

Senior Laboratory

## ATOMS AND MEASUREMENT



St. John's College  
Annapolis, MD

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Annapolis, MD — Santa Fe, NM

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## Acknowledgements and Notes

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The illustration on the cover shows Millikan's oil-drop apparatus. This is the design he describes as having achieved "the limit of its possible precision" (*The Electron*, p.115).

Throughout the manual, explanatory footnotes added to the original texts are indicated by being enclosed in square brackets. Ellipses of up to several sentences are similarly indicated, and longer ellipses by a line with asterisks as below.

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# TABLE OF CONTENTS

<b>1</b>	<b>On the Absolute Quantity of Electricity Associated with the Particles or Atoms of Matter</b>	<b>1</b>
	<i>Michael Faraday</i>	
<b>2</b>	<b>Cathode Rays</b>	<b>13</b>
	<i>J. J. Thomson</i>	
<b>3</b>	<b>The Electron</b>	<b>25</b>
	<i>R. A. Millikan</i>	
<b>4</b>	<b>The Scattering of <math>\alpha</math> and <math>\beta</math> Particles by Matter and the Structure of the Atom</b>	<b>45</b>
	<i>Ernest Rutherford</i>	
<b>5</b>	<b>The Quantum Hypothesis</b>	<b>61</b>
	<i>Max Planck</i>	
<b>6</b>	<b>The Photoelectric Effect</b>	<b>75</b>
	<i>Albert Einstein</i>	
<b>7</b>	<b>On the Spectrum of Hydrogen</b>	<b>85</b>
	<i>Niels Bohr</i>	
<b>8</b>	<b>Matter Waves</b>	<b>99</b>
	<i>Louis de Broglie</i>	
<b>9</b>	<b>Four Lectures on Wave Mechanics</b>	<b>123</b>
	<i>Erwin Schrödinger</i>	
<b>10</b>	<b>Critique of the Physical Concepts of the Particle Picture</b>	<b>137</b>
	<i>Werner Heisenberg</i>	
<b>11</b>	<b>The Polarization of Light</b>	<b>157</b>
	<i>Optics Practicum 1</i>	
<b>12</b>	<b>The Principles of Quantum Mechanics</b>	<b>163</b>
	<i>Paul Dirac</i>	
<b>13</b>	<b>Optics Lab: Introduction</b>	<b>175</b>
	<i>Optics Practicum 2</i>	
<b>14</b>	<b>Single Photon Interference And Superposition</b>	<b>181</b>
	<i>Optics Practicum 3</i>	

<b>15 The “Quantum Eraser”</b>	<b>183</b>
<i>Optics Practicum 4</i>	
<b>16 Can Quantum-Mechanical Description of Reality Be Considered Complete?</b>	<b>185</b>
<i>Einstein, Podolsky, and Rosen</i>	
<b>17 Bell’s Theorem</b>	<b>189</b>
<i>J. S. Bell</i>	
<b>18 Appendix: ESU, EMU, and SI</b>	<b>203</b>
<i>Units and Systems of Measurement</i>	



## CHAPTER 1

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# ON THE ABSOLUTE QUANTITY OF ELECTRICITY ASSOCIATED WITH THE PARTICLES OR ATOMS OF MATTER

MICHAEL FARADAY<sup>1</sup>

852. The theory of definite electrolytical or electro-chemical action appears to me to touch immediately upon the *absolute quantity* of electricity or electric power belonging to different bodies. It is impossible, perhaps, to speak on this point without committing oneself beyond what present facts will sustain; and yet it is equally impossible, and perhaps would be impolitic, not to reason upon the subject. Although we know nothing of what an atom is, yet we cannot resist forming some idea of a small particle, which represents it to the mind; and though we are in equal, if not greater, ignorance of electricity, so as to be unable to say whether it is a particular matter or matters, or mere motion of ordinary matter, or some third kind of power or agent, yet there is an immensity of facts which justify us in believing that the atoms of matter are in some way endowed or associated with electrical powers, to which they owe their most striking qualities, and amongst them their mutual chemical affinity. As soon as we perceive, through the teaching of Dalton, that chemical powers are, however varied the circumstances in which they are exerted, definite for each body, we learn to estimate the relative degree of force which resides in such bodies: and when upon that knowledge comes the fact, that the electricity, which we appear to be capable of loosening from its habitation for awhile, and conveying from place to place, *whilst it retains its chemical force*, can be measured out, and being so measured out is found to be *as definite in its action* as any of those portions which, remaining associated with the particles of matter, give them their *chemical relation*; we seem to have found the link which connects the proportion of that we have evolved to the proportion of that belonging to the particles in their natural state.

853. Now it is wonderful to observe how small a quantity of a compound body is decomposed by a certain portion of electricity. Let us, for instance, consider this and a few other points in relation to water. One grain<sup>2</sup> of water, acidulated to facilitate conduction, will require an electric current to be continued for three minutes and three quarters of time to effect its decomposition, which current must be powerful enough to retain a platina wire 1/104 of an inch in thickness,<sup>3</sup> red hot, in the air during the whole time; and if interrupted anywhere by charcoal points, will produce a very brilliant and

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<sup>1</sup>[*Experimental Researches in Electricity*, VIIth series, section 13. Dover edition, Vol.I, 249ff.]

<sup>2</sup>[One grain is about .065 grams.]

<sup>3</sup>I have not stated the length of wire used, because I find by experiment, as would be expected in theory, that it is indifferent. The same quantity of electricity which, passed in a given time, can heat an inch of platina wire of a certain diameter red hot, can also heat a hundred, a thousand, or any length of the same wire to the same degree, provided the cooling circumstances are the same for every part in all cases. This I have proved by the volta-electrometer. I found that whether half an inch or eight inches were retained at one constant temperature of dull redness, equal quantities of water were decomposed in equal times. When the half-inch was used, only the center portion of wire was ignited. A fine wire may even be

constant star of light. If attention be paid to the instantaneous discharge of electricity of tension, as illustrated in the beautiful experiments of Mr. Wheatstone,<sup>4</sup> and to what I have said elsewhere on the relation of common and voltaic electricity (371. 375.),<sup>5</sup> it will not be too much to say that this necessary quantity of electricity is equal to a very powerful flash of lightning.<sup>6</sup> Yet we have it under perfect command; can evolve, direct, and employ it at pleasure; and when it has performed its full work of electrolyzation, it has only separated the elements of *a single grain of water*.

854. On the other hand, the relation between the conduction of the electricity and the decomposition of the water is so close, that one cannot take place without the other. If the water is altered only in that small degree which consists in its having the solid instead of the fluid state, the conduction is stopped, and the decomposition is stopped with it. Whether the conduction be considered as depending upon the decomposition, or not (413. 703.), still the relation of the two functions is equally intimate and inseparable.

855. Considering this close and twofold relation, namely, that without decomposition transmission of electricity does not occur; and, that for a given definite quantity of electricity passed, an equally definite and constant quantity of water or other matter is decomposed; considering also that the agent, which is electricity, is simply employed in overcoming electrical powers in the body subjected to its action; it seems a probable, and almost a natural consequence, that the quantity which passes is the *equivalent* of, and therefore equal to, that of the particles separated; i.e. that if the electrical power which holds the elements of a grain of water in combination, or which makes a grain of oxygen and hydrogen in the right proportions unite into water when they are made to combine, could be thrown into the condition of *a current*, it would exactly equal the current required for the separation of that grain of water into its elements again.

856. This view of the subject gives an almost overwhelming idea of the extraordinary quantity or degree of electric power which naturally belongs to the particles of matter; but it is not inconsistent in the slightest degree with the facts which can be brought to bear on this point. To illustrate this I must say a few words on the voltaic pile.<sup>7</sup>

857. Intending hereafter to apply the results given in this and the preceding series of Researches to a close investigation of the source of electricity in the voltaic instrument, I have refrained from forming any decided opinion on the subject; and without at all meaning to dismiss metallic contact, or the contact of dissimilar substances, being conductors, but not metallic, as if they had nothing to do with the origin of the current, I still am fully of the opinion with Davy, that it is at least continued by chemical action, and that the supply constituting the current is almost entirely from that source.

used as a rough but ready regulator of a voltaic current; for if it be made part of the circuit, and the larger wires communicating with it be shifted nearer to or further apart, so as to keep the portion of wire in the circuit sensibly at the same temperature, the current passing through it will be nearly uniform.

<sup>4</sup>Literary Gazette, 1833, March 1 and 8. Philosophical magazine, 1833, 204. L'Institute, 1833, 261.

<sup>5</sup>[Faraday refers to numbered paragraphs in earlier series of the *Experimental Researches*.]

<sup>6</sup>[This amount of charge is indeed comparable to that in a typical lightning bolt.]

<sup>7</sup>By the term voltaic pile, I mean such apparatus or arrangement of metals as up to this time have been called so, and which contain water, brine, acids, or other aqueous solutions or decomposable substances (476.), between their plates. Other kinds of electric apparatus may hereafter be invented, and I hope to construct some not belonging to the class of instruments discovered by Volta. [Note: The voltaic pile is an instance of what we know as the *electric battery*; and indeed Faraday also uses the term "battery" in paragraphs 858ff. below.]

