qx}$  we get a  $\psi$  pattern which approaches the  $W$  axis asymptotically, therefore, the following Fig. 13 gives us the picture.

In order to plot the patterns we first determine the pattern of the tails and then the pattern inside the box.

Assume a certain  $W$  level to remain constant and plot the pattern. Since the curves fail to meet at the center we can have no continuous probability of finding a particle hence no matter can exist for this value of energy level and particular momentum. In (a) we know that the momentum  $p = mv$  is too large, and in (b)  $p$  is too small. As  $p$  increases the wave length

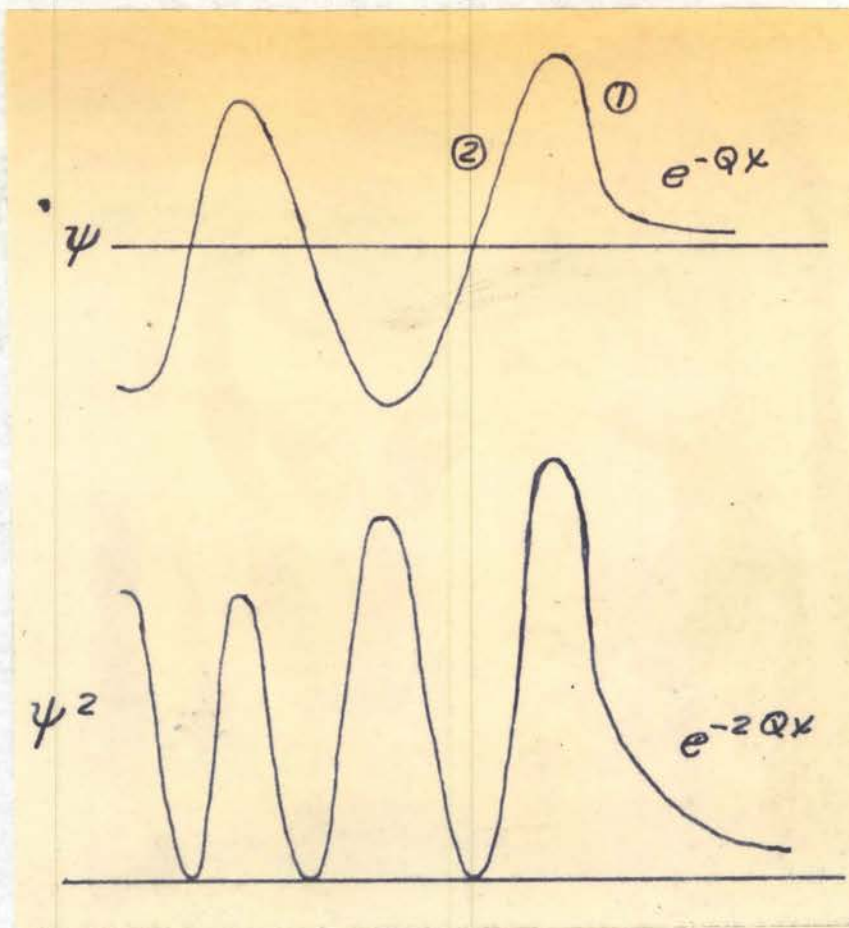


Fig. 13. Steps in Plotting  $\psi$  and  $\psi^2$  Curves

increases, therefore, a smaller value of  $p$  for case (a) would lead to an acceptable solution. Since  $p = \sqrt{2m(W-V)}$  the only quantity we can vary to make the curves fit is  $W$ ,  $m$  and  $V$  being fixed for the particular case at hand. Therefore, our originally assumed total energy level  $W$  was in an unallowed region where no particle could exist. In quantum mechanics terms  $W$  must evidently be quantized or exist only in certain discrete levels even inside the potential box. It follows then that some level of higher energy would have also led to a satisfactory solution.

Thus all finite matter microscopic or macroscopic must exist in a quantized state if at all--the fact that matter is existant is then evidence



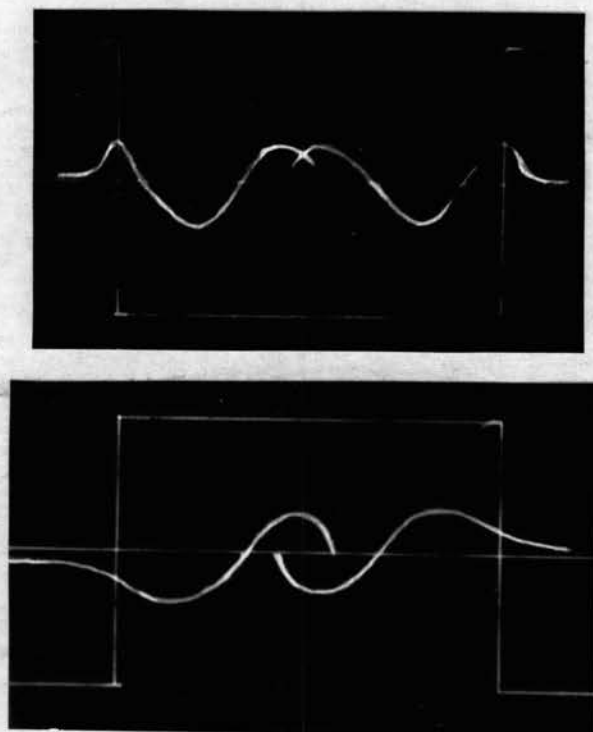


Fig. 14. Quantitization

of quantization. It is only seldom, however, out of the endless possibilities in nature that the curves in the preceding figure will meet therefore when they do the event is important enough to be considered unique. The quantum mechanics or wave mechanics-- a product of the mind of man--not predicated upon logic has been found to be one of the fundamental formulations of all nature.

Returning now to the allowed energy levels or quantization of matter, we proceed quite naturally to the thought of lower and higher energy states of atomic particles. The lowest energy state that a particle can exist in (which is also the most often encountered state of nature) has a half wave length slightly greater than the width of the confining box so that the tails can be added.

The actual  $\psi$  patterns are independent of the form of the box (straight sides, parabola, etc.) but the box does determine the  $W$  level at which the

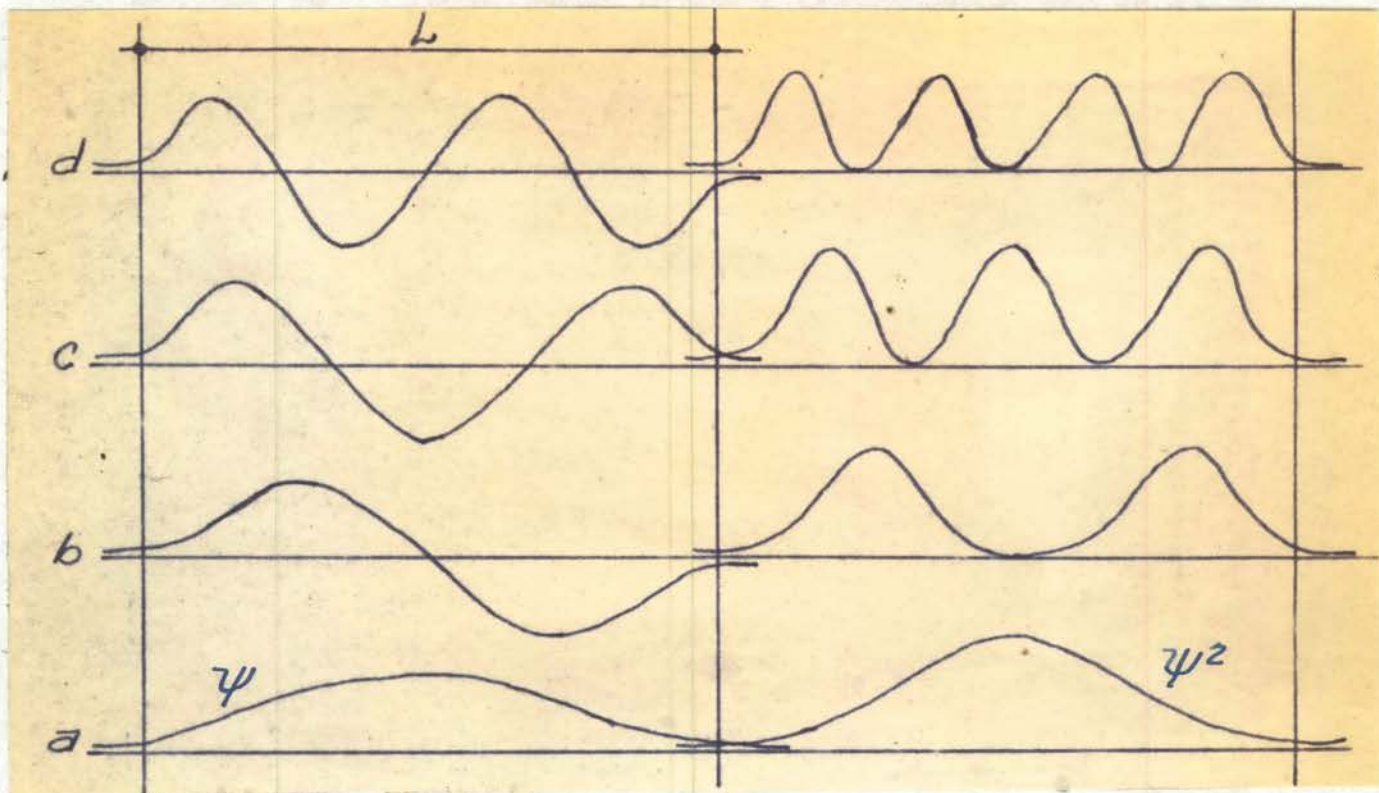


Fig. 15. Patterns for Fundamental and Harmonics 2

Lowest level possible is at a above for (a)  $\frac{\lambda}{2} > L$   
 for (b)  $\frac{2\lambda}{2} > L$       for (c)  $\frac{3\lambda}{2} > L$       for (d)  $2\lambda > L$

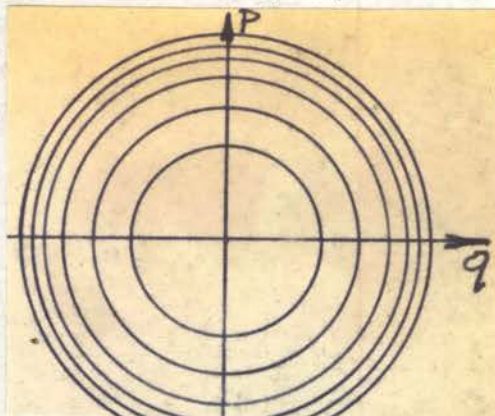
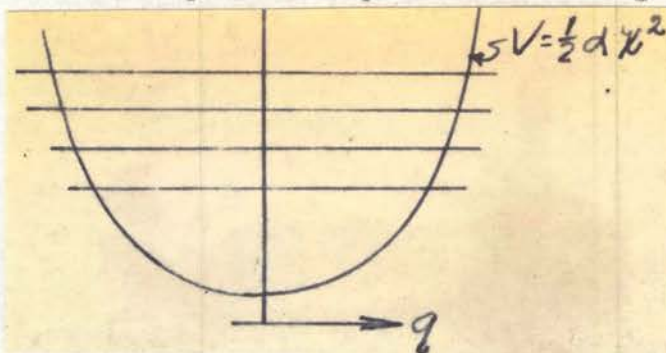
pattern will fit. The  $\psi$  pattern for the lowest level a above is without a node or zero value on the W axis. The first node appears in b and is called the first mode, c is mode 2 and d is mode three. Mode = 1- harmonic. The solutions in Fig. 15 are for a box in the form of a parabola and an electron confined to this box. Particles in a metal sample are almost analogous to a harmonic oscillator, because  $\psi x^2$  defines the V boundary curve. It is to this extent only that  $\psi$  patterns for any one type of potential box differ from another type.

✓ The spacing of the energy levels depends upon the size and shape of the



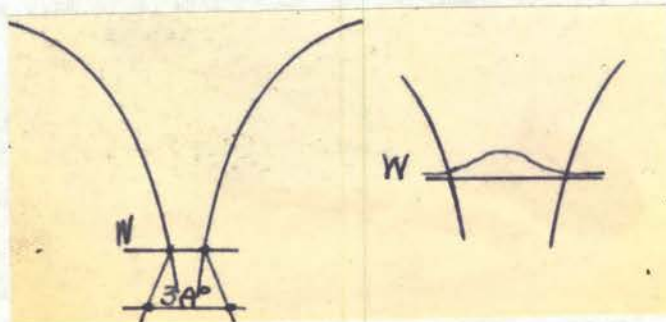
potential box. Look at the harmonic oscillator where  $V = \frac{1}{2}\alpha x^2$  ( $\alpha = \text{force}$ ).

This corresponds to a parabola as in Fig. 4.



It so happens that this particular potential box results in energy levels which are equally spaced the energy of the  $n$ th level being  $W_n = (n + \frac{1}{2}) \frac{h}{2\pi} \sqrt{\frac{\alpha}{m}}$  Where  $n$  takes on integral values 0, 1, 2, --- for successive levels and is known as the principal quantum number. The set of levels then has uniform spacing throughout, the interval being  $\frac{h}{2\pi} \sqrt{\frac{\alpha}{m}}$ . If the  $V$  curve is determined by  $-e^2/r$  as in Fig. 8 the box first increases slowly and then rapidly and soon becomes infinite. The levels then will be widely spaced at the bottom and will become more and more close as the top is approached, and finally converge to a limit or continuous spectrum symbolical of a free electron.

The energy levels in an atom are spaced about 100 times as widely apart as they are in the molecule. Patterns like those in Fig. 15 will be used to represent an electron in an atom or in a molecule, but the wavelength will be very much different since the wavelength varies inversely with the mass ( $\lambda = h/mv$ ). The spacing of the levels can very conveniently be calculated and should correspond with experimental data showing a spacing of a few electron volts. For an electron in an atomic box of  $3A^0$  width the ground state





will give  $\frac{1}{2} \lambda = 3 \times 10^{-8}$  cm., then the kinetic energy T from equation 1 is <sup>2</sup>

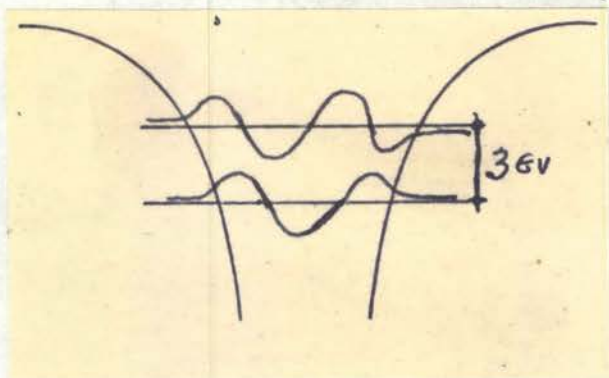
$$\lambda = \frac{h}{\sqrt{2m(W-V)}} \quad \& \quad W-V = \frac{1}{2} m v^2 \quad \lambda^2 = \frac{h^2}{2m(\frac{1}{2} m v^2)}$$

$$\lambda^2 = \frac{h^2}{m^2 v^2}$$

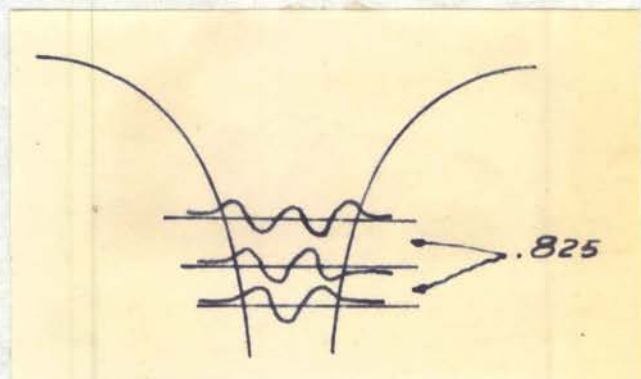
$$W-V = T = \frac{h^2}{2m\lambda^2}$$

$$W-V = 5 \times 10^{-12} \text{ Ergs}$$

$$\approx 3 \text{ eV spacing}$$



Rotational energy lines may be from .1 to .01 of this amount giving rotational levels with a spacing = .3 to .03. The proton due to greater mass will give vibrational levels with a much smaller interval between the spacings. From the same data we get



We must now extend these methods to problems of three dimensions, the harmonic oscillator as discussed above being confined to one dimension only. In the three dimensional picture we must bring in the x, y, z, cartesian coordinates so that equation 2 now becomes

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2} (W-V)\psi = 0 \quad \text{Equation 6}$$

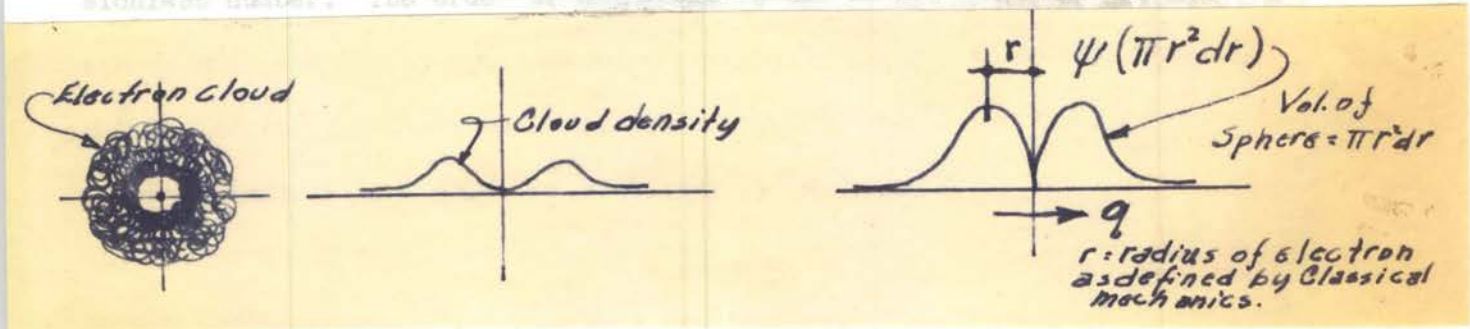
<sup>2</sup> Ibid., p. 24.

and the kinetic energy  $W-V = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$  Equation 7

(See Appendix D)

Our new picture of the three dimensional potential box will be a region where  $W > V$  is surrounded on all sides by a forbidden region where  $W < V$ . The boundary will now be a three dimensional surface inside of which the  $\psi$  pattern will have a character similar to that of the one dimensional problem, when the three dimensional pattern is projected in a single axis, and outside the surface the  $\psi$  pattern will terminate in exponential tails as before.

Since charged particles such as an atomic nucleus, has a spherically symmetrical field they become particularly interesting. The hydrogen atom consisting of one proton forming the potential box for the single electron has been completely solved by the methods of quantum mechanics. The knowledge gained here has caused the statement to be made that the electron is by far the most versatile of all atomic particles in fact of all the particles of nature. For the purposes of the  $\psi$  patterns the electron may be thought of as existing in the form of a cloud whose density is proportional to  $\psi^2$  and which thins out rapidly in all directions. The following sketch will serve to illustrate an electron in the first excited state of the hydrogen atom.



If the electron cloud is rotated we get a spherical shell of variable density, and if the distribution curve is rotated we get a funnel in which the radius is given by the distance from the center to the position of highest density. If the cloud density is given by  $\rho$  then  $\rho \psi$  is the probability density since



$\psi$  is proportional to the probability and is merely a graph of the intensity of the density from point to point.  $e$  gives the probability of the electron being at a particular point when you photograph it. The  $\psi$  pattern for the hydrogen atom must be normalized, however, to give the probability of finding exactly one electron; i.e. the value of  $\psi$  must be adjusted so that the integral over all time space is equal to unity. In three dimensions  $\psi\psi^*$  is used in the place of  $\psi^2$  and the probability per unit of volume becomes

$$\int \psi\psi^* dv = 1 \quad \text{Equation 8}$$

The electron still makes occasional long excursions from the nucleus but the probability of finding the electron very far outside what we ordinarily regard as an atomic volume is very small. Therefore, if we multiply the value of  $\psi$  at every point by "e", the charge of the electron we may picture the cloud as a distribution of negative electricity, the total quantity of which when integrated over all space is equal to e. When normalized as in equation 8 above  $\psi^2$  or  $\psi\psi^*$  must have a definite numerical value at every point, and we may consider in what units it is expressed. It's dimensions must clearly be the reciprocal of volume in order that equation 8 be a dimensionless number. The order of magnitude of the normalized  $\psi$  pattern for an atomic electron may be obtained by a rough calculation.<sup>3</sup> If the atomic volume inside the  $\psi$  pattern has a value ordinarily associated with atomic volumes of approximately  $10^{-22} \text{ cm.}^3$ , we could obtain unity by multiplying by  $10^{22} \text{ cm.}^{-3}$ , this value would therefore be a suitable value for  $\psi$  in the atom; and its square root  $10^{11} \text{ cm.}^{-3/2}$ , would be a satisfactory mean value of  $\psi$ . As a matter of fact, in the pattern belonging to the lowest level of the hydrogen atom  $\psi$  has been found to be  $5 \times 10^{11} \text{ cm.}^{-3/2}$ , at the center and falls off exponentially in all directions. Evidently then the  $\psi$  pattern in Fig. 11 will not

<sup>3</sup> Ibid., p. 26.



be the same as this  $\psi$  pattern which has the form as follows.



This shape is due to the fact that the positive nucleus is situated at the center of the potential box. This type of curve is characteristic of the S state or lowest energy state of the electron. In this state a plot of the electron gives the density shadow graph in the form of a fluffy ball as follows.



This pattern shows that in the lowest energy state the electron tries to stay around the nucleus. Therefore, the electron in the S state sits on the nucleus and vibrates or oscillates in all directions. This is a very different picture from a classical orbit, in fact, Bohr's quantum mechanics was almost perfect, his one omission being that classical mechanics could not allow the possibility of the electron passing through the nucleus (actually it flows around the nucleus as it vibrates). Most of the patterns in any of the excited states bear a greater relationship to an orbit than does the first S state. The reason for this is the part played by the angular momentum, hence it will now be convenient to observe more closely this atomic property.

d. Potential Boxes from Elliptical Orbits, and Similar Boxes from Attraction and Repulsion Curves.

Bohr in his work of constructing an atomic model was able to justify atomic relationships by considering the angular and radial momentum of the particles. In his model the potential box departs from the familiar inverse Coulomb curve which is a plot of  $-e^2/r$  as is shown in Fig. 8 and Fig. 16.

After the newer quantum mechanics came into use it was found that potential boxes similar to those derived from Bohr's elliptical orbits, could be constructed from consideration of the attraction repulsion forces between two particles. Furthermore these new potential boxes allowed the formation of the ground state, a condition not possible with the elliptical orbit boxes. Let us start with the familiar elliptical orbit from the field of astronomy, and used so effectively by Bohr in his work. In this picture the electron never goes nearer the nucleus than some prescribed amount, nor further away than another prescribed amount, indicating that some balance is present causing the electron to oscillate between these limits as it follows the elliptical orbit. Bohr connected this balance with the astronomical science of his day and attributed the phenomena to the angular and radial momentum of the particle. Let us look at Fig. 16.

The electron never goes nearer the nucleus  $O$  than  $OP$ , nor further from it than  $OQ$ . Values of  $r$  between  $r = OP$  and  $r = OQ$  are then allowed and values outside these limits are not allowed or are forbidden. This indicates that there exists a potential curve similar to  $ABC$  in the place of the Coulomb curve  $EFG$ , which is a plot of  $-e^2/r$  similar to Fig. 8. Returning to the orbit  $P-Q$ , we see that at  $Q$  the radial velocity is zero but the particle still possesses an amount of energy represented by  $A-F$ . The boundary at  $C$  is also to be expected, for it is, of course, the angular momentum about  $O$  which prevents the electron from colliding with the nucleus; and in determining the allowed value of  $r$  this kinetic energy associated with the angular momentum must be subtracted from the total kinetic energy,  $W-V$ . Taking any vertical line  $HG$ ,  $HG$ , represents the total kinetic energy;  $BG$  represents the angular part of the kinetic energy, and  $H, B$ , the radial part. As  $H$  approaches  $A$  and  $C$ ,  $HB$  tends to approach zero, giving a boundary at  $A$  or  $C$ . In this way  $ABC$