858. Those bodies which, being interposed between the metals of the voltaic pile, render it active, *are all of them electrolytes* (476.); and it cannot but press upon the attention of every one engaged in considering this subject, that in those bodies (so essential to the pile) decomposition and the transmission of a current are so intimately connected, that one cannot happen without the other. This I have shown abundantly in water, and in numerous other cases (402. 476.). If, then, a voltaic trough have its extremities connected by a body capable of being decomposed, as water, we shall have a continuous current through the apparatus; and whilst it remains in this state we may look at the part where the acid is acting upon the plates, and that where current is acting upon the water, as the reciprocals of each other. In both parts we have the two conditions *inseparable in such bodies as these*, namely, the passing of a current, and decomposition; and this is as true of the cells in the battery as of the water cell; for no voltaic battery has as yet been constructed in which the chemical action is only that of combination: *decomposition is always included*, and is, I believe, an essential chemical part.

859. But the difference in the two parts of the connected battery, that is, the decomposition or experimental cell, and the acting cells, is simply this. In the former we urge the current through, but it, apparently of necessity, is accompanied by decomposition: in the latter we cause decompositions by ordinary chemical actions (which are, however, themselves electrical), and, as a consequence, have the electrical current; and as the decomposition dependent upon the current is definite in the former case, so is the current associated with the decomposition also definite in the latter (862. &c.).

860. Let us apply this in support of what I have surmised respecting the enormous electric power of each particle or atom of matter (856.). I showed in a former series of these Researches on the relation by measure of common and voltaic electricity,<sup>8</sup> that two wires, one of platina and one of zinc, each one eighteenth of an inch in diameter, placed five-sixteenths of an inch apart, and immersed to the depth of five eighths of an inch in acid, consisting of one drop of oil of vitriol and four ounces of distilled water at a temperature of about 60° Fahr., and connected at the other extremities by a copper wire eighteen feet long, and one eighteenth of an inch in thickness,<sup>9</sup> yielded as much electricity in little more than three seconds of time as a Leyden battery<sup>10</sup> charged by thirty turns of a very large and powerful plate electric machine in full action (371.). This quantity, though sufficient if passed through the head of a rat or cat to have killed it, as by a flash of lightning, was evolved by the mutual action of so small a portion of the zinc wire and water in contact with it, that the loss of weight sustained by either would be inappreciable by our most delicate instruments; and as to the water which could be decomposed by that current, it must have been insensible in quantity, for no trace of hydrogen appeared upon the surface of the platina during those three seconds.

861. What an enormous quantity of electricity, therefore, is required for the decomposition of a single grain of water! We have already seen that it must be in quantity sufficient to sustain a platina wire 1/104 of an inch in thickness, red hot, in contact with the air, for three minutes and three quarters (853.), a quantity which is almost infinitely

<sup>8</sup>[By "common" electricity Faraday means *static* electricity; while "voltaic" electricity is what is produced by the voltaic battery. Until Faraday showed their equivalence, it was uncertain whether the two "electricities" were same or different.]

<sup>9</sup>[The eighteen-foot length of wire formed the coil of a galvanometer. See *Experimental Researches*, Vol. I, 105.]

<sup>10</sup>["Leyden battery": an array (a "battery") of Leyden jars.]

greater than that which could be evolved by the little standard voltaic arrangement to which I have just referred (860. 371.). I have endeavored to make a comparison by the loss of weight of such a wire in a given time in such an acid, according to a principle and experiment to be almost immediately described (862.); but the proportion is so high that I am almost afraid to mention it. It would appear that 800,000 such charges of the Leyden battery as I have referred to above, would be necessary to supply electricity sufficient to decompose a single grain of water; or, if I am right, to equal the quantity of electricity which is naturally associated with the elements of that grain of water, endowing them with their mutual chemical affinity.

862. In further proof of this high electric condition of the particles of matter, and the *identity as to quantity of that belonging to them with that necessary for their separation*, I will describe an experiment of great simplicity but extreme beauty, when viewed in relation to the evolution of an electric current and its decomposing powers.

863. A dilute sulphuric acid, made by adding about one part by measure of oil of vitriol to thirty parts of water, will act energetically upon a piece of zinc plate in its ordinary and simple state: but, as Mr. Sturgeon has shewn,<sup>11</sup> not at all, or scarcely so, if the surface of the metal has in the first instance been amalgamated; yet the amalgamated zinc will act powerfully with platina as an electromotor,<sup>12</sup> hydrogen being evolved on the surface of the latter metal, as the zinc is oxidized and dissolved. The amalgamation is best effected by sprinkling a few drops of mercury upon the surface of the zinc, the latter being moistened with the dilute acid, and rubbing with the fingers or tow so as to extend the liquid metal over the whole of the surface. Any mercury in excess, forming liquid drops upon the zinc, should be wiped off.<sup>13</sup>

864. Two plates of zinc thus amalgamated were dried and accurately weighed; one, which we shall call A, weighed 163.1 grains; the other, to be called B, weighed 148.3 grains.<sup>14</sup> They were about five inches long, and 0.4 of an inch wide. An earthenware pneumatic trough was filled with dilute sulphuric acid, of the strength just described (863.), and a gas jar, also filled with the acid, inverted in it.<sup>15</sup> A plate of platina of nearly the same length, but about three times as wide as the zinc plates, was put up into this jar. The zinc plate A was also introduced into the jar, and brought in contact with the platina, and at the same moment the plate B was put into the acid of the trough, but out of contact with other metallic matter.

865. Strong action immediately occurred in the jar upon the contact of the zinc and platina plates. Hydrogen gas rose from the platina, and was collected in the jar, but no hydrogen or other gas rose from *either* zinc plate. In about ten or twelve minutes, sufficient hydrogen having been collected, the experiment was stopped; during its progress a few small bubbles had appeared upon plate B, but none upon plate A. The plates were washed in distilled water, dried, and reweighed. Plate B weighed 148.3 grains, as before, having lost nothing by the direct chemical action of the acid. Plate A

<sup>11</sup>Recent Experimental Researches, &c., 1830, 74, &c.

<sup>12</sup>[“electromotor”: something that moves or tends to move electricity (1827).]

<sup>13</sup>The experiment may be made with pure zinc, which, as chemists well know, is but slightly acted upon by dilute sulphuric acid in comparison with ordinary zinc, which during the action is subject to an infinity of voltaic actions. See De la Rive on this subject, Bibliothèque Universelle, 1830, 391.

<sup>14</sup>[Or, since one grain equals about .065 grams, plate A weighs about 10.6 grams and plate B about 9.6 grams.]

<sup>15</sup>The acid was left during a night with a small piece of unamalgamated zinc in it, for the purpose of evolving such air as might be inclined to separate, and bringing the whole into a constant state.



[A representation of Faraday's apparatus.]

weighed 154.65 grains, 8.45 grains of it having been oxidized and dissolved during the experiment.

866. The hydrogen gas was next transferred to a water-trough and measured; it amounted to 12.5 cubic inches, the temperature being 52°, and the barometer 29.2 inches. This quantity, corrected for temperature, pressure, and moisture, becomes 12.15453 cubic inches of dry hydrogen at mean temperature and pressure,<sup>16</sup> which, increased by one half for the oxygen that must have gone to the *anode*, i.e. to the zinc, gives 18.232 cubic inches as the quantity of oxygen and hydrogen evolved from the water decomposed by the electric current.<sup>17</sup> According to the estimate of the weight of the mixed gas before adopted (791.),<sup>18</sup> this volume is equal to 2.3535544 grains, which therefore is the weight of water decomposed; and this quantity is to 8.45 [grains], the quantity of zinc oxidized, as 9 is to 32.31. Now taking 9 as the equivalent number of water, the number 32.5 is given as the equivalent number of zinc;<sup>19</sup> a coincidence sufficiently near to show, what indeed could not but happen, that for an equivalent of zinc oxidized an equivalent of water must be decomposed.<sup>20</sup>

867. But let us observe *how* the water is decomposed. It is electrolyzed, i.e. is decomposed voltaically, and not in the ordinary manner (as to appearance) of chemical decompositions; for the oxygen appears at the *anode* and the hydrogen at the *cathode* of the body under decomposition, and these were in many parts of the experiment above an inch asunder. Again, the ordinary chemical affinity was not enough under the circumstances to effect the decomposition of the water, as was abundantly proved by the inaction on plate B; the voltaic current was essential. And to prevent any idea that the chemical affinity was almost sufficient to decompose the water, and that a smaller current of electricity might, under the circumstances, cause the hydrogen to

<sup>16</sup>[Faraday uses the gas laws to reduce the measured volume of hydrogen to the equivalent volume at 50° F. and 30 in Hg; these are "mean" conditions which he takes as standard. The measurement is first "corrected for moisture" by subtracting the known vapor pressure of water at 52° F. from the measured barometric pressure.]

<sup>17</sup>[Since decomposition of water yields hydrogen and oxygen in a 2:1 ratio by volume, the total volume of both gases will be 1.5 times the volume of hydrogen alone.]

<sup>18</sup>[In an earlier paragraph 791, Faraday had reported about .129 grains per cubic inch as the density of a mixture of 2 volumes hydrogen and 1 volume oxygen at "mean" temperature and pressure.]

<sup>19</sup>[The equivalent weight of zinc currently accepted is 32.69, about .5% higher than the figure 32.5 accepted by Faraday.]

<sup>20</sup>The experiment was repeated several times with the same results.

pass to the *cathode*, I need only refer to the results which I have given (807. 813.), to shew that the chemical action at the electrodes has not the slightest influence over the *quantities* of water or other substances decomposed between them, but that they are entirely dependent upon the quantity of electricity which passes.

868. What, then, follows as a necessary consequence of the whole experiment? Why, this: that the chemical action upon 32.31 parts, or one equivalent of zinc, in this simple voltaic circle, was able to evolve such quantity of electricity in the form of a current as, passing through water, should decompose 9 parts, or one equivalent of that substance: and considering the definite relations of electricity as developed in the preceding parts of the present paper, the results prove that the quantity of electricity which, being naturally associated with the particles of matter, gives them their combining power, is able, when thrown into a current, to separate those particles from their state of combination; or, in other words, that *the electricity which decomposes, and that which is evolved by the decomposition of, a certain quantity of matter, are alike*.

869. The harmony which this theory of the definite evolution and the equivalent definite action of electricity introduces into the associated theories of definite proportions and electro-chemical affinity, is very great. According to it, the equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity, or have naturally equal electric powers; it being the ELECTRICITY which *determines* the equivalent number, *because* it determines the combining force. Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalent to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them. But I must confess I am jealous<sup>21</sup> of the term *atom*; for though it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature, especially when compound bodies are under consideration.

870. I cannot refrain from recalling here the beautiful idea put forth, I believe, by Berzelius (703.) in his development of his views of the electro-chemical theory of affinity, that the heat and light evolved during cases of powerful combination are the consequence of the electric discharge which is at the moment taking place. The idea is in perfect accordance with the view I have taken of the *quantity* of electricity associated with the particles of matter.

871. In this exposition of the law of the definite action of electricity, and its corresponding definite proportion in the particles of bodies, I do not pretend to have brought, as yet, every case of chemical or electro-chemical action under its dominion. There are numerous considerations of a theoretical nature, especially respecting the compound particles of matter and the resulting electrical forces which they ought to possess, which I hope will gradually receive their development; and there are numerous experimental cases, as, for instance, those of compounds formed by weak affinities, the simultaneous decomposition of water and salts, &c., which still require investigation. But whatever the results on these and numerous other points may be, I do not believe that the facts which I have advanced, or even the general laws deduced from them, will suffer any serious change; and they are of sufficient importance to justify their publication, though much may yet remain imperfect or undone. Indeed, it is the great beauty of our science, CHEMISTRY, that advancement in it, whether in a degree great or small, instead of exhausting the subjects of research, opens the doors to further and more abundant knowledge, overflowing with beauty and utility, to those who will

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<sup>21</sup>[“jealous:” here, *suspicious*.]

be at the easy personal pains of undertaking its experimental investigation.

872. The definite production of electricity (868.) in association with its definite action proves, I think, that the current of electricity in the voltaic pile is sustained by chemical decomposition, or rather by chemical action, and not by contact only. But here, as elsewhere (857.), I beg to reserve my opinion as to the real action of contact, not having yet been able to make up my mind as to whether it is an exciting cause of the current, or merely necessary to allow of the conduction of electricity, otherwise generated, from one metal to the other.

873. But admitting that chemical action is the source of electricity, what an infinitely small fraction of that which is active do we employ in our voltaic batteries! Zinc and platina wires, one eighteenth of an inch in diameter and about half an inch long, dipped into dilute sulphuric acid, so weak that it is not sensibly sour to the tongue, or scarcely to our most delicate test papers, will evolve more electricity in one twentieth of a minute (860.) than any man would willingly allow to pass through his body at once. The chemical action of a grain of water upon four grains of zinc can evolve electricity equal in quantity to that of a powerful thunder-storm (868. 861.). Nor is it merely true that the quantity is active; it can be directed and made to perform its full equivalent duty (867. &c.). Is there not, then, great reason to hope and believe that, by a closer *experimental* investigation of the principles which govern the development and action of this subtle agent, we shall be able to increase the power of our batteries, or invent new instruments which shall a thousandfold surpass in energy those which we at present possess?

874. Here for a while I must leave the consideration of the *definite chemical action of electricity*. But before I dismiss this series of experimental Researches, I would call to mind that, in a former series, I showed the current of electricity was also *definite in its magnetic action* (216. 366. 367. 376. 377.); and, though this result was not pursued to any extent, I have no doubt that the success which has attended the development of the chemical effects is not more than would accompany an investigation of the magnetic phenomena.

Royal Institution  
December 31st, 1833.

## A NOTE ON CHEMICAL EQUIVALENCE

Faraday confesses he is "jealous," that is, suspicious, of the term *atom*. When he wrote in 1833, there was no agreement among natural philosophers as to a formula for, say, water, which would specify the atomic constituents of a single smallest particle (molecule) of water: was it HO, or H<sub>2</sub>O, or something else? What Faraday *was* sure of was that chemical substances reacted in definite proportions by weight and, further, that the weights of various substances reacting with one another formed a series of "equivalent" or "combining" weights. And since oxygen combines with so many different substances, taking oxygen as the standard of comparison allowed indirect extension of the series to include *all* elements.

For example, 8 parts by weight of oxygen will combine with 1 part by weight of hydrogen (to form water). But 8 parts by weight of oxygen will also combine with 32.69 parts by weight of zinc (to form zinc oxide). Then the 32.69 of zinc, the 8 of oxygen, and the 1 of hydrogen are all said to be "equivalent" weights—equivalent, that is to

say, in *combining power*—because either any two of those quantities will combine with one another or each will combine with the specified weight of the remaining substance. Equivalent weights are relative only to one another and may therefore be expressed in arbitrary units of weight. But it is particularly convenient to express them in *grams*, with 8 *grams of oxygen* taken as the standard. The figures so obtained are called, not merely equivalent weights, but *gram-equivalent weights*; thus 1 gram, 8 grams, and 32.69 grams are the *gram-equivalent weights* of hydrogen, oxygen, and zinc, respectively.

If, like Faraday, one is skeptical of the atomic view, there cannot be assumed any natural “unit” of chemical combining power. Thus it is for him illuminating in the highest degree to be able to interpret the chemically equivalent weights of various substances as amounts which contain “equal quantities of electricity” (cf. his paragraph 869 above).

If the atomic view is accepted, there are consequences even more far-reaching. The molecular formulas finally propounded by Cannizzaro (*A Course in Chemical Philosophy*, 1859) show that one atom of an element may hold in combination one, two or more atoms of other elements by establishing an integral number of *atomic bonds*, where the bond to a hydrogen atom is taken as unit.<sup>22</sup> Since, on the atomic view, an atom that forms a single atomic bond manifests a *natural unit of combining power*, then under Faraday’s interpretation of chemical powers as ultimately electrical, such a unitary combining power would appear to be associated with and perhaps even explained by a *natural unit of electricity*.

Might there really be a natural unit of electricity, an “atom of charge”? The papers to follow by Thomson and Millikan will bear on this question.

## EXPERIMENT: ELECTRODEPOSITION OF COPPER

In order to simplify the relations between chemical and electrical power in our apparatus, we use a cell in which no overall chemical reaction occurs. This is achieved by using electrodes made of the same metal as the metal in the electrolytic solution. Under the action of electric current metal from the positive electrode (anode) dissolves into solution, while at the negative electrode (cathode) metal leaves the solution and is deposited there. The net result is transfer of material from one electrode to the other. We normally use copper electrodes, with a copper sulfate solution as electrolyte. If available, silver electrodes with a silver nitrate solution can be employed for comparison with another element.<sup>23</sup>

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<sup>22</sup>The number of bonds an atom has formed is known as its *valence*. Thus in H<sub>2</sub>O (water) and NH<sub>3</sub> (ammonia), the oxygen atom is said to be *bivalent* and the nitrogen atom *tervalent*. Some elements combine under different conditions to form more than one compound, allowing a single element to exhibit multiple valences. For example, a carbon atom is bivalent in CO but quadrivalent in CO<sub>2</sub>.

Since “equivalent weights” of elements are amounts which display the same combining power, then on the atomic view they must also be amounts that form the same total number of atomic bonds. But any number of bivalent atoms will form as many bonds as *twice* that number of univalent atoms; and in general, equivalent weights of different elements must contain numbers of atoms inversely proportional to their respective valences. Therefore we may state that *the relative weights of the atoms of different elements are as the products of their equivalent weights times their valences*, respectively; or:

$$\text{Atomic weight} = \text{Equivalent weight} \times \text{Valence.}$$

<sup>23</sup>The experiment can easily be done with silver, provided the silver nitrate solution is protected from light; however the supplies are much more expensive and harder to recover after use.



With this wiring, the suspended copper electrode is an anode; the fixed copper electrode a cathode. Copper is lost at the anode and gained at the cathode. To reverse anode and cathode, run the current from the power supply in the reverse directions, remembering that current in the ammeter runs from positive (terminal) to negative.

You may choose to weigh either the cathode, which gains material, or the anode, which loses it. It is theoretically advantageous to weigh the *cathode*, since the anode is subject to secondary reactions in the presence of an acid solution, producing excessive weight loss. On the other hand, material removed from the anode may fail to adhere to the cathode, resulting in deficient measurement of the weight gain. Whichever your choice, results will be greatly improved if you start with clean electrodes and avoid excessive currents.

The electrolyte solution is cupric sulfate dissolved in distilled water, with the addition of a small quantity of sulfuric acid, which enhances the conductivity of the solution.

Power is furnished by a standard supply. A rheostat of about 20 ohms is used to help regulate the current. Typically 1-2 amperes is the current used. Higher values will require constant readjustment of the rheostat and may cause decomposition of the water, as well as other problems.