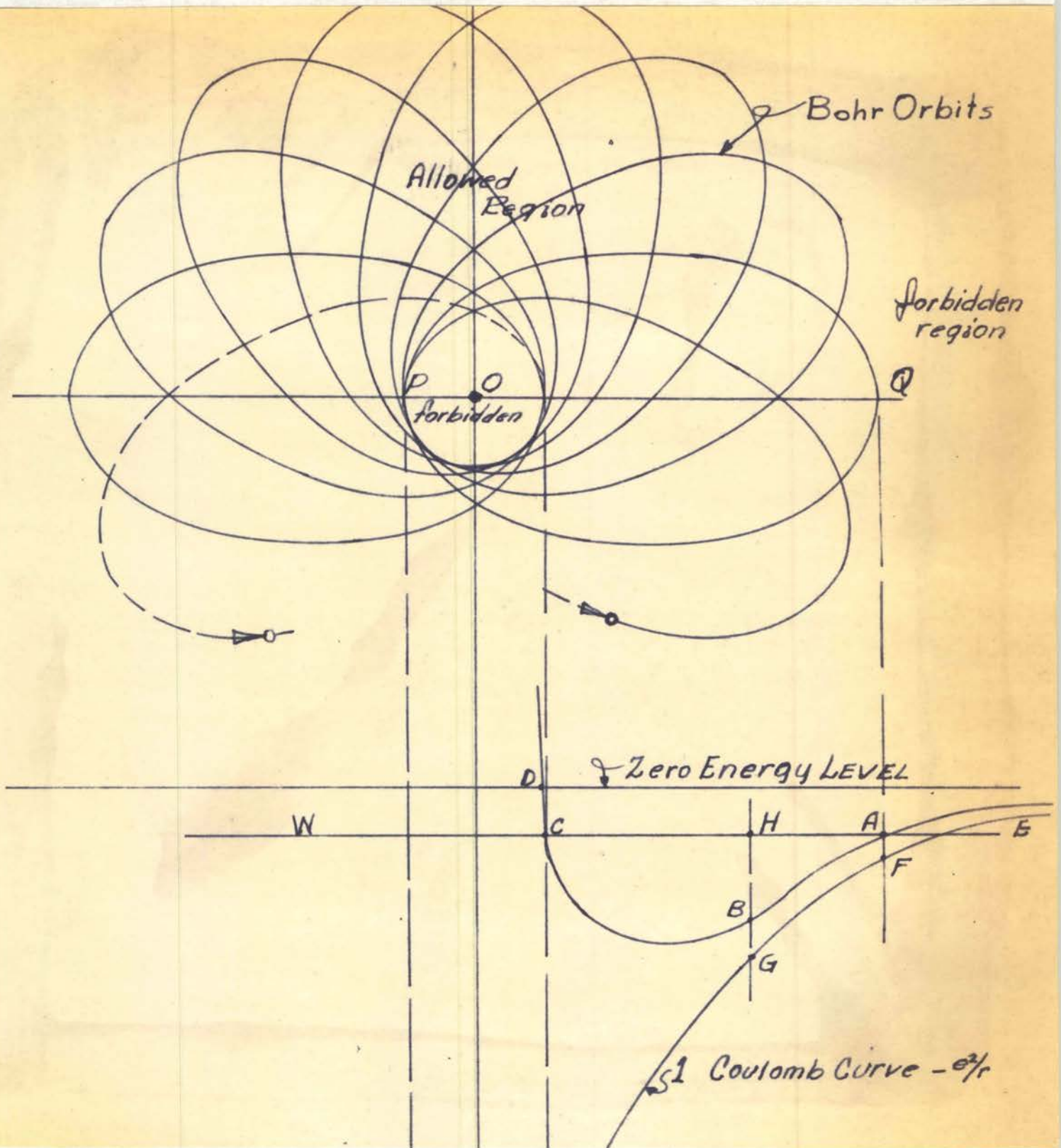


Fig. 16. Potential Box from a Particle in an Orbit



becomes a potential box. This then is a pictorial representation of some excited state of the hydrogen atom and is the picture to be used instead of Fig. 8, for all except the ground or S energy state or level, when the electron is considered to be in an orbit.

Inspection of Fig. 16 will reveal that the potential box ABC could have been obtained without the use of orbits. It has been established that in equilibrium conditions between charged particles there exists attraction forces tending to bring the particles together, and repulsion forces preventing the particles from approaching each other more closely than some small amount. Referring to Fig. 16 if we add to the Coulomb curve, which is an attraction potential, a repulsion curve whose slope increases rapidly as we approach the position of the nucleus; we get upon adding these two curves a potential box similar to that of Fig. 17. In the absence of the repulsion curve or  $l = 0$  we immediately obtain  $\psi$  patterns of the ground state as shown by the S energy levels of Fig. 17.

In the alkali atoms such as Li, Na, K, etc., their atomic arrangement is such as to cause them to be referred to as hydrogen like atoms. Each atom consists of a positive core and a single valence electron. In any atom the core or nucleus consists of a single positive charge  $Ze$  where  $Z$  is the atomic number of the element. In considering the alkali atoms, then the core which forms the potential box consists of  $Z-1$  electrons surrounded by a positive  $Ze$  charge. The valence electron spends most of its time outside the core in a field almost identical to that provided to the electron by the proton in the hydrogen atom.

To account for the complicated series of spectra lines emitted by the hydrogen like atoms Bohr postulated the existence of several series of energy

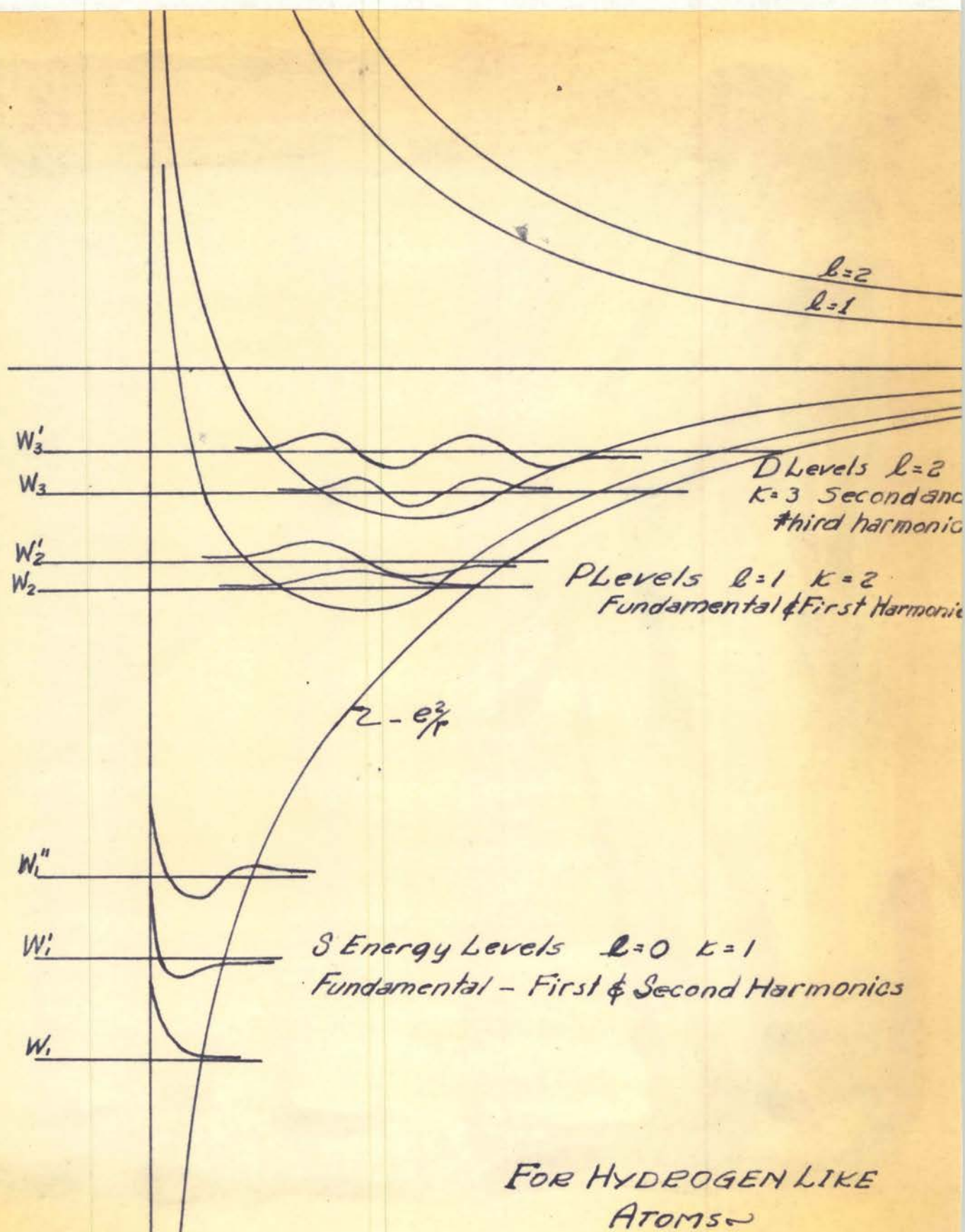


Fig. 17, Potential Boxes from Attraction Repulsion Curves

levels, of which the most important are known as the S-series, the P-series and the D-series. These letters were taken from the initial letters of the words "sharp", "principal" and "diffuse;" these terms being used to classify spectrum lines. The same letters later came to be used to denote the energy levels which were believed to give rise to the various spectra lines. Using this idea of Bohr's we may at once state roughly how it is that the  $\psi$  patterns belonging to these varying series arise. We obtain the S-series by fitting  $\psi$  patterns into the simple potential box like Fig. 8 or the  $W_1$  levels of Fig. 17. We obtain the P-series levels by fitting a set of  $\psi$  patterns into a potential box like the  $W_2$  levels, and the D-series by another set of  $\psi$  patterns similar to  $W_3$  levels in Fig. 17.

e. Two Potential Boxes.

We have previously limited our discussion to one potential box and have determined the pattern of the particles confined therein. Let us look at the case where two boxes are brought into close relationship with each other. Referring to Fig. 18 let the two boxes be separated by the barrier distance QR and assume OP and ST to extend to infinity. If the barrier was complete as in classical mechanics particles could not transfer from one of the boxes to the other, and the boxes would be independent of each other. In quantum mechanics the  $\psi$  pattern extends to infinity therefore for any energy level there is a possibility of finding the particle passing from one box to the other. In the lowest energy state we find that the  $\psi$  pattern can either be symmetrical as in Fig. 18, b or anti-symmetrical as in Fig. 18, c. Both patterns have the same possibility of existing and the composite pattern is given by the summation as is shown in Fig. 18, d. The total area or  $\psi^2$  value for b and c is about identical. The only discrepancy comes in the



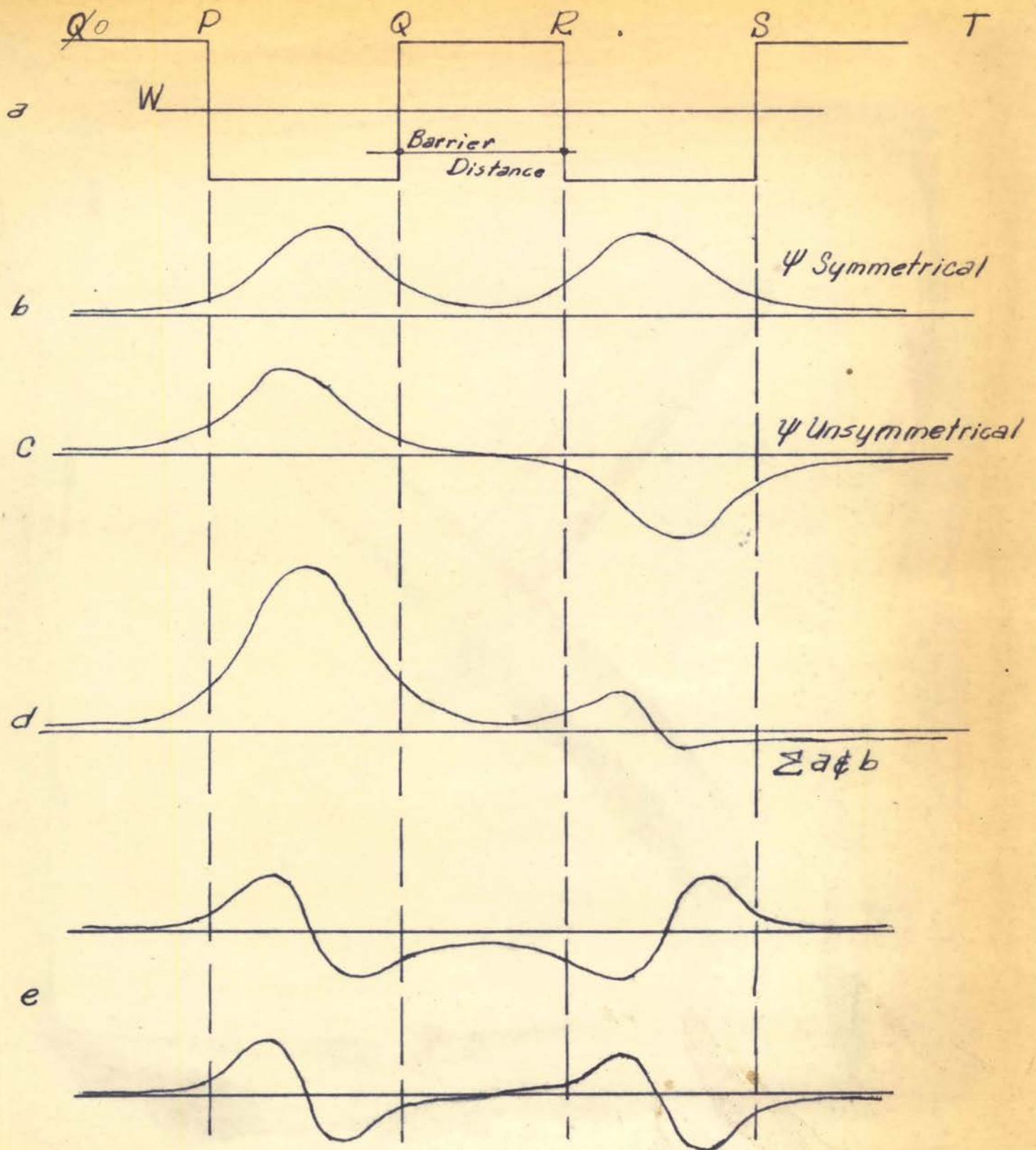


Fig. 18., Two Potential Boxes

actual zero value of the antisymmetrical wave where it goes through zero in the Q R region. Values of  $k$  must change as well as the constants  $C$  and  $D$  in the  $\psi$  equation for 18, b and 18, c. The two  $\psi$  patterns will give different discrete  $W$ 's or energy levels. The  $W$  of b will be slightly lower than the  $W$  of c. If Q R were infinite we would have the equivalent of 1 box giving one  $W$ .

for 1 box we have 1 Energy Level  $W$  —————  $\frac{W_c}{W_b}$  for 2 boxes we have 2 possible energy levels

The symmetrical  $\psi$  of the last figure gives  $\psi_k = C e^{-kx} + D e^{+kx}$  neither of which disappear between Q R.