The plate to be weighed will be suspended directly from a metal stand. The beaker, containing the electrolyte solution and the fixed electrode, rests on the workbench. The fixed electrode is cut from a strip of pure copper sheet and is about 1 inch wide; it must be long enough to run along the bottom of the beaker.<sup>24</sup> It should be bent to fit the edge of the beaker and guided far enough away from the suspended plate to prevent accidental contact.

Weigh both plates on the electronic balance. Then fit the fixed plate into the beaker, and adjust the length of the suspension hook so that the suspended plate can swing freely without touching the fixed plate. You will have to make at least two plating trials.

Some groups will attach the spring clips—as suggested in the sketch—others will reverse them. Attach the fixed plate to the desired pole of the power supply.

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<sup>24</sup>This is to establish an electric field on both sides of the suspended plate; otherwise the action may be slow or erratic.

Next clip the remaining power supply lead to the fixed electrode. Start a stopwatch as you turn on the power supply, and quickly bring the current to some value between 1 and 2 amperes.<sup>25</sup> During the run, continually adjust the rheostat to maintain a uniform current through the solution.<sup>26</sup> In order to transfer an amount of material that will be large compared with the sensitivity of the balance, it is best to plate for at least 20 minutes if a 1-ampere current is used, at least 10 minutes if a 2-ampere current is used. Longer times give greater precision of measurement, since the weights of material transferred are then larger in relation to the uncertainty of the weight measurements.

At the conclusion of the first timed run, turn off the power and remove the beam clip and the electrical connection to the pan. Gently remove the suspended electrode and dry it with a hair dryer before measuring its change in weight.

Carry out a second run similar to the first. It is not necessary to keep either the current or the plating time the same as before.

We are now in a position to investigate two relations which Faraday observed to hold in electrolysis:

### Proportionality Between Weight and Charge for a Single Element

According to Faraday, the quantity of charge that is supplied to an electrochemical reaction during any time will be directly proportional to the quantity of material decomposed (or transferred) in that time. We first attempt to exhibit that proportionality.

Calculate the *weight* of material transferred to or from the weighing plate during the first run, and cumulatively over both runs.

Calculate the quantity of *charge* passed during the first run, and cumulatively over both runs:

$$\text{Charge in coulombs} = \text{uniform current in amperes} \times \text{time in seconds}$$

If the expected proportionality holds, the weight of material transferred during the first run will be to the total weight transferred as the charge calculated for the first plating is to the total charge passed. Do the weights have to one another the same ratio as the calculated charges?

### The Ratio of Charge to Weight for Multiple Elements

We have, it is hoped, observed in electrolysis a constant relation between charge and weight for a single element. But as Faraday also described, the weights of two or more elements liberated or transferred by the same quantity of charge are to one another in the same ratio as their *chemically equivalent weights*. Or, differently expressed, *the ratio between charge and equivalent weight is the same for all elements*.

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<sup>25</sup>Don't waste time trying to target a "round number." In this age of pocket calculators, round numbers carry no advantage whatever. It is not important that the current have any particular value, but that it be *steady*.

<sup>26</sup>Note that our rheostat illustrates the very technique Faraday mentioned in his note 3 above for using a fine (and hence high-resistance) wire as a current regulator!

Faraday recognized this constant proportion, but he could not express it in terms of a conventional unit of charge since at that time no such standard had been defined.<sup>27</sup> Using a modern unit, it has subsequently been determined that a charge of about 96,500 coulombs<sup>28</sup> is required to liberate one gram-equivalent weight of any element. That quantity, 96,500 C, was named the *faraday* in that investigator's honor. The measurements we have already taken in electrodeposition of copper will permit us to calculate the faraday for ourselves.

For we found in that experiment that a charge  $Q$  was required to transfer  $\Delta W$  of copper. Now 1 faraday,  $F$ , is the charge required to transfer one gram-equivalent weight of copper—31.78 g. But the charges are to one another as the weights, as presumably we have just confirmed; therefore

$$Q : F :: \Delta W : 31.78 \text{ grams}$$

Or, expressed algebraically,

$$F = \frac{31.78 \cdot Q}{\Delta W}.$$

Thus the faraday will equal the product of the charge passed in any run of the electrodeposition experiment, times the gram-equivalent weight of copper, divided by the weight of copper deposited in that run.

As we shall see, the actual size of the faraday—that is, the quantity of charge found to be associated with one gram-equivalent weight of an element in electrolysis—will become pivotal in some speculations which J. J. Thomson allows himself in his paper that follows.

(It is, as Faraday himself keenly appreciated, extremely large: two one-faraday charges placed one kilometer apart—if it were possible to do this—would electrostatically attract each other with a force of *trillions* of pounds.)

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<sup>27</sup>Hence his recourse to such expressions as: “sufficient to keep a platinum wire red hot,” “more than any man would willingly allow to pass through his body at once,” “thirty turns of a very large and powerful plate machine.”

<sup>28</sup>See the Appendix for information about the various systems of measurement of electrical quantities.



## CHAPTER 2

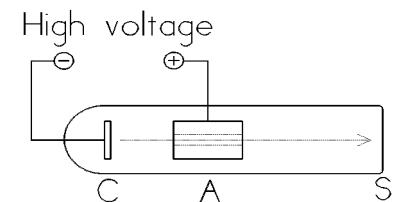
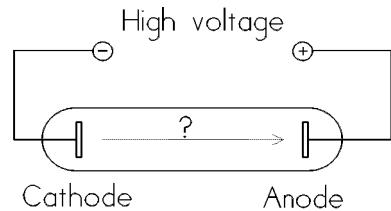
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# CATHODE RAYS

J. J. THOMSON

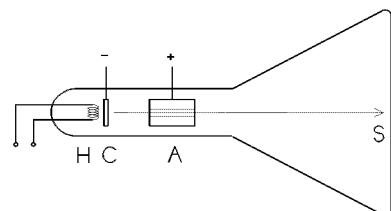
## REMARKS

We pursue further the investigation of "charge," particularly its relation to matter. An avenue for investigation of this question was opened by the discovery of the so-called "cathode rays." If a glass tube into which two electrodes had been sealed was evacuated, and if a high potential difference was placed across the two electrodes, a mysterious emanation issued from the cathode (negative electrode), evidenced, among other manifestations, by its ability to cause phosphors and even certain types of glass to *glow*. These rays, like the ionic motions in electrolysis, served to complete the circuit and thus in a sense to "separate the current from the wire" and make it available for independent study. J. J. Thomson, making the initial hypothesis that the rays consisted of a flow of electrified particles, showed that they did indeed exhibit properties of both mass and charge, related in a definite manner.



The next sketch shows a modern form of cathode-ray tube, much like an oscilloscope or television picture tube. Here H is an electrically-heated wire mounted close to cathode C, for it is found that production of rays is greatly increased if the cathode is heated. One cylindrical anode A is drawn in the figure, but in practice additional anodes are sometimes used to bring the beam to a sharp focus on screen S. The beam may be deflected magnetically or, as Thomson shows, electrostatically. It becomes then a delicate and versatile pencil capable of drawing patterns on the screen which faithfully reflect conditions in the circuits governing the electric or magnetic deflection.

Thomson's 1897 paper on cathode rays is reproduced in part below. He assumes the reader to be familiar with the cathode ray phenomenon. We have sketched two forms of the cathode-ray apparatus here. First depicted is the simplest version: C is the cathode and A the anode of an evacuated tube. The anode contains a small slit; and that a ray of some sort passes through the slit is shown by a bright spot on the zinc sulfide screen S. The spot (and hence the "ray") can be deflected by bringing a magnet near the tube in the region between A and S.



# CATHODE RAYS<sup>1</sup>

J. J. THOMSON

The experiments discussed in this paper were undertaken in the hope of gaining some information as to the nature of the Cathode Rays. The most diverse opinions are held as to these rays; according to the almost unanimous opinion of German physicists they are due to some process in the æther to which—inasmuch as in a uniform magnetic field their course is circular and not linear—no phenomenon hitherto observed is analogous: another view of these rays is that, so far from being wholly æthereal, they are in fact wholly material, and that they mark the paths of particles of matter charged with negative electricity. It would seem at first sight that it ought not to be difficult to discriminate between views so different, yet experience shows that this is not the case, as amongst physicists who have most deeply studied the subject can be found supporters of either theory.

The electrified-particle theory has for purposes of research a great advantage over the æthereal theory, since it is definite and its consequences can be predicted; with the æthereal theory it is impossible to predict what will happen under any given circumstances, as on this theory we are dealing with hitherto unobserved phenomena in the æther, of whose laws we are ignorant.

The following experiments were made to test some of the consequences of the electrified-particle theory.

## Charge Carried by the Cathode Rays

If these rays are negatively electrified particles, then when they enter an enclosure they ought to carry into it a charge of negative electricity. This has been proved to be the case by Perrin, who placed in front of a plane cathode two coaxial metal cylinders which were insulated from each other: the outer of these cylinders was connected with the earth, the inner with a gold-leaf electroscope. These cylinders were closed except for two small holes, one in each cylinder, placed so that the cathode rays could pass through them into the inside of the inner cylinder. Perrin found that when the rays passed into the inner cylinder the electroscope received a charge of negative electricity, while no charge went to the electroscope when the rays were deflected by a magnet so as no longer to pass through the hole.