There can be only one curve of  $W$  or one  $\psi$  which will satisfy the lower energy level  $W'$  for the symmetrical curve. For the anti-symmetrical pattern Fig. 18, c  $\psi$  may be positive or negative therefore  $W$  can have two values. Irregardless the value of  $\psi$  squared will have all positive values. Since the node occurs between the potential boxes this is not an overtone or shift to a higher energy state.

For the next higher energy level we would get  $\psi$  patterns as in Fig. 18, e.

Up to this point we have considered the potential box and  $\psi$  patterns, and the probability of finding the particle somewhere in the  $\psi$  pattern. If we expect to find an electron or particle at a particular place we must by some means interrupt the  $\psi$  pattern to examine the particle. Heisenberg found that for a particle moving at the tremendous velocities of say  $10^7$  or  $10^8$  cm per second at which electrons can travel--if the pattern is made stationary at one point so that a coordinate of the electron is fixed with



certainty, then little information can be obtained about the momentum of the electron from it's  $\psi$  pattern. On the other hand if we determine the momentum of the electron we cannot place the particle at any particular point. Heisenberg found that an expression of the above statement is

$$(\Delta x)(\Delta p) \cong h \quad \text{Equation 9}$$

In brief equation 9 implies that if we know the position of a particle, there results a great uncertainty as to it's velocity or momentum  $p$ . As an example if an electron is accelerated to a velocity of  $10^7$  cm/sec with an allowable error of 20% in the determination of the velocity, then the value of  $mv$  is about  $10^{-20}$ , therefore we find the uncertainty of the position of the electron to be more than 300  $\text{\AA}$  units.<sup>1</sup> (One angstrom unit =  $10^{-8}$  centimeters).

f. Extension of Boxes to Crystals, Solids, and liquids in Contact With Solids.

As we proceed from single electron problems to those of heavier elements we make the assumption that all of the electrons from the electron cloud are at aphelion and that the remaining valence electron or electrons are captured in the box. In this way we progress from the hydrogen atom to the alkali elements and on to crystals and solids.

Consider a solid cube of macroscopic dimensions. If the positive nuclei be represented by  $N$  then we must have  $N-1$  electrons in the sample. If the valence electron is allowed to move throughout the solid and suffer reflection

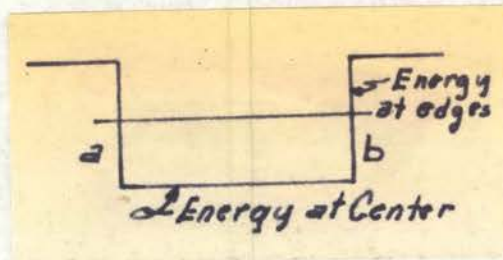


at the surface then the particle itself becomes a huge potential box. Inside

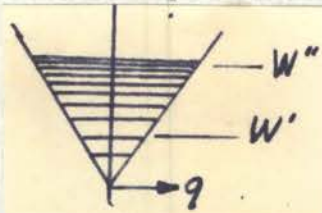
<sup>1</sup> Ibid., p. 51.



the metal is the lower potential region and the surface becomes the sides of the potential box.



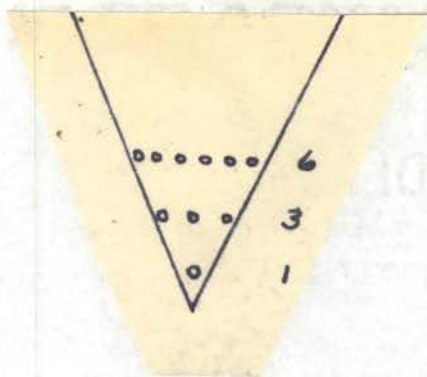
This box considers all of the electrons to be bound except one, this one being the valence electron and belonging to all possible  $\psi$  patterns that the energy  $W$  will allow. At room temperature we have the following picture,



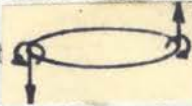
with most of the  $\psi$  patterns being in the higher energy states. As we reduce the temperature and approach absolute zero the tip of the cone begins to fill in. The high energy electrons around  $W''$  settle down into  $\psi$  patterns. At absolute zero all motion ceases and the fuzzy top begins to become a plane surface.


At ordinary temperatures only a small percent of the electrons are in the low energy pockets or holes. Chances are that they are bound electrons being bound to the nucleus to characterize the element. All of those in the neighborhood of  $W''$  are free electrons and those near  $W'$  are bound, those between are the valence electrons and are in a semi-bound state.

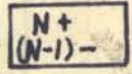
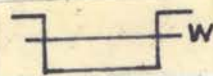
As the temperature approaches absolute zero the lower levels fill in according to the following scheme. The Pauli exclusion principle determines the manner in which the levels fill in. In any system there are a definite number of holes, only one identical electron can be accompanied in a given hole, therefore the holes are vacant  $\psi$  patterns. Pauli said that when we



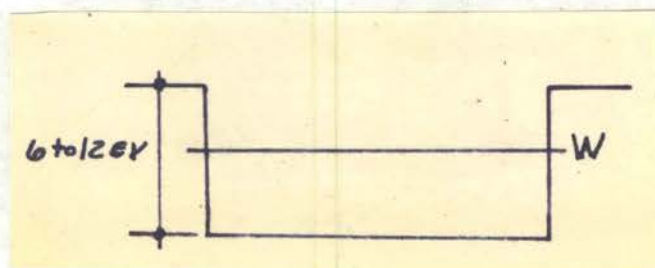
| x | y | z |     |
|---|---|---|-----|
| 0 | 0 | 0 | ) 1 |
| 1 | 0 | 0 | } 3 |
| 0 | 1 | 0 |     |
| 0 | 0 | 1 |     |
| 2 | 0 | 0 | } 6 |
| 0 | 2 | 0 |     |
| 0 | 0 | 2 |     |
| 1 | 1 | 0 | } 6 |
| 1 | 0 | 1 |     |
| 0 | 1 | 1 |     |

have more electrons than holes they can be matched in pairs to form a closed shell. The criterion is that for the same  $\psi$  pattern to accommodate two electrons, their direction of spin must be different  They then cancel their magnetic effect, therefore closed shells with paired electrons never react with magnetic moments or give rise to Zeeman effect.

Returning to the microscopic piece of metal each nucleus gives rise to an intense field with the charge smeared  throughout.

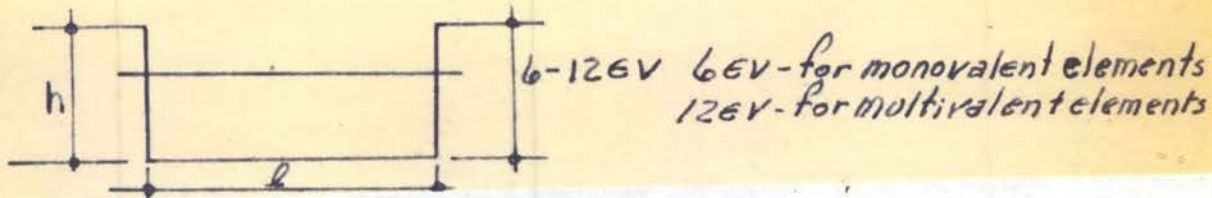
The charges and nuclei give rise so  Net = +1 and the particle forms a potential box. 

Take the 1 (plus) net charge and build a potential curve for the charge or valence electron. This charge must seek and find its  $W$  level. The depth  $h$  of the box varies from 6 to 12 ev.

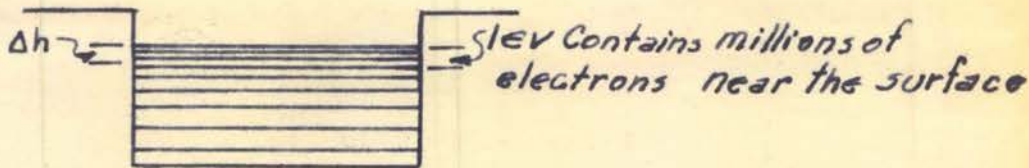




For the higher valence elements we have as many electrons in the box as the element has valence. The De Broglie wavelength for the lower level will be enormously large  $\lambda = 2L$ , (where  $L$  = length of metal and also the width of the potential box).



Therefore, for all the billions of electrons contained in the macroscopic particle each electron volt must have at least millions of  $\psi$  patterns or electrons if the total depth of the box is only 6 to 12 ev.



The larger the piece of metal the more closely the levels become. In the natural or unexcited state the box is approximately  $2/3$  full of solids such as metals and crystals.

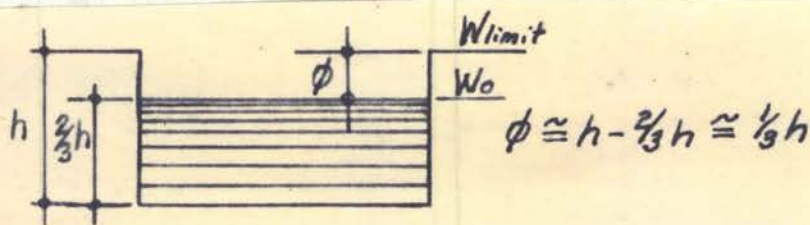


Fig. 19. Work Function in Solids

The  $\phi$  distance in Fig. 19 above is completely void of all electrons at absolute zero. This space  $\phi$  provides the characteristic work function of the metal. Comparison with Fig. 6 shows that  $\phi$  is the latent heat of the electron gas.



For alkali metals  $\phi$  has a range of about 2 ev. and goes as high as 6 ev. for platinum. The work function does not depend upon gas density or the number of electrons. Therefore,  $\phi$  is a characteristic of the element itself.

In order to extend our previous work to the absorption or radiation of energy we must bring into our  $\psi$  patterns or wave equation a time component. We have noted that the value of  $\psi$  have previously been fixed as a standing wave. Consider the amplitude of a vibrating string from which we observe that the amplitude change with time from positive to negative  $v$  time per second or becomes a traveling wave. Returning to the problem of two potential boxes we have Fig. 20.

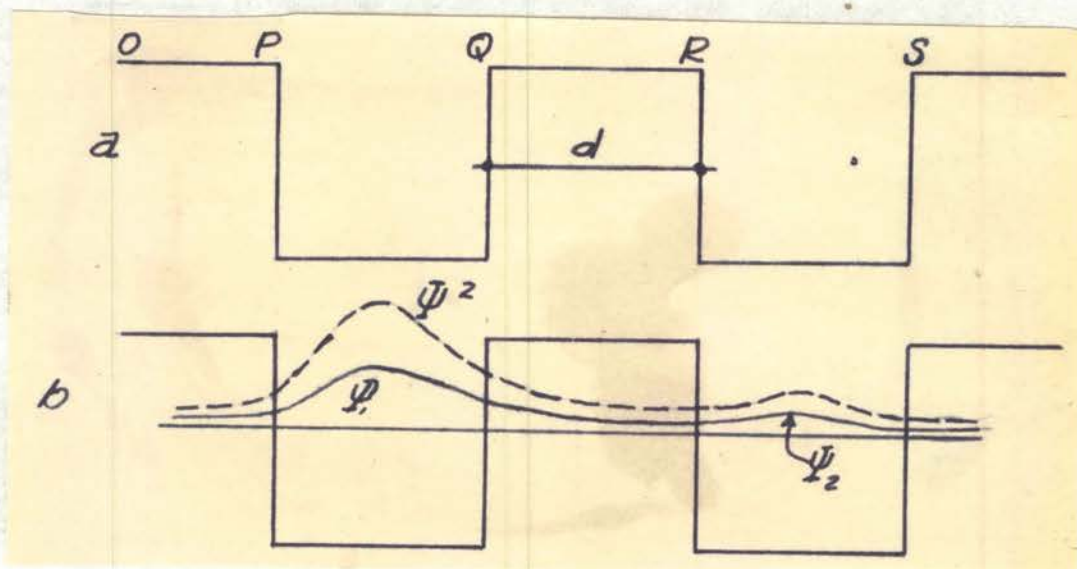


Fig. 20. Two Potential Boxes

With Time Considered

In this case where the two boxes share electrons the  $\psi$  patterns at some time will be similar to Fig. 20, b. If the square of the amplitude of the  $\psi$  pattern gives the probability of locating the electrons along the  $x$  axis then we see that at this instant the probability of the electrons being in box 1 is much greater than the probability of its being in box 2. The

probability of the electrons being in the second box is given by  $P \approx e^{-2kd}$  or  $e^{-2kL}$ . Since  $d$  is not infinite then at some time later the probability of the electrons being in box 2 will increase. The factor  $e^{-2kd}$  is termed the leaking factor giving the probability of the particles leaking through the boundary and appearing in the other box. Since this process takes place with time we must introduce the time factor in the Schroedinger equation whose solutions become

$$\Psi(x,t) = \Psi_1 + \Psi_2 = a_1 \psi_1 e^{-2\pi i \nu_1 t} + a_2 \psi_2 e^{2\pi i \nu_2 t} \quad \text{Equation 10}$$