This experiment proves that something charged with negative electricity is shot off from the cathode, travelling at right angles to it, and that this something is deflected by a magnet; it is open, however, to the objection that it does not prove that the cause of the electrification in the electroscope has anything to do with the cathode rays. Now the supporters of the æthereal theory do not deny that electrified particles are shot off from the cathode; they deny, however, that these charged particles have any more to do with the cathode rays than a rifle-ball has with the flash when a rifle is fired. I have therefore repeated Perrin's experiment in a form which is not open to this objection. The arrangement used was as follows:—

Two coaxial cylinders (Fig. 1) with slits in them are placed in a bulb connected with the discharge-tube; the cathode rays from the cathode A pass into the bulb through a slit in a metal plug fitted into the neck of the tube; this plug is connected with the

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<sup>1</sup>[*Philosophical Magazine*, 44 (1897), 293–311.]



Figure 1

anode and is put to earth. The cathode rays thus do not fall upon the cylinders unless they are deflected by a magnet. The outer cylinder is connected with the earth, the inner with the electrometer. When the cathode rays (whose path was traced by the phosphorescence on the glass) did not fall on the slit, the electrical charge sent to the electrometer when the induction-coil producing the rays was set in action was small and irregular; when, however, the rays were bent by a magnet so as to fall on the slit there was a large charge of negative electricity sent to the electrometer. I was surprised at the magnitude of the charge; on some occasions enough negative electricity went through the narrow slit into the inner cylinder in one second to alter the potential of a capacity of 1.5 microfarads by 20 volts. If the rays were so much bent by the magnet that they overshot the slits in the cylinder, the charge passing into the cylinder fell again to a very small fraction of its value when the aim was true. Thus this experiment shows that however we twist and deflect the cathode rays by magnetic forces, the negative electrification is indissolubly connected with the cathode rays.

When the rays are turned by the magnet so as to pass through the slit into the inner cylinder, the deflexion of the electrometer connected with this cylinder increases up to a certain value, and then remains stationary although the rays continue to pour into the cylinder. This is due to the fact that the gas in the bulb becomes a conductor of electricity when the cathode rays pass through it, and thus, though the inner cylinder is perfectly insulated when the rays are not passing, yet as soon as the rays pass through the bulb the air between the inner cylinder and the outer one becomes a conductor, and the electricity escapes from the inner cylinder to the earth. Thus the charge within the inner cylinder does not go on continually increasing; the cylinder settles down into a state of equilibrium in which the rate at which it gains negative electricity from the rays is equal to the rate at which it loses it by conduction through the air. If the inner cylinder has initially a positive charge it rapidly loses that charge and acquires a negative one; while if the initial charge is a negative one, the cylinder will leak if the initial negative

potential is numerically greater than the equilibrium value.

### Deflexion of the Cathode Rays by an Electrostatic Field

An objection very generally urged against the view that the cathode rays are negatively electrified particles, is that hitherto no deflexion of the rays has been observed under a small electrostatic force, and though the rays are deflected when they pass near electrodes connected with sources of large differences of potential, such as induction-coils or electrical machines, the deflexion in this case is regarded by the supporters of the ætherial theory as primarily due to the discharge passing between the electrodes, and not primarily to the electrostatic field. Hertz made the rays travel between two parallel plates of metal placed inside the discharge-tube, but found that they were not deflected when the plates were connected with a battery of storage-cells; on repeating this experiment I at first got the same result, but subsequent experiments showed that the absence of deflexion is due to the conductivity conferred on the rarefied gas by the cathode rays. On measuring this conductivity it was found that it diminished very rapidly as the exhaustion increased; it seemed then that on trying Hertz's experiment at very high exhaustions there might be a chance of detecting the deflexion of the cathode rays by an electrostatic force.

The apparatus used is represented in Figure 2.



Figure 2

The rays from the cathode C pass through a slit in the anode A, which is a metal plug fitting tightly into the tube and connected with the earth; after passing through a second slit in another earth-connected metal plug B, they travel between two parallel aluminium plates about 5 cm long by 2 broad and at a distance of 1.5 cm apart; they then fall on the end of the tube and produce a narrow well-defined phosphorescent patch. A scale pasted on the outside of the tube serves to measure the deflexion of this patch. At high exhaustions the rays were deflected when the two aluminium plates were connected with the terminals of a battery of small storage-cells; the rays were depressed when the upper plate was connected with the negative pole of the battery, the lower with the positive, and raised when the upper plate was connected with the positive, the lower with the negative pole. The deflexion was proportional to the difference of potential between the plates, and I could detect the deflexion when the potential-difference was as small as two volts. It was only when the vacuum was a good one that the deflexion took place, but that the absence of deflexion is due to the conductivity of the medium is shown by what takes place when the vacuum has just arrived at the stage at which the deflexion begins. At this stage there is a deflexion of

the rays when the plates are first connected with the terminals of the battery, but if this connexion is maintained the patch of phosphorescence gradually creeps back to its undeflected position. This is just what would happen if the space between the plates were a conductor, though a very bad one, for then the positive and negative ions between the plates would slowly diffuse, until the positive plate became coated with negative ions, the negative plate with positive ones; thus the electric intensity between the plates would vanish and the cathode rays be free from electrostatic force.

\* \* \*

### Magnetic Deflexion of the Cathode Rays in Different Gases

\* \* \*

As the cathode rays carry a charge of negative electricity, are deflected by an electrostatic force as if they were negatively electrified, and are acted on by a magnetic force in just the way in which this force would act on a negatively electrified body moving along the path of these rays, I can see no escape from the conclusion that they are charges of negative electricity carried by particles of matter. The next question arises, What are these particles? are they atoms, or molecules, or matter in a still finer state of subdivision? To throw some light on this point, I have made a series of measurements of the ratio of the mass of these particles to the charge carried by it. To determine this quantity, I have used two independent methods.<sup>2</sup>

\* \* \*

I shall describe another method of measuring<sup>3</sup> the quantities  $m/e$  and  $v$  of an entirely different kind from the preceding; this method is based upon the deflexion of the cathode rays in an electrostatic field. If we measure the deflexion experienced by the rays when traversing a given length under a uniform electric intensity, and the deflexion of the rays when they traverse a given distance under a uniform magnetic field, we can find the values of  $m/e$  and  $v$  in the following way:—

Let the space passed over by the rays under a uniform electric intensity  $F$  be  $l$ ,<sup>4</sup> the time taken for the rays to traverse this space is  $l/v$ , the [component of the final] velocity in the direction of  $F$  is therefore

$$\frac{Fe}{m} \cdot \frac{l}{v}$$

so that  $\theta$ , the angle through which the rays are deflected when they leave the electric field and enter a region free from electric force, is given by the equation

$$\theta = \frac{Fe}{m} \cdot \frac{l}{v^2}.$$

<sup>2</sup>[We shall consider only the second and more accurate of Thomson's two methods.]

<sup>3</sup>[In the following,  $m$  and  $e$  are the mass and charge, respectively, and  $v$  is the velocity, of a cathode ray particle. All of the electric quantities here are expressed in the *electromagnetic system of units* (e.m.u.). Thus  $e$  is in *abcoulombs*, and so on. See Appendix.]

<sup>4</sup>[Thus  $l$  is the length of the parallel plates D and E in Figure 2.]

<sup>5</sup>[For this and the next expression see note 6, which follows.]

<sup>6</sup>[The force on the particle is always vertical and of magnitude  $Fe$ . When applied for a time  $l/v$  it will impart a final vertical velocity  $v'$ , given by  $l/v$  times the vertical acceleration, which is  $Fe/m$ ; thus

$$v' = \frac{Fe}{m} \frac{l}{v}.$$

Then the vector resultant of horizontal velocity  $v$  and vertical velocity  $v'$  will be directed at an angle  $\theta$

If, instead of the electric intensity, the rays are acted on by a magnetic force  $H$  at right angles to the rays, and extending across the distance  $l$ , then the [component of the final] velocity at right angles to the original path of the rays is

$$\frac{Hev}{m} \cdot \frac{l}{v},^7$$

so that  $\phi$ , the angle through which the rays are deflected when they leave the magnetic field, is given by the equation

$$\phi = \frac{He}{m} \cdot \frac{l}{v}.^8$$

From these equations we get

$$v = \frac{\phi F}{\theta H}$$

and

$$\frac{m}{e} = \frac{H^2 \theta l}{F \phi^2}.$$

In the actual experiments  $H$  was adjusted so that  $\phi = \theta$ ; in this case the equations become

$$v = \frac{F}{H}$$

$$\frac{m}{e} = \frac{H^2 l}{F \theta}.$$

The apparatus used to measure  $v$  and  $m/e$  by this means is that represented in Figure 2. The electric field was produced by connecting the two aluminium plates to the terminals of a battery of storage-cells. The phosphorescent patch at the end of the tube was deflected, and the deflection measured by a scale pasted to the end of the tube. As it was necessary to darken the room to see the phosphorescent patch, a needle coated with luminous paint was placed so that by a screw it could be moved up and down the scale; this needle could be seen when the room was darkened, and it was moved until it coincided with the phosphorescent patch. Thus, when light was admitted, the deflection of the phosphorescent patch could be measured.

The magnetic field was produced by placing outside the tube two coils whose diameter was equal to the length of the plates[...].<sup>9</sup>

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A series of experiments was made to see if the electrostatic deflection was proportional to the electric intensity between the plates; this was found to be the case. In the

such that

$$\tan \theta = \frac{v'}{v} = \frac{Fe}{m} \cdot \frac{l}{v^2}$$

Moreover for small angles,  $\tan \theta$  is nearly equal to  $\theta$  (measured in radians); hence the formula in the text.]