(See Appendix D)

$\psi_1$  Symmetrical     $\psi_2$  Nonsymmetrical

If we select a time where the electrons are in one box with small probability of them being in the other box we know that they vibrate even at room temperature. At some particular instant they may be in phase but their frequencies differ  $\nu_1 \neq \nu_2$  hence their synchronism gets worse and worse with increasing time. The small probability amplitude box 2 will grow as  $\psi_1, \psi_2$

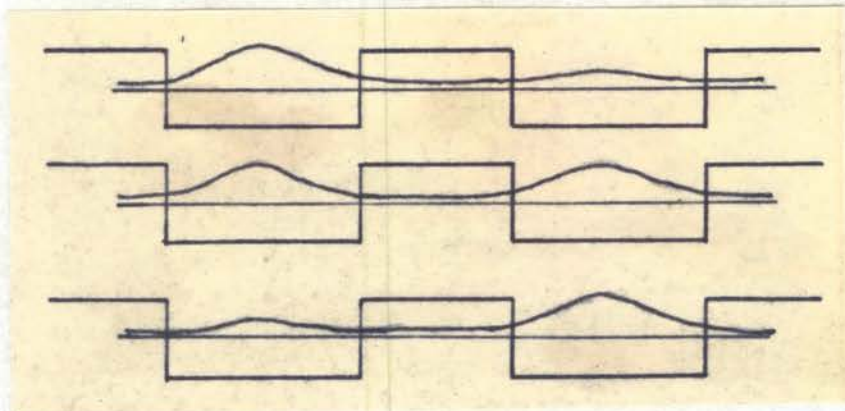


Fig. 21. Leaking Between Boxes

add. This change is described as a physical event, one which the physicist can detect. This "leaking" or tunneling effect where  $W < V$  is not allowed and cannot be accounted for in classical mechanics. The rate of leakage

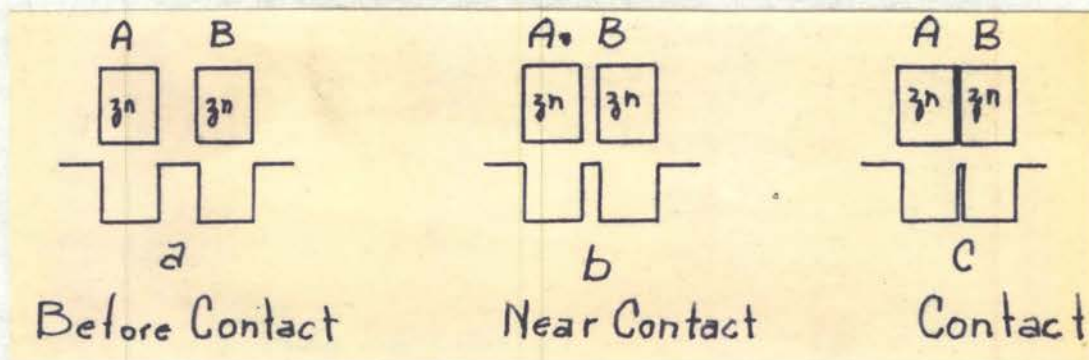


from quantum mechanics is the same as the group velocity of the two  $\Psi$  patterns or the net wave. It is, therefore, proportional to the beat frequency in vibration per second.

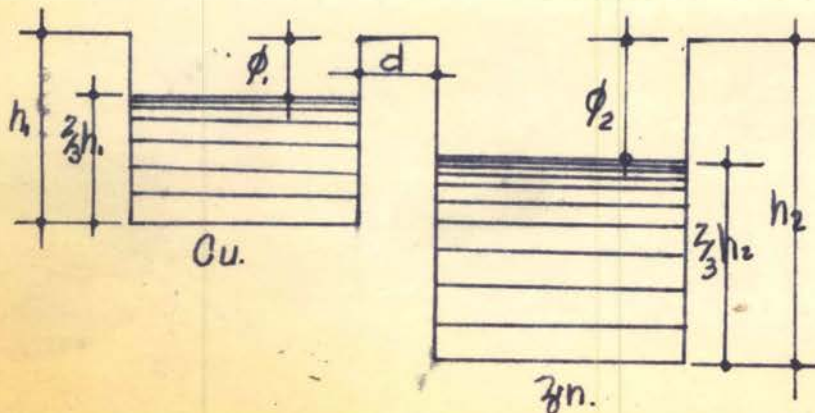
$$B.F. = \text{Number of Vibrations/Sec} = (\nu_2 - \nu_1) = \left(\frac{W_2}{h} - \frac{W_1}{h}\right) = \frac{1}{h}(W_2 - W_1)$$

The probability  $P_1$  is proportional to  $e^{-kd}$  where  $d$  is the distance separating the boxes. As the boxes are far apart the electron cannot go from one box to the other, but as  $d$  decreases the barrier becomes less and less effective and hence the electrons start to leak through the barrier even though their total energy is insufficient to allow their going over the top of the barrier as would be necessary by classical mechanics.

Let us now consider two metallic samples as they approach each other.



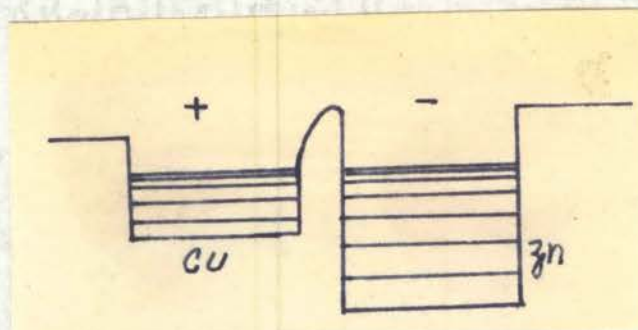
These bodies form a potential box system which varies as shown in the above figure. The depths of the potential boxes are equal, therefore, no electron exchange takes place hence there is no net current flow. In the case of dissimilar metallic cubes, the depth of the boxes depends upon the element of the cube and we have



*d - approaching atomic dimensions.*



When  $d$  is small but the barrier is still present we find that the electrons from the higher energy level of the copper will leak through the wall and establish an equilibrium level as follows.



The copper will lose enough electrons to cause equilibrium to be established. The loss in electrons (negative) from the copper causes the copper cube to become positive with respect to the zinc cube. The barrier changes character as shown in the sketch so that the electrons from the zinc find the barrier thickness easier and easier to penetrate while the electrons from the copper find the barrier harder and harder to penetrate so that at equilibrium the resulting potential difference is the familiar contact potential of the elements.

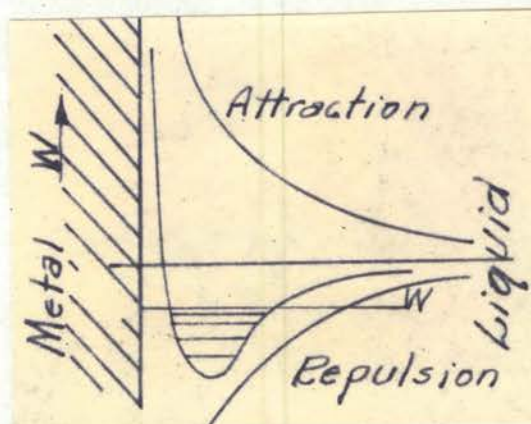
Sommerfeld's theory of metals in conjunction with the Fermi-Dirac statistics and the quantum mechanics enables us to visualize what takes place at a metal to metal junction or liquid solid, or liquid-liquid interface.<sup>1</sup> As we have previously found the valence electrons are quasi-free or semi-bound; i.e. they are wandering about the parent material somewhat like the molecules of a gas and belong to no particular atom. The atoms are then actually ions and as such occupy definite crystal positions in a solid or wander about in a liquid.

When a positive ion is removed from a solid surface or when a positive

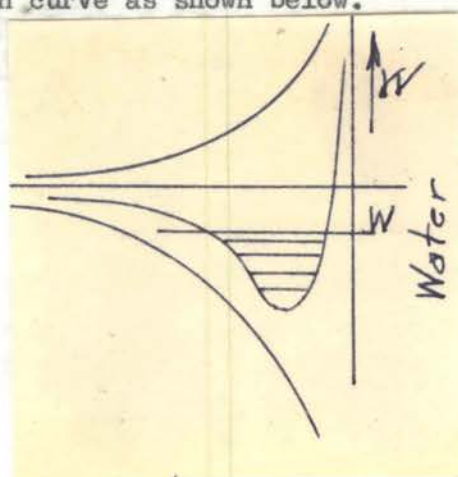
<sup>1</sup> Dole, Malcolm, Experimental and Theoretical Electrochemistry, pp. 505-512.

ion goes into solution it must do work against the net attraction of the electrons and other ions in the solid. Very close to the solid perhaps just at the solid surface the forces are repulsive, but these repulsive forces fall off very rapidly as the distance from the surface increases and soon give way to the attractive forces previously mentioned.

The latter also decreases as the distance increases so that the potential energy curve of a positive ion along a line perpendicular to the metal surface assumes the form similar to Fig. 17 or as follows:



Consider the situation where the metal is submerged in water. As a positive ion approaches a water molecule, it polarizes the water molecule, i.e. it induces a temporary electric moment in the water molecule and is, therefore, attracted to the water molecule or water molecules until, at very close distances, the repulsive forces become effective. Therefore, the potential energy curve of the positive ion near a water molecule is a similar attraction repulsion curve as shown below.





From what we have learned from quantum mechanics we know that positive ions can make spontaneous transitions from the surface of the metal to the solution and vice versa despite the existence of a potential barrier at the surface of the metal. Considering a single positive ion we know that there is a definite probability of finding this ion in the solution. Suppose that it leaves the metal surface and makes the transition to the solution. If it does not make an inelastic collision in the solution, it will have enough energy to get back to the metal, but the chances are very great that the ion will lose some of its energy by colliding with a water molecule, and in this way be trapped in the potential energy box in the neighborhood of the water molecule. It will accordingly stay in the solution; this is the mechanism by which an ion makes a metal to solution transfer. Not all ions on the metal surface can make transitions; the possibility of a transition taking place is based on the existence of a lower energy level in the solution. If the energy level in the solution that the ion must go to is higher than the level which the ion occupies in the metal, the metallic ions cannot make the transition to the solution. However, the reverse transition could take place, in fact, both transitions occur all the time until at equilibrium the number of ions depositing becomes equal to the number of ions dissolving. The possibility of ions depositing or dissolving can be illustrated by Fig. 22. These boxes are obtained by uniting the previous two boxes or by bringing the water molecule close to the metal surface. The potential curves begin to overlap giving three types of potential curves as below.

In the case of a the normal levels are the same potential-energy level: Hence the transitions of the ions in either direction are in equilibrium and the transitions take place reversibly. In the case of b transitions will



take place only from the metal to the solution, and these transitions are irreversible because the ions are not able to make spontaneous transition from a lower energy level to a higher energy level. As the ions leave the metal surface the metal becomes negative, with the result that the energy levels are shifted in such a direction that the equilibrium situation shown in b is attained. This causes the establishment of an interfacial potential difference during the adjustment. In the case of c, ions will deposit on the metal shifting the levels and producing an opposite potential difference, the metal becoming positive.

If a potential difference is applied to a cell in equilibrium such as Fig. 22, a the potential boxes will change such that either Fig. 22, b or c results. Either condition will result in a polarized current flow which accompanies the movement of the partially fixed film at the interface.

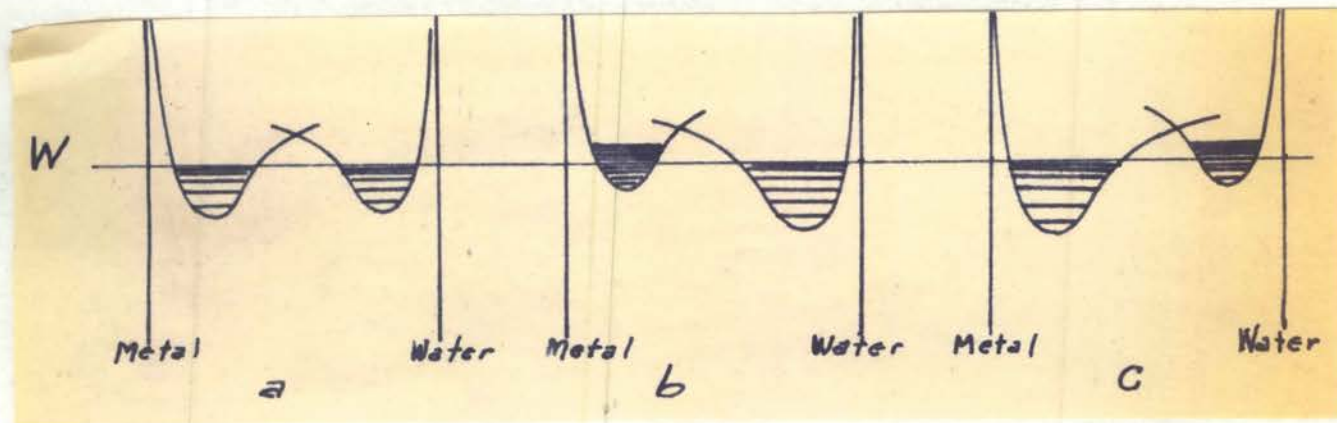


Fig. 22. Overlapping Potential Curves

Conversely if by mechanical means the film is caused to move the potential boxes will be altered either in accordance with Fig. 22 b or c. These alterations then give rise to a current flow resulting in the establishment of a polarized potential between the solution and the metal.

Mention should also be made of the fact that the potential curves shown in Fig. 22 can also be considered as a pressure value curve. When the volume of a metal or liquid contains positive ions in potential boxes is reduced the shape of the potential box is latered becoming more narrow at the top forcing the energy levels up to a higher level.

$$\text{When Compressed } \frac{\text{Energy}}{\text{Volume}} = \frac{W}{V} = \frac{PAU}{V}$$

$$\frac{PAU}{V} \sim \frac{PV}{V} \sim P \quad \text{Equation 11}$$

Therefore, potential curve can be considered as a pressure curve.

It follows then that if the water in contact with a solid is acted upon by a variable pressure the effect will be the same as if the fluid were mechanically driven with respect to the metal.

## CHAPTER IV

### THEORY OF ELECTROKINETIC TRANSDUCER OPERATION

As has been previously stated on page 6 a proposed theory should represent a plausible explanation of the phenomena and substantiate the experimental evidence. The value of the proposed theory lies not only in its ability to account for the experimental facts, but also in its suggestiveness of new modes of attack or application to other phenomena.

From the last part of the quantum mechanics summary we have arrived at the conclusion that when a solid is in contact with a liquid the system will reach an equilibrium condition wherein the two potential boxes overlap reducing the boundary height. From Electro-Chemistry by Creighton and Koehler<sup>1</sup> we find that when two heterogeneous substances are brought into contact the one having the higher dielectric constant will in general assume a positive charge with respect to the other at equilibrium--this again being accounted for by the influence on the shape of the potential box. Returning to the operation of the Electrokinetic Transducer we have a situation wherein two metallic electrodes are inserted in a glass tube with a fritted disc superimposed between the electrodes, see Fig. 1. When filled with water the higher dielectric constant of the water with respect to either the metallic electrodes or the pyrex glass causes the water to assume a positive charge. The potential boxes between the electrodes and the water and the water and the fritted disc cause an abundance of positive ions whose mobilities are much in excess of the ordinary positive ion mobility because

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<sup>1</sup> Ibid., p. 144.



of the influence of the potential systems. The theory of operation of the Electrokinetic Transducer proposed by the author is as follows: IN A SYSTEM CONSISTING OF METALLIC ELECTRODES CONTAINED IN A GLASS TUBE FILLED WITH WATER, THE ELECTRODES AND THE WATER PRESENT TO THE POSITIVE IONS FROM THE METAL AND THE GLASS OVERLAPPING POTENTIAL BOXES WHOSE EFFECT IS THE LOWERING OF THE POTENTIAL BARRIER ALLOWING MUTUAL TRANSITION OF IONS UNTIL A CONDITION OF EQUILIBRIUM IS ESTABLISHED. DISTURBANCE OF THIS EQUILIBRIUM CONDITION BY MECHANICAL AGITATION OR VARIABLE PRESSURE RESULTS IN AN EXCESS OF POSITIVE IONS IN ONE POTENTIAL BOX WHICH GIVES RISE TO A POTENTIAL DIFFERENCE BETWEEN THE WATER AND THE ELECTRODE. THE SUPERPOSITION OF THE FRITTED DISC BETWEEN THE ELECTRODES HAS THE SAME EFFECT AS HEATING THE FILAMENT OF A VACUUM TUBE. THIS DISC BECOMES THE SOURCE OF A CONCENTRATION POSITIVE IONS WHICH PRESENTS AN ELECTRIC FIELD TO THE WATER-ELECTRODE POTENTIAL BOXES SUCH AS TO CAUSE A FURTHER LOWERING OF THE BOUNDARY AND HENCE A GREATER MOBILITY FOR IONIC TRANSMISSION. It should be noted here that in accordance with equation 11 and previous reasoning that ionic transition will result either from mechanical movement of the water with respect to the electrodes, or with a change in pressure within the water. Therefore, one would expect an output from either movement or pressure variation. Pressure variation can arise either from diaphragm movement, shock waves, or sound waves transversing the liquid. The following figure shows the condition existing in the Electrokinetic Transducer.

In Fig. 23, a we find two metallic electrodes submerged in water. The nominal energy level previous to contact is represented by some line as W. Upon contact and establishment of equilibrium condition the potential boxes overlap so as to lower the potential barrier, thereby allowing exchange of

ions and equilibrium at some level such as  $W$ . In Fig. 23, b the addition of the fritted disc causes greater overlapping of the potential boxes thereby lowering still further the potential barrier and giving greater mobility to the ions. Fig. 23, c is the same as b except the water is assumed to be under pressure. An increase in pressure has the effect of increasing the ordinates from the  $W$  level to the potential box as well as a reduction in the volume which decreases the radius  $r$ . Hence an increase or decrease in pressure will result in a potential difference between the electrodes.

Experimental observations previously mentioned are in agreement with the theory of operation. For instance, the useful output has been found to vary directly with the spacing of the electrodes when no fritted disc is used and with the distance from the disc when the disc is used. Moving the electrodes out results in separating the potential boxes allowing a higher barrier and accompanying resistance to transition of the ions. Increasing the electrode area gives a proportional increase in output because greater use is made of the potential field presented to the water-metal potential boxes by the fritted disc. By properly varying the areas and spacing different characteristics can be built into a given transducer.

The observed increased output from the transducer when used as a microphone with its axis perpendicular to the sound source is compatible with the proposed theory because a greater area is presented to the sound source resulting in a greater variation in pressure throughout the transducer. This pressure variation alters the potential boxes giving rise to the observed potential. In a like manner the difference observed between the light blow of the screwdriver blade and the heavy blow of the plastic handle are explainable. The handle causes more deflection and undoubtedly some flow



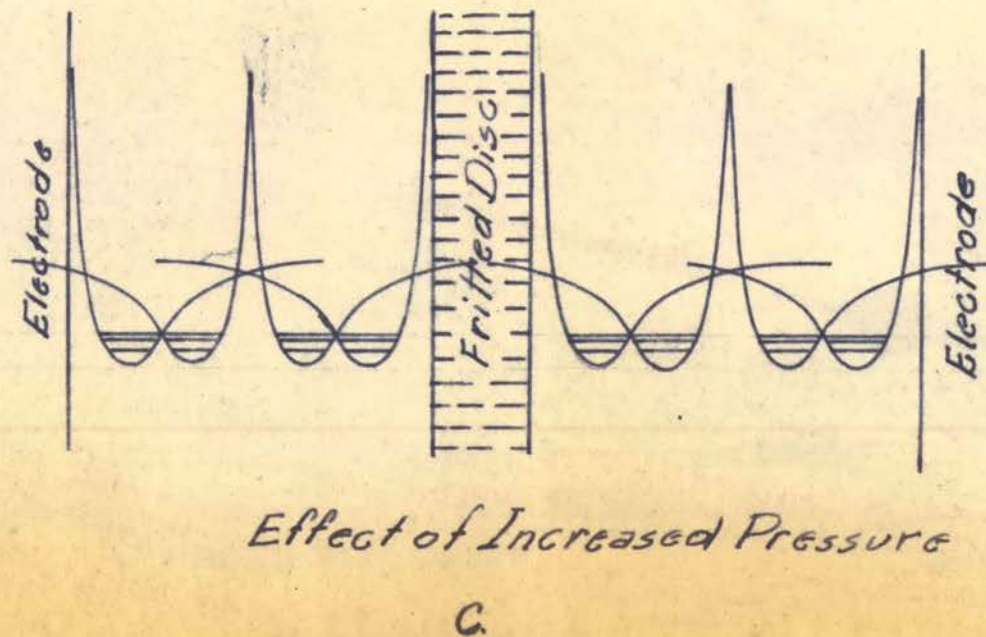
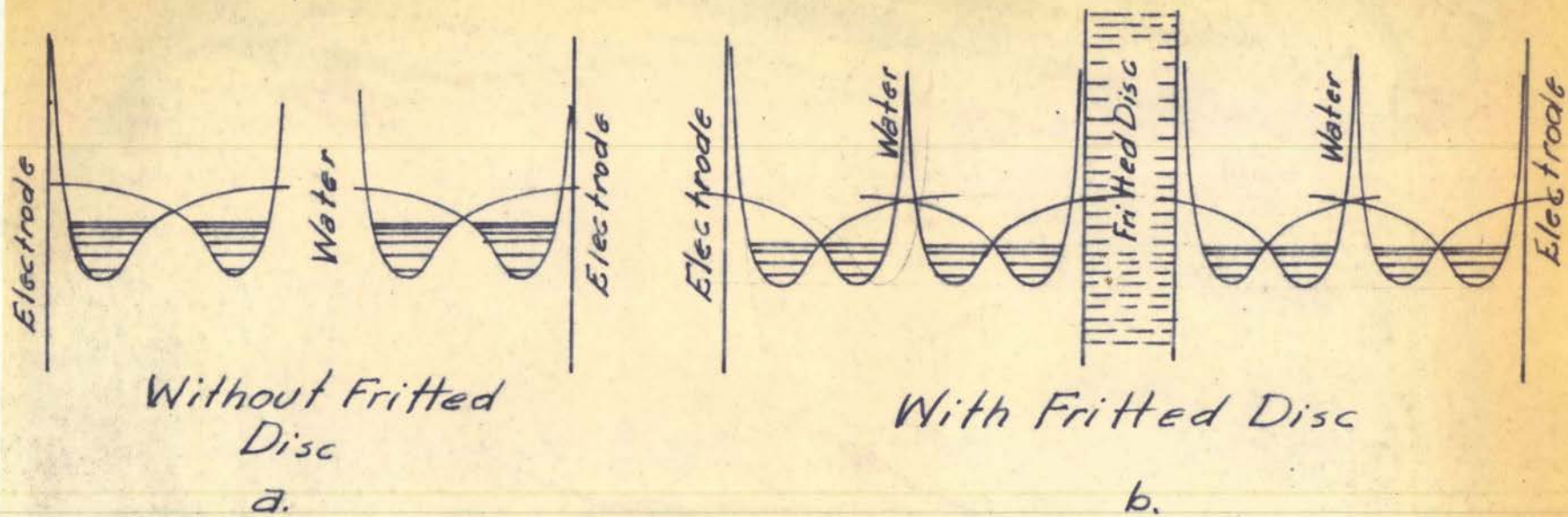


Fig. 23., Potential Curves for Electrokinetic Transducer



through the disc, these effects, however, do not have as much to do with the useful output as the sharp shock wave and resulting pressure variation in the alteration of the shape of the potential boxes.

In order to prove the proposed theory experimentally the author first thought of constructing a transducer in which the two ends of the tube were brought out to a common outlet. This outlet could be fitted with a diaphragm or subjected to variable pressure, however, the results from such an apparatus would only be indigative since both branches would not be absolutely identical. This would leave open to question the fact that minute flow might take place across the electrodes. Giving more consideration to Fig. 23, it was decided that the fritted disc was important only in supplying an intensified field to aid in ionic transfer, and that flow did not have to take place through the disc. This immediately suggested that the porous diaphragm could be replaced by a solid diaphragm. A tube was made consisting of a pyrex tube divided into two sections by a solid pyrex disc. Proper electrodes and stand pipes were fitted as shown in Fig. 24 and accompanying photographs.

Previous to use it was expected that the output of this tube would be less than a fritted disc. Furthermore if the theory of the potential boxes is correct then one should be able to predict the polarity of the output. Looking at Fig. 25 we see that when a pressure increase approaches from the right we expect the first potential box to decrease in volume, causing a general rise in the energy levels and hence a flow of ions to the second box.

This ionic exchange should leave electrode one more negative than it was in equilibrium conditions. Following this reasoning through as many boxes as we desire we always find electrode 2 to be more positive than it was at equilibrium conditions.