<sup>7</sup>[A charge  $e$  (e.m.u.), moving with velocity  $v$  at right angles to the direction of a magnetic field  $H$ , will experience a force  $f = Hev$ , directed perpendicularly to both  $v$  and  $H$ . (For a discussion see the Note at the end of this chapter.) Now since  $a = f/m$  and  $t = l/v$ , the charge will attain a [component of the] final velocity  $v' = at = \frac{f}{m} \cdot \frac{l}{v}$  in the direction perpendicular to  $v$  and  $H$ . Substitution yields the expression cited.]

<sup>8</sup>[Obtained by taking the ratio of vertical to horizontal components of velocity, just as was done previously for angle  $\theta$ .]

<sup>9</sup>[We here omit Thomson's description of his method of measuring the magnetic field.]

following experiments the current through the coils was adjusted so that the electrostatic deflexion was the same as the magnetic:—

TABLE 1

Gas.	$\theta.$	H.	F.	$l.$	$m/e.$	$v.$
Air	8/100	5.5	$1.5 \times 10^{10}$	5	$1.3 \times 10^{-7}$	$2.8 \times 10^9$
Air	9.5/100	5.4	$1.5 \times 10^{10}$	5	$1.1 \times 10^{-7}$	$2.8 \times 10^9$
Air	13/110	6.6	$1.5 \times 10^{10}$	5	$1.2 \times 10^{-7}$	$2.3 \times 10^9$
Hydrogen	9/110	6.3	$1.5 \times 10^{10}$	5	$1.5 \times 10^{-7}$	$2.5 \times 10^9$
Carbonic acid	11/110	6.9	$1.5 \times 10^{10}$	5	$1.5 \times 10^{-7}$	$2.2 \times 10^9$
Air	6/110	5	$1.8 \times 10^{10}$	5	$1.3 \times 10^{-7}$	$3.6 \times 10^9$
Air	7/110	3.6	$1 \times 10^{10}$	5	$1.1 \times 10^{-7}$	$2.8 \times 10^9$

The cathode in the first five experiments was aluminium, in the last two experiments it was made of platinum; in the last experiment Sir William Crookes's method of getting rid of the mercury vapour by inserting tubes of pounded sulphur, sulphur iodide, and copper filings between the bulb and the pump was adopted. In the calculation of  $m/e$  and  $v$  no allowance has been made for the magnetic force due to the coil in the region outside the plates; in this region the magnetic force will be in the opposite direction to that between the plates, and will tend to bend the cathode rays in the opposite direction: thus the effective value of H will be smaller than the value used in the equations, so that the values of  $m/e$  are larger and those of  $v$  less than they would be if this correction were applied. . . .<sup>10</sup>

From these determinations we see that the value of  $m/e$  is independent of the nature of the gas, and that its value  $10^{-7}$  is very small compared with the value  $10^{-4}$ , which is the smallest value of this quantity previously known, and which is the value for the hydrogen ion in electrolysis.<sup>11</sup>

Thus for the carriers of the electricity in the cathode rays  $m/e$  is very small compared with its value in electrolysis. The smallness of  $m/e$  may be due to the smallness of  $m$  or the largeness of  $e$ , or to a combination of these two. That the carriers of the charges in the cathode rays are small compared with ordinary molecules is shown, I think, by Lenard's results as to the rate at which the brightness of the phosphorescence produced by these rays diminishes with the length of path traveled by the ray. If we regard this phosphorescence as due to the impact of the charged particles, the distance through which the rays must travel before the phosphorescence fades to a given fraction (say,  $1/e$ , where  $e = 2.71$ ) of its original intensity, will be some moderate multiple of the mean free path.<sup>12</sup> Now Lenard found that this distance depends solely upon the

<sup>10</sup>[The value of  $m/e$  accepted today is  $0.5685 \times 10^{-7}$  g/abC, less than half the average of the values given in Thomson's table above. Thomson acknowledges that he has neglected the magnetic field *outside* the parallel plates. Although he does not appear to regard that as a serious omission, it may in fact account for much of the discrepancy between his results and subsequent determinations.]

<sup>11</sup>[Thomson here alludes to the results of electrolysis experiments such as our electroplating exercise: that one gram-equivalent weight of any element is associated with a charge of 96,500 coulombs (9,650 abcoulombs). Then since 1 gram is the gram-equivalent weight of hydrogen, the quotient  $m/e$  for hydrogen will be  $1/9,650$  g/abC, or approximately  $10^{-4}$ , as Thomson cites.]

<sup>12</sup>[Here,  $e$  is the base of the natural log system, approximately 2.71, and should not be confused with  $e$ , the charge carried by a cathode ray "corpuscle." The *mean free path* of a molecule in a gas is the average distance it can travel before colliding with another molecule. For air at atmospheric pressure this distance is of the order of one millionth of 1 cm.]

density of the medium, and not upon its chemical nature or physical state. In air at atmospheric pressure the distance was about half a centimetre, and this must be comparable with the mean free path of the carriers through air at atmospheric pressure. But the mean free path of the molecules of air is a quantity of quite a different order. The carrier, then, must be small compared with ordinary molecules.

\* \* \*

The explanation which seems to me to account in the most simple and straightforward manner for the facts is founded on a view of the constitution of the chemical elements which has been favourably entertained by many chemists: this view is that the atoms of the different chemical elements are different aggregations of atoms of the same kind. In the form in which this hypothesis was enunciated by Prout,<sup>13</sup> the atoms of the different elements were hydrogen atoms; in this precise form the hypothesis is not tenable, but if we substitute for hydrogen some unknown primordial substance X, there is nothing known which is inconsistent with this hypothesis[...].

If, in the very intense electric field in the neighborhood of the cathode, the molecules of the gas are dissociated and are split up, not into the ordinary chemical atoms, but into these primordial atoms, which we shall for brevity call corpuscles; and if these corpuscles are charged with electricity and projected from the cathode by the electric field, they would behave exactly like the cathode rays. They would evidently give a value of  $m/e$  which is independent of the nature of the gas and its pressure, for the carriers are the same whatever the gas may be[...].

Thus we have in the cathode rays matter in a new state, a state in which the subdivision of matter is carried very much further than in the ordinary gaseous state: a state in which all matter—that is, matter derived from different sources such as hydrogen, oxygen, &c.—is of one and the same kind; this matter being the substance from which all the chemical elements are built up.

\* \* \*

## EXPERIMENT: THE RATIO OF CHARGE TO MASS IN CATHODE RAYS

The cathode-ray tube described here operates on the same principles as does that described by Thomson. However, the experiment is made somewhat more elegant by causing the cathode-ray particles to orbit in a circular path under the action of the magnetic field alone. This happens because in a magnetic field  $H$  the force on a charge  $e$  moving with velocity  $v$  is always perpendicular to both  $H$  and  $v$ . Thus if  $v$  is initially perpendicular to  $H$  and if  $H$  is uniform, the forces on  $e$  will always deflect it in a single plane perpendicular to  $H$ , as diagrammed in the figure below.<sup>14</sup> Moreover, since force  $f$  is also normal to  $v$ , the charge  $e$  will never be accelerated in the direction of its motion, and  $v$  will therefore remain constant in magnitude and vary only in direction. But these

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<sup>13</sup>[William Prout (1785-1850), English chemist and physician, pointed out in an anonymous article in the *Annals of Philosophy* in 1815 that the atomic weights of a number of elements are multiples of that of hydrogen. In a second article in the following year he suggested that hydrogen was the "prime matter" of the ancients.]

<sup>14</sup>If in the figure the indicated direction for the force  $f$  seems to be reversed, recall that the charge on the hypothetical cathode-ray particle is *negative*.

are exactly the conditions for circular motion with constant speed; in such an orbit the force is always normal to the velocity and is directed to a virtual center, O.



Now the acceleration  $a$  towards the center of circular motion is  $a = v^2/r$ ,<sup>15</sup> so that the central force will be given by

$$f = ma = mv^2/r. \quad (1)$$

In the present case the force  $f$  is supplied by the magnetic field and is therefore<sup>16</sup>

$$f = Hev \quad (2)$$

(compare Thomson's equation for magnetic deflection). Combining equations (1) and (2), we find

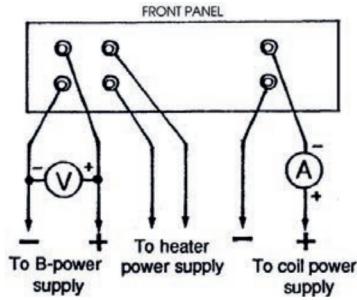
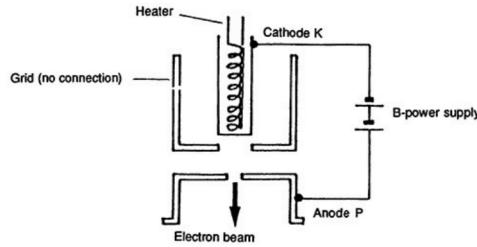
$$\frac{e}{m} = \frac{v}{rH}; \quad (3)$$

the ratio  $e/m$  will thus be known if  $r$ ,  $H$ , and  $v$  are known. We use a tube in which several radii  $r$  are marked on a phosphor-coated scale running the length of the tube; the magnetic field  $H$  is adjusted until the ray orbit intersects the scale at a predetermined marking indicating the diameter (e.g., 10 cm), and thus  $r$  is known. It remains only to determine  $H$  and  $v$ .