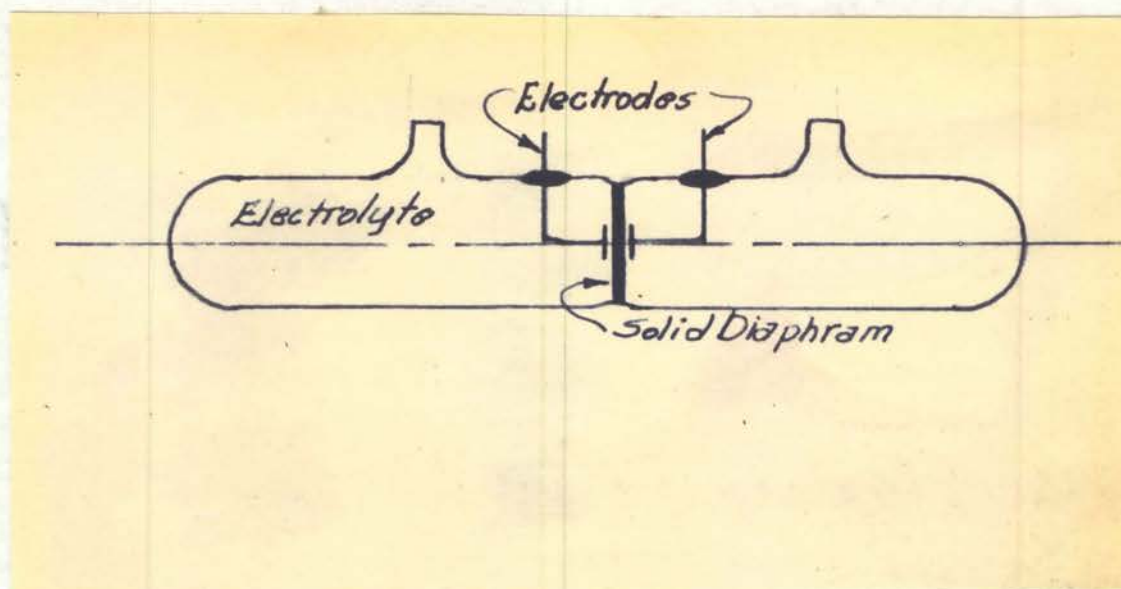
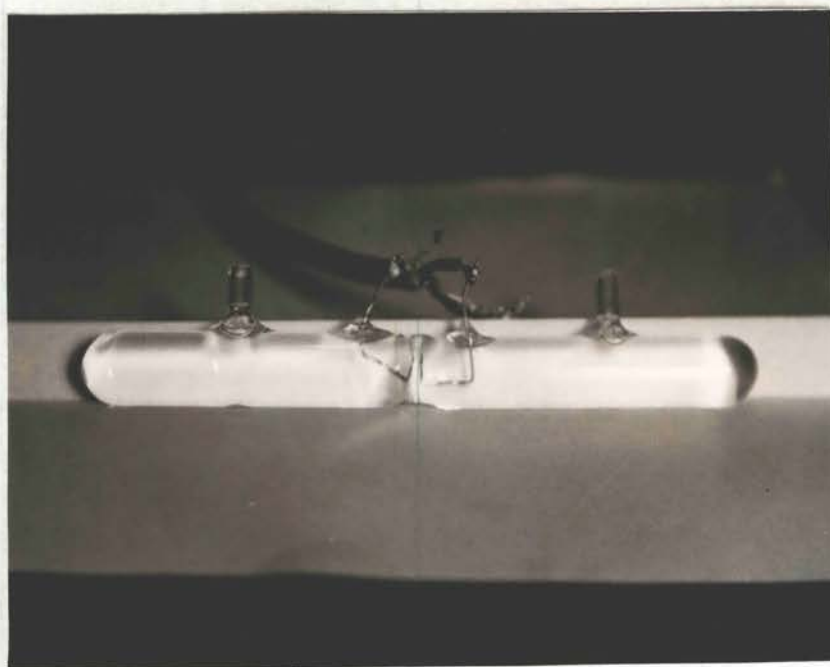


Fig. 24., Transducer Without Fritted Disc



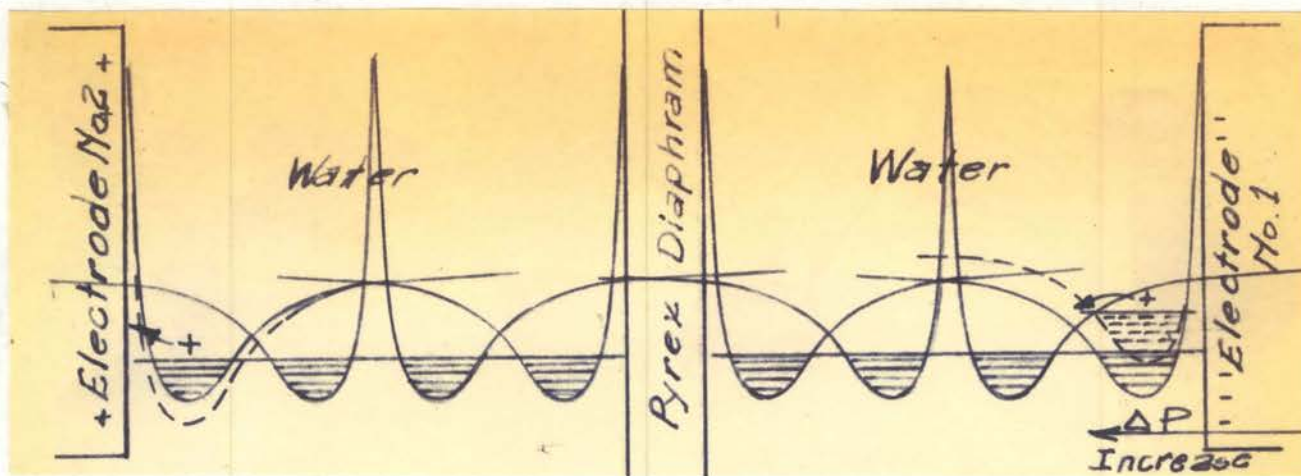
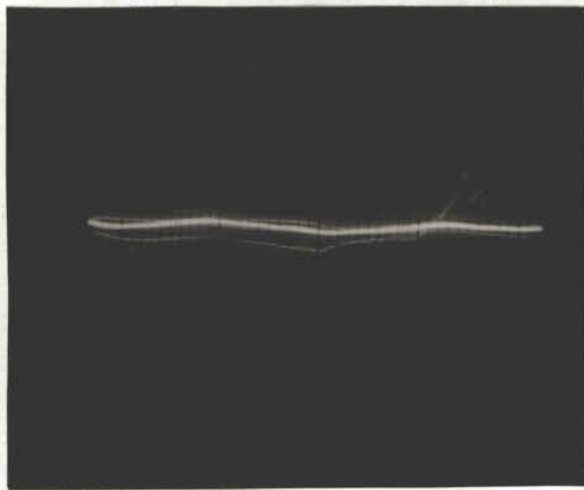
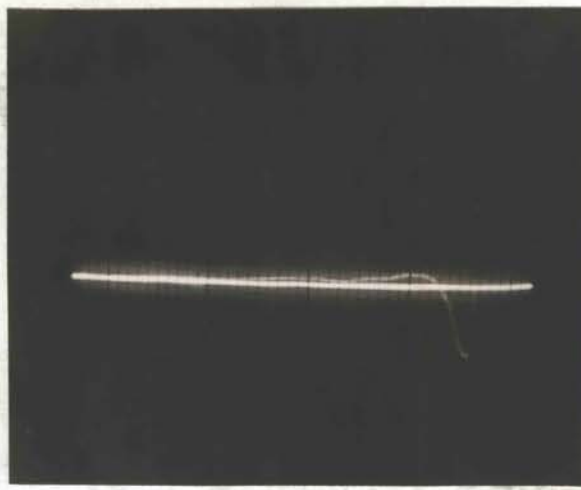


Fig. 25. Potential Curves for Pressure Variation

The following photographs show the direction of the potential on an oscilloscope in which the upward direction corresponds to a positive potential. Print A shows a pressure wave approaching from the left with reference to Fig. 25, and print B shows the approach of the pressure wave from the right hand side.



Print A.



Print B.

The author then offers these exhibits in support of the theory that the output does not depend upon flow through the fritted diaphragm, and further that the idea of the potential boxes must be substantially correct as is evidenced by the prediction of the polarity of the potential difference.



## CHAPTER V

### CONCLUSIONS

The object of this study was to derive a theory of operation of the Electrokinetic Transducer which would explain the apparent discrepancy between the potential difference at the electrodes and flow through the fritted disc. At the outset it was not certain that the potential difference did not depend upon flow to some extent, being modified by the tube and diaphragm characteristics. It was thought however that if another explanation was to be made quantum mechanics offered a valuable tool for the investigation.

Having developed the theory of quantum mechanics to the point where quantitative application could be made it was evident that the ideas of potential boxes could offer an explanation of the developed potential. Analysis of the potential boxes accompanying the electrodes, electrolyte and fritted disc immediately suggested that verification, of the proposal that the potential difference did not depend upon flow, offered itself in the form of a transducer as in Fig. 24.

The postulation that this transducer having a solid diaphragm should have a similar but reduced output, and furthermore that the output should be polarized and appear in a definite relation to the oncoming pressure wave offers strong evidence that the proposed theory is correct and applicable.

In evaluating the transducer for pressure pickup work it is the author's opinion that, since the prime mode of operation is alteration of the

potential boxes by the pressure waves, the pickup should be able to faithfully record the pressure variation. Some of these transducers have been driven as high as 100 Kilocycles therefore their frequency response for pressure pickup work should be extremely good.

Cognizance should be taken of the fact that in these experiments only platinum electrodes, distilled water and pyrex tubing have been used. Since it is possible to use a solid diaphragm, prudent selection of component materials and electrolytes should enable output manyfold.

This work has been on a qualitative basis only, but the potential usefulness of the proposed theory in the explanation of physical phenomena and in the development of engineering apparatus, is such as to demand that the work be pursued to the point that quantitative predictions can be made.

## CHAPTER VI

### SUGGESTED ENGINEERING APPLICATIONS OF QUANTUM MECHANICS

If we examine the profession of Engineering as it is today we will realize that technically the profession utilizes to the utmost the classical mechanics that was developed largely in the field of Physics. Furthermore Engineering has been responsible in both the application of physical discoveries and in the suggestion of basic physical investigations. This is as it should be, however, if we closely examine our college curricula we will find that the mechanics in present day use stops at about the state Physics was in some twenty five years ago.

In the author's library searches he found two texts used in engineering work that utilized the concepts of the newer quantum mechanics. These were in the field of Chemical Engineering where one would expect to find the first application. The future no doubt will see the Engineers utilize newer approaches as they are confronted with more fundamental problems. From these uses the newer approaches will formulate themselves and gradually come into general use just as the process has gone on in the past. In the next few pages the author wishes to present a few of the engineering applications to which he feels that quantum mechanics is particularly adaptable.

#### 1. Chemical Engineering

Electrochemical phenomena could be explained or the concepts expanded by use of quantum mechanics. Energy releases and equilibrium conditions



in chemical reactions likewise could be explained by use of quantum mechanics. Much of the present controversial data now in existence concerning colloidal phenomena could profit by use of quantum mechanics. Practically all electrokinetic phenomena should be capable of lending itself to a quantum mechanics explanation. The text Experimental and Theoretical Electrochemistry by Malcom Dole has proposed the application of Gurneys quantum mechanics to such subjects as Quantum Mechanics and Electromotive Force, Statistical Mechanics and the Glass Electrode, Quantum Mechanics and Overvoltage, Quantum Mechanics and Electrical Conductance.

## 2. Civil Engineering

In the field of soil mechanics such subjects as plasticity of soils, seepage and settlement could conceivably profit from a more fundamental approach for an explanation of the accompanying physical phenomena. The engineering application of bacteriology to sanitation offers a fruitful field for economic considerations in conjunction with filter effectiveness.

## 3. Electrical Engineering

The theories of quantum mechanics find particular application in a better explanation of the following electrical phenomena.

- a. Electron emitters
- b. Phorphorescent and phorescent screens and emitters
- c. Skin effect
- d. Corona
- e. Lighting
- f. Insulators
- g. Semiconductors

#### h. Conductors

#### 4. Mechanical Engineering

A better understanding should be had in the field of evaporation and condensation by recourse to quantum mechanics. It is known that when certain surface conditions exist that dropwise condensation can be promoted which condition makes a given condenser surface as much as 6 to 12 times as effective in rate of heat transfer. Throughout the history of lubrication continued attempts have been made to correlate the physical and chemical properties of a lubricant with its performance under service conditions. In the instance where clearances are small, pressures high and a thin film separates two dissimilar materials, the phenomena can only be explained and understood by employing the use of potential boxes energy levels and/or quantum mechanic methods. While progress is being made in the field of radiant heating the present basis of calculation, wherein most emphasis is placed on the emitting surface, considers only part of the problem. For a given room not only the emitting surface and its characteristics, but also the furnishings in the room and the disposition of the furnishings and occupants must be considered.