The tube with its connections is diagrammed in the sketches. It contains an anode and a heated cathode. A power supply maintains the anode at a positive potential with respect to the cathode, so that negative particles emitted by it are accelerated towards the anode and pass through the slit with considerable velocity. Current is run through a pair of coils that surrounds the tube, arranged so that their magnetic fields combine to form a nearly uniform field in the region of the tube. The beam of particles is indicated by the glow of vapor in the tube; coil current is adjusted until the orbit of the particles lines up with one of the marks for measurement.

<sup>15</sup>Cf. Newton, *Principia*, Prop. IV, Corollary 1.

<sup>16</sup>See the Note at the end of this chapter.



Energy considerations determine the velocity  $v$ . Since particles emitted from the cathode are accelerated to the anode, they gain kinetic energy equal to the work done by the electric field on them. This work equals the product of the potential difference and the charge on the particle,<sup>17</sup> so that in electromagnetic units ( $V$  in abvolts and  $e$  in abcoulombs), we have

$$Ve = \frac{1}{2}mv^2 \quad \text{or} \quad v = \sqrt{\frac{2Ve}{m}}. \quad (4)$$

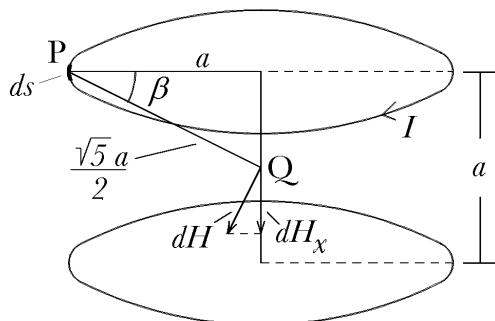
If  $V$  represents the measurement in *volts* as per our meters, a conversion factor must be introduced (1 volt =  $10^8$  abvolts), and the equation becomes

$$v = \sqrt{\frac{2V_{volt}e \cdot 10^8}{m}} \quad (5)$$

Substitution of this value in equation (3) yields for  $e/m$ :

$$\frac{e}{m} = \frac{2V_{volt}}{r^2 H^2} \cdot 10^8 \text{ abC/g}. \quad (6)$$

Finally, the magnetic field  $H$  must be found. The pair of coils we use, known as Helmholtz coils, is so designed that the distance between them is equal to the coil radius  $a$ . (This makes the magnetic field between the coils relatively uniform.) The tube is placed at  $Q$ , which is at a distance  $a/2$  from the center of each coil. The contribution  $dH$  that a current element  $I ds$  at  $P$



<sup>17</sup>See Appendix.

makes to the field at Q will be

$$dH = \frac{I ds}{PQ^2} = \frac{I ds}{(5/4)a^2} = \frac{4 I ds}{5 a^2}$$

(using the Pythagorean Theorem to give us  $PQ^2$ ). As successive current elements are considered, components of  $dH$  perpendicular to the axis cancel one another, so that only axial components  $dH_x$  are effective. But

$$\cos \beta = a/PQ = 2/\sqrt{5},$$

whence

$$dH_x = dH \cos \beta = \frac{2}{\sqrt{5}} dH = \frac{8}{5\sqrt{5}} \frac{I ds}{a^2}. \quad (7)$$

Integrating, we obtain

$$H = \int_0^{2\pi a} \frac{8}{5\sqrt{5}} \frac{I}{a^2} ds = \frac{8}{5\sqrt{5}} \frac{2\pi a I}{a^2} = \frac{16\pi I}{5\sqrt{5}a}.$$

For *two* coils of  $N$  turns each, therefore,

$$H = \frac{32\pi IN}{5\sqrt{5}a}.$$

If the current  $I$  is stated in *amperes* as per our meter readings, the above equation becomes

$$H = \frac{3.2\pi NI_{amp}}{5\sqrt{5}a}. \quad (8)$$

For our coils,  $N = 130$ .

Thus we use equation (8) to determine the magnetic field  $H$ ; then we substitute this value into equation (6) to determine the charge-to-mass ratio  $e/m$ .

### Operation

When the apparatus is wired, orient the coils so their axis is aligned with magnetic north in the room (use a compass for this purpose). Slowly raise  $V$ , the anode voltage, to some value between 200 and 300 volts. Record this voltage, and vary the coil current  $I$  until the beam falls on one of the markers. Half of this diameter will be your radius  $r$  for equation (6). With known  $I$  we calculate  $H$  using equation (7); then with known  $H$  and  $V$  and  $r$  we calculate  $e/m$  using equation (5). It makes sense to determine  $e/m$  several times using different radii and different voltages. Although by our theory the values thus obtained ought to agree, in practice they may differ. If so, look for any suggestive regularities in the differences; for example, are measurements taken at higher voltages uniformly greater or less than those taken at lower voltages? What might cause such an effect?

### NOTE: ON MAGNETIC FIELDS AND MOVING CHARGED BODIES

A current-carrying wire, because of the magnetic field which it generates, will exert a force on any magnet placed near it. By Newton's Third Law, the magnet will necessarily exert *an equal and opposite force back on the wire*. Thus, magnetic fields exert force

on current-carrying wires. If a long straight wire carrying a current of 1 abampere is placed in a perfectly uniform magnetic field of unit strength with the field lines perpendicular to the wire, then it will experience *a force of one dyne for every centimeter of its length*. The force will be perpendicular to both the wire and the field lines.

An analogous situation holds for *moving charged bodies* in a magnetic field. A body carrying 1 abcoulomb and moving at 1 centimeter per second through a magnetic field of unit strength will experience a force of 1 dyne perpendicular to both the field lines and the direction of motion. We cannot argue rigorously for this here, but note that in one second this charged body makes one abcoulomb "flow" a distance of one centimeter—just as does a 1-cm-long wire carrying 1 abamp, which also would experience a force of one dyne. At any rate, in general

$$f = Hev,$$

where  $f$  is the force,  $H$  is the magnetic field strength,  $e$  is the charge *in abampères* and  $v$  is the velocity in cm./sec.

For both the current-carrying wire and the moving charged particle, the direction of the force is more or less conveniently given by the "left hand rule," also known as the "*fBI*" rule. Arrange the thumb, forefinger and middle fingers on your left (your *left*) hand so that they are mutually perpendicular, like 3-dimensional coordinate axes. Then your thumb will give the direction of  $f$  the force if your forefinger points in the direction of  $B$  the magnetic field and your middle finger in the direction of  $I$  the current. (Remember that for a cathode-ray current,  $I$  is in the opposite direction of the motion of the electrons, since they are negatively charged.)

## CHAPTER 3

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# THE ELECTRON

R. A. MILLIKAN

## REMARKS

We turn now to the examination of "charge" itself, in particular to the question whether charge is discrete or continuous in its ultimate composition. That question was effectively answered with R. A. Millikan's discovery of a fundamental unit of charge—the so-called "electron."

The instrument Millikan employed for that delicate task of measurement is a tiny droplet of oil bearing a minute electrical charge, alternately hoisted up by an applied electric field, then allowed to fall back down under its own weight with the field turned off. From observations of the motion of such drops Millikan was able, first, to show that a fundamental unit of charge exists; second, to determine the magnitude of that unit.

In the selection that follows, Millikan takes as granted the equations governing the motion of the oil drop. Therefore the first phase in our reasoning must be to work out in a general way the forces that act on the drop and to derive the equation of its motion under those forces. It will be assumed at this point that the size and mass of the drop are known; actually their determination constitutes an important second phase of the analysis.



The forces which act on a falling drop in the absence of an electric field are sketched on the left side of the diagram, marked (a). The mass of the drop is  $\mu$  and the weight is therefore  $\mu g$ . The drop falls through the air, which we shall regard as a very thin homogeneous fluid that both buoys up a body and resists motion through itself. We also assume, with Millikan, that this resisting force is *directly proportional to the velocity* of the moving drop. This proportionality characterizes the special type of friction called a "viscous" force, exerted by a "viscous" fluid on any body moving through it. The

measure of a fluid's capacity for applying such a force is called its "viscosity." Millikan had good reason to believe that air exhibited this viscosity quite strictly.

With some constant of proportionality,  $R$ , then, the viscous force  $r$  resisting the droplet's fall will be

$$r = Rv \quad (3.1)$$

as shown in Fig. (a).

At the same time, the drop is buoyed up by a force equal to the weight of air which it displaces.<sup>1</sup> Thus a droplet of volume  $V$  will have mass  $\mu = V\sigma$ , but it will displace a mass  $V\rho$  of air, where  $\sigma$  is the density of the oil and  $\rho$  is the density of the air. Hence the three forces acting on the falling drop are:

$$\begin{aligned} \text{Weight} & W = V\sigma g \\ \text{Buoyancy} & \beta = V\rho g \\ \text{Retarding force} & r = Rv \end{aligned}$$

for a total downward force  $f$  of

$$\begin{aligned} f &= V\sigma g - V\rho g - Rv \\ &= V(\sigma - \rho)g - Rv \end{aligned}$$

On analogy with  $V\sigma$ , the actual mass of the oil drop, Millikan will call  $V(\sigma - \rho)$  in the expression above the "effective" gravitational mass,  $m$ —as though the reduced downward tendency of the drop in the buoyant medium were due to a reduced gravitational mass  $m = V(\sigma - \rho)$  rather than, as is actually the case, to the presence of an upward buoyant force  $\beta = V\rho g$ . The expression for the net downward force can then be written

$$f = mg - Rv \quad (3.2)$$

where  $m = V(\sigma - \rho)$ . There will be a downward acceleration—that is, a continuing increase in velocity  $v$ —so long as the resistance  $Rv$  of the medium is less than the effective weight  $mg$ .