#### 5. General

The fields of fluid flow, creep stresses, plastic or elastic deformation, friction, transparency and translucence must also ultimately resort to quantum mechanics for an explanation. The February 1951 issue of Scientific American, page 54<sup>1</sup> gives an account of our present knowledge of friction. Friction like the common cold has long been with

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<sup>1</sup> Fredric Palmer, "Friction," Scientific American Vol. 184, No. 2 (February 1951), pp. 54-58.

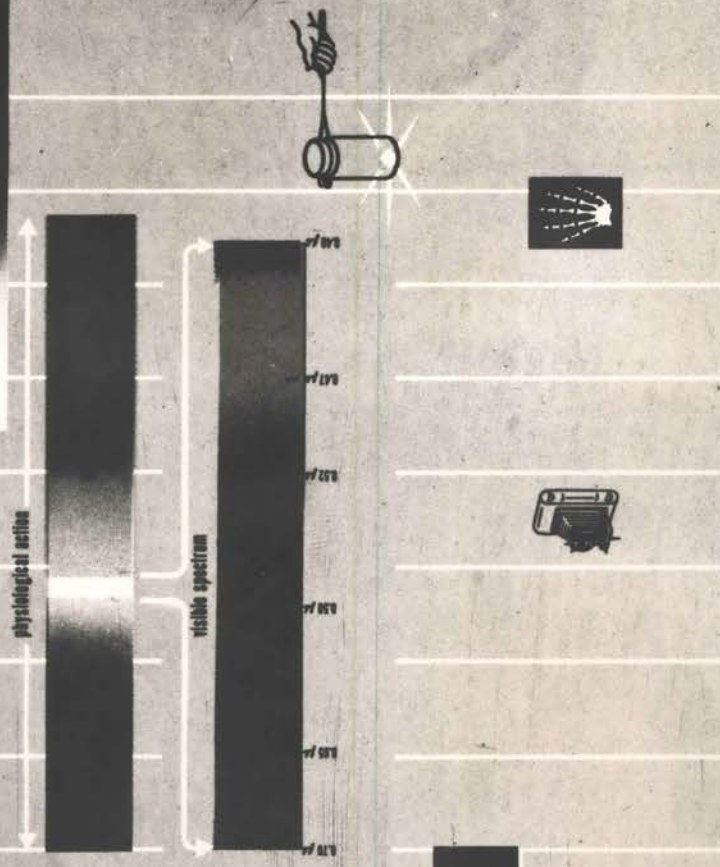
us yet our knowledge of both is of a meager nature. We are still pondering whether friction manifests itself by means of surface conditions or primarily molecular attraction. Since we have no idealized homogeneous materials to which we apply our theories a student of quantum mechanics would be prone to suggest that friction is a manifestation of the action of the potential boxes established along the contact planes of two materials and/or their lubricants. We know that roughness of surface increases friction but it is not axiomatic that superimproved surfaces decrease friction. On the contrary with smoother bearings as surfaces continue to improve and the closeness of fits becomes less friction increases. Is it too remote to believe then that on the deformed and high stress areas of a rough surface that the potential boxes exert an even stronger influence?

The engineering research man of today who despairs of the lack of fruitful fields is in the same position the Patent Office Clerk in the 1800's was in when he tendered his resignation because everything worthwhile had already been invented. The author is thankful of the opportunity to be privileged to live at this time and to be associated with research when the philosophy is really "Research Horizons Unlimited," with quantum mechanics becoming one of the more important approaches to fundamental knowledge.



# electromagnetic frequency spectrum

reference data for radio engineers third edition



|                     |                   |                   |                   |                   |        |          |                 |                 |                 |                      |                    |                    |                    |                    |                    |                    |                    |                     |                        |
|---------------------|-------------------|-------------------|-------------------|-------------------|--------|----------|-----------------|-----------------|-----------------|----------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------|------------------------|
| 0.01 kc/s           | 0.1               | 1                 | 10                | 100 kc/s          | 1 mc/s | 10       | 10 <sup>2</sup> | 10 <sup>3</sup> | 10 <sup>4</sup> | 10 <sup>5</sup>      | 10 <sup>6</sup>    | 10 <sup>7</sup>    | 10 <sup>8</sup>    | 10 <sup>9</sup>    | 10 <sup>10</sup>   | 10 <sup>11</sup>   | 10 <sup>12</sup>   | 10 <sup>13</sup>    | 10 <sup>14</sup> mc/s  |
| 3x10 <sup>8</sup> m | 3x10 <sup>7</sup> | 3x10 <sup>6</sup> | 3x10 <sup>5</sup> | 3x10 <sup>4</sup> | 30     | 3 meters | 30 cm           | 3               | 0.3             | 3x10 <sup>-2</sup>   | 3x10 <sup>-3</sup> | 3x10 <sup>-4</sup> | 3x10 <sup>-5</sup> | 3x10 <sup>-6</sup> | 3x10 <sup>-7</sup> | 3x10 <sup>-8</sup> | 3x10 <sup>-9</sup> | 3x10 <sup>-10</sup> | 3x10 <sup>-11</sup> cm |
|                     |                   |                   |                   |                   |        |          |                 |                 |                 | frequency $f$        |                    |                    |                    |                    |                    |                    |                    |                     |                        |
|                     |                   |                   |                   |                   |        |          |                 |                 |                 | wavelength $\lambda$ |                    |                    |                    |                    |                    |                    |                    |                     |                        |
|                     |                   |                   |                   |                   |        |          |                 |                 |                 | microseconds $\mu$   |                    |                    |                    |                    |                    |                    |                    |                     |                        |
|                     |                   |                   |                   |                   |        |          |                 |                 |                 | Angstroms $\text{Å}$ |                    |                    |                    |                    |                    |                    |                    |                     |                        |

APPENDIX A

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## APPENDIX B

If the surface of a solid absorbs energy in the form of light, heat, or some other radiation we have

$$\mathcal{E} = h\nu = e = PM$$

where

$$\mathcal{E} = \text{Energy ergs}$$

$$h = \text{Planck Constant - erg-second}$$

$$\nu = \text{Frequency - cycles per second}$$

$$e = \text{Epsilon potential - volts}$$

Referring to Fig 6 P M is known as the photoelectric effect if the figure is considered to be for a metal. Photoelectric effect is equal to  $C P + H = e = \text{energy absorbed.}$

## APPENDIX C

The De Broglie equation is derived from the Schroedinger equation as follows:

In simplified form we have

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(W-V)\psi = 0$$

for a free particle traveling at a velocity  $v$  in the  $x$  direction. The potential energy,  $V$  is a constant and may be set equal to zero.  $W$  then becomes equal to the kinetic energy  $T = mv^2/2$ .

The equation may be rewritten as follows:

$$\frac{d^2\psi}{dx^2} + \left(\frac{2\pi m v}{h}\right)^2 \psi = 0$$

This equation has a solution in the form

$$\psi = A \sin \frac{2\pi x}{\lambda}$$

Provided  $\lambda$  is given by

$$\lambda = h/mv$$

Therefore the  $\lambda$  of the De Broglie equation is contained in the solution of the Schroelinger wave equation.

In a similar manner if we use one of Raleighs equations where he has shown that  $\Delta x \cdot \Delta(1/\lambda) \approx 1$ , we can arrive at, by use of De Broglie's equation, Heisenbergs uncertainty principle. Refer to the sketch showing phase velocities and group velocity. Let the wave lengths of the individual waves be  $\lambda_1, \lambda_2, \lambda_3$ , etc., and their reciprocals the wave numbers be  $1/\lambda_1, 1/\lambda_2, 1/\lambda_3$ , etc. Then let  $\Delta(1/\lambda)$  be the extreme difference between the wave numbers, i.e.,  $1/\lambda_1 - 1/\lambda_n$ . In other words the length of the wave packet  $\Delta x$  in the sketch is inversely proportional to the maximum difference in the number of waves per centimeter,  $\Delta(1/\lambda)$ , of the individual waves.

From De Broglie Equation we find

$$\begin{aligned}\lambda &= \frac{h}{mv} = \frac{h}{p} \\ d\lambda &= \frac{h}{dp} \\ d(1/\lambda) &= \frac{dp}{h} \\ \text{or } \Delta(1/\lambda) &= \frac{\Delta p}{h}\end{aligned}$$

Substituting in Raleigh Equation

$$\begin{aligned}\Delta x \cdot \Delta(1/\lambda) &\cong 1 \\ \Delta x \cdot \frac{\Delta p}{h} &\cong 1 \\ \Delta x \cdot \Delta p &\cong h \quad \text{or Heisenbergs Principle}\end{aligned}$$

#### APPENDIX D

Starting with the Heisenberg Equation and the general form of the equation (Equation 10) we can derive the general Schroelinger equation 6.

$$\Delta x \cdot \Delta p \cong h$$



Also since  $W = h\nu$  or  $\nu = \frac{W}{h}$

from equation 10 we get

$$\begin{aligned}\Psi &= \psi e^{-2\pi i \nu t} = \psi e^{-2\pi i \frac{W}{h} t} \\ \Psi^* &= \psi e^{2\pi i \nu t} = \psi e^{2\pi i \frac{W}{h} t}\end{aligned}$$

Differentiation of  $\Psi$  and  $\Psi^*$  is equivalent to multiplying by  $\frac{2\pi}{i h} W$

then  $\frac{\partial \Psi}{\partial t} = \Psi \frac{2\pi}{i h} W$  or  $\frac{\partial}{\partial t} = \frac{2\pi W}{i h}$

$$W = \frac{\partial}{\partial t} \frac{i h}{2\pi}$$

$$\Delta W \approx h/\Delta t \quad \Delta W \cdot \Delta t \approx h$$

from the correspondence principle we find that in the limit quantum mechanics and classical mechanics must have a 1 to 1 correspondence, therefore

$$W \approx \frac{i h}{2\pi} \frac{\partial}{\partial t}$$

$$\Delta W = h/\Delta t$$

if these have 1 to 1 correspondence

then

$$\Delta P = h/\Delta x$$

$$P = \frac{i h}{2\pi} \frac{\partial}{\partial x}$$

these should also have 1 to 1 correspondence

and

we then have

$$\begin{aligned}p_x &= \frac{i h}{2\pi} \frac{\partial}{\partial x} & p_x^2 &= -\frac{h^2}{4\pi^2} \frac{\partial^2}{\partial x^2} \\ p_y &= \frac{i h}{2\pi} \frac{\partial}{\partial y} & p_y^2 &= -\frac{h^2}{4\pi^2} \frac{\partial^2}{\partial y^2} \\ p_z &= \frac{i h}{2\pi} \frac{\partial}{\partial z} & p_z^2 &= -\frac{h^2}{4\pi^2} \frac{\partial^2}{\partial z^2}\end{aligned}$$

we have already found that  $W - V = \frac{p^2}{2m}$

Let  $p^2 = p_x^2 + p_y^2 + p_z^2 = 2m(W - V)$

$$\text{or } p_x^2 + p_y^2 + p_z^2 - 2m(W - V) = 0$$

$$\text{then } -\frac{h^2}{4\pi^2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi - 2m(W - V)\psi = 0$$

$$\text{or } \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + \frac{8\pi^2 m}{h^2} (W - V)\psi = 0$$

$$\text{or } \nabla^2 \psi + \frac{8\pi^2 m}{h^2} (W - V)\psi = 0$$

Thus we have arrived at the Schroedinger equation by means of the Heisenberg principle.

#### APPENDIX E

Equation 9 was arrived at as follows: In 1922 Dr. A. H. Compton demonstrated that the wave length of an incident beam of X-Rays colliding with a particle suffered a modification of wave length in the reflected wave. The X-Ray was considered to be made up of quanta or photons each having an energy  $h\nu$  and a momentum  $h\nu/c$ . When the photon collides with a free particle or electron it gives up part of its momentum or energy, causing the electron to recoil. The energy given to the recoil electron comes from the original X-Ray photon decreasing the value of  $h\nu$ , i.e., decreasing the wavelength since  $h$  is constant. Thus, the wavelength  $\lambda$  of the modified spectra line is greater than that of the incident ray. From conservation of energy and momentum Dr. Compton predicted that the increase in wavelength should be

$$\Delta\lambda = \frac{h}{m c} (1 - \cos \theta)$$

in terms of momentum this amounts to

$$p_x = \frac{h\nu}{c} (1 - \cos \theta)$$

from optics we know that

$$\Delta x = \frac{c}{\nu \sin \alpha} \quad \sin \alpha < \cos \theta$$

Therefore, the recoil moment lies between

$$\begin{aligned} & h\nu/c (1 - \sin \alpha) \\ \text{and} & h\nu/c (1 + \sin \alpha) \end{aligned}$$

$$\Delta P_k = 2h\nu/c \sin \alpha$$

Therefore

$$\Delta X \cdot \Delta P = \frac{c}{\nu \sin \alpha} \cdot \frac{2h\nu}{c} \sin \alpha \approx h$$



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