However, as the velocity of the drop increases, so will the resistance; as  $Rv$  increases it will approach  $mg$  and the net force  $f$  will approach zero, as is clear from equation (3.2) above. The acceleration will become very small, and the droplet will continuously approach the *constant* velocity  $v_1$ ,<sup>2</sup> characterized as the velocity at which

$$Rv = mg.$$

This gives

$$v_1 = \frac{mg}{R}. \quad (3.3)$$

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<sup>1</sup>Archimedes, *On Floating Bodies*, I, Prop. 7.

<sup>2</sup>In practice, the drop almost immediately accelerates to a velocity immeasurably close to its terminal velocity.

Suppose now that the droplet bears electric charge  $e_n$ . In the absence of an electric field, that charge will not affect the drop's motion. But when a field  $F$  tending to raise the drop is applied, an upward force  $Fe_n$  will act on the drop; and if it is strong enough to overbalance the effective weight of the drop, the drop will stop falling and begin to rise. Then while the drop is rising both the effective weight and the viscous force will be *downwards*, and there will act on the drop (see Fig. (b)) a net *upward* force equal to

$$Fe_n - mg - Rv.$$

Then by an argument similar to that for the drop when falling, the rising drop will shortly attain a constant upward velocity  $v_2$ , where

$$v_2 = \frac{Fe_n - mg}{R} \quad (3.4)$$

It is a striking characteristic of motion in a viscous medium that a body under the action of a constant force attains a *constant velocity proportional to that force*.

Equations (3.3) and (3.4) constitute all the theory that Millikan requires to establish from his observations that the electron *exists*; although calculation of its *quantity* involves, as we shall see, considerably more reasoning. Actually Millikan uses the *quotient* of equation (3.3) by equation (3.4), which is

$$\frac{v_1}{v_2} = \frac{mg}{Fe_n - mg} \quad \text{or} \quad e_n = \frac{mg}{Fv_1} (v_1 + v_2) \quad (1)$$

It will be called equation (9) in the selection that follows.

A final remark: unlike Thomson (who had to deal with both electric and magnetic qualities in his calculations), Millikan, who deals with the electron only in its electrostatic relations, accordingly uses the *electrostatic system of units* (e.s.u.) in what we are about to read. Thus he will eventually state his fundamental unit of charge in *statcoulombs*. In order to relate Millikan's and Thomson's results, recall that the electromagnetic and the electrostatic systems of units are related by the constant  $c$  (the speed of light in centimeters per second), so that one abcoulomb equals  $3.00 \times 10^{10}$  statcoulombs. (See Appendix below for a fuller discussion of the relation between the "electrostatic" and "electromagnetic" system of units.)

## THE ELECTRON

### R. A. MILLIKAN

#### **General Proof of the Atomic Nature of Electricity<sup>3</sup>**

Although the "balanced droplet method" just described<sup>4</sup> had eliminated the chief sources of uncertainty which inhered in preceding work on  $e$  and had made it possible to assert with much confidence that the unit charge was a real physical entity and not merely a "statistical mean," it was yet very far from an exact method of studying the

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<sup>3</sup>[Chapter IV of *The Electron*, University of Chicago Press (1924). Although we are reading his 1924 account, Millikan developed the methods here described from 1909 to 1913.]

<sup>4</sup>[Millikan here refers to an earlier technique, omitted here.]

properties of gaseous ions. The sources of error or uncertainty which still inhered in it arose from (1) the lack of stagnancy in the air through which the drop moved; (2) the lack of perfect uniformity of the electrical field used; (3) the gradual evaporation of the drops, rendering it impossible to hold a given drop under observation for more than a minute or to time a drop as it fell under gravity alone through a period of more than five or six seconds; and (4) the assumption of the validity of Stokes's Law.

The method which was devised to replace it was not only entirely free from all of these limitations, but it constituted an entirely new way of studying ionization and one which at once yielded important results in a considerable number of directions. This chapter deals with some of these by-products of the determination of  $e$  which are of even more fundamental interest and importance than the mere discovery of the exact size of the electron.

### I. Isolation of Individual Ions and Measurement of Their Relative Charges

In order to compare the charges on different ions, the procedure adopted was to blow with an ordinary commercial atomizer an oil spray into the chamber C (Fig. 3). The air with which this spray was blown was first rendered dust-free by passage through a tube containing glass wool. The minute droplets of oil constituting the spray, most of them having a radius of the order of a one-thousandth of a millimeter, slowly fell in the chamber C, and occasionally one of them would find its way through the minute pinhole  $p$  in the middle of the circular brass plate M, 22 cm in diameter, which formed



Figure 3

one of the plates of the air condenser. The other plate, N, was held 16 mm. beneath it by three ebonite posts  $a$ . By means of the switch S these plates could be charged, the one positively and the other negatively, by making them the terminals of a 10,000-volt storage battery B, while throwing the switch the other way (to the left) short-circuited

them and reduced the field between them to zero. The oil droplets which entered at  $p$  were illuminated by a powerful beam of light which passed through diametrically opposite windows in the encircling ebonite strip  $c$ . As viewed through a third window in  $c$  on the side toward the reader, it appeared as a bright star on a black background. These droplets which entered  $p$  were found in general to have been strongly charged by the frictional process involved in blowing the spray, so that when the field was thrown on in the proper direction they would be pulled up toward  $M$ . Just before the drop under observation could strike  $M$  the plates would be short-circuited and the drop allowed to fall under gravity until it was close to  $N$ , when the direction of motion would be again reversed by throwing on the field. In this way the drop would be kept traveling back and forth between the plates. The first time the experiment was tried an ion<sup>5</sup> was caught within

TABLE IV

$t_g$	$t_F$
13.6	12.5
13.8	12.4
13.4	21.8
13.4	34.8
13.6	84.5
13.6	85.5
13.7	34.6
13.5	34.8
13.5	16.0
13.8	34.8
13.7	34.6
13.8	21.9
13.6	
13.5	
13.4	
13.8	
13.4	
Mean 13.595	

a few minutes, and the fact of its capture was signaled to the observer by the change in the speed with which [the oil drop] moved up when the field was on. The significance of the experiment can best be appreciated by examination of the complete record of one of the early experiments when the timing was done merely with a stop watch.

<sup>5</sup>[“Ion” was Faraday’s term for the particles of matter which seemed, in electrolysis, to migrate from one region of the solution to another. Although Faraday himself distrusted the atomic view, researchers of a later generation collected much evidence that “ions” were actually *electrically-charged atoms* (or groups of atoms), which were not only found in electrolytes but could also be produced in gases by various causes including x-rays and the presence of radioactive substances. In an earlier chapter of *The Electron*, Millikan wrote: “In a word, then, the act of ionization in gases appears to consist in the detachment from a neutral atom of one or more negatively charged particles, called by Thomson *corpuscles*. The residuum of the atom is of course positively charged.... The detached corpuscle must soon attach itself, in a gas at ordinary pressure, to a neutral atom.” Thus some of the air molecules in Millikan’s chamber carry either a positive or a negative charge, and it is these charged molecules—ions—that periodically collide with the oil drop and yield to it whatever charges they bear.]

The column headed  $t_g$  gives the successive times which the droplet required to fall [under the force of gravity,  $g$ ] between two fixed cross-hairs in the observing telescope whose distance apart corresponded in this case to an actual distance of fall of .5222 cm. It will be seen that these numbers are all the same within the limits of error of a stop-watch measurement. The column marked  $t_F$  gives the successive times which the droplet required to rise under the influence of the electrical field [ $F$ ] produced by applying in this case 5,051 volts of potential difference to the plates M and N. It will be seen that after the second trip up, the time changed from 12.4 to 21.8, indicating, since in this case the drop was positive, that a negative ion had been caught from the air. The next time recorded under  $t_F$ , namely, 34.8, indicates that another negative ion had been caught. The next time, 84.5, indicates the capture of still another negative ion. This charge was held for two trips, when the speed changed back again to 34.6, showing that a positive ion had now been caught which carried precisely the same charge as the negative ion which before caused the inverse change in time, i.e., that from 34.8 to 84.5.

In order to obtain some of the most important consequences of this and other similar experiments we need make no assumption further than this, that the velocity with which the drop moves is proportional to the force acting upon it and is independent of the electrical charge which it carries. Fortunately this assumption can be put to very delicate experimental test, as will presently be shown, but introducing it for the time being as a mere assumption, as Townsend, Thomson, and Wilson had done before, we get

$$\frac{v_1}{v_2} = \frac{mg}{Fe_n - mg} \quad \text{or} \quad e_n = \frac{mg}{Fv_1}(v_1 + v_2) \quad (9)$$

The negative sign is used in the denominator because  $v_2$  will for convenience be taken as positive when the drop is going up in the direction of  $F$ , while  $v_1$  will be taken as positive when it is going down in the direction of  $g$ .  $e_n$  denotes the charge on the drop, and must not be confused with the charge on an ion. If now by the capture of an ion the drop changes its charge from  $e_n$  to  $e_{n'}$ , then the value of the captured charge  $e_i$  is

$$e_i = e_{n'} - e_n = \frac{mg}{Fv_1}(v'_2 - v_2) \quad (10)$$

and since  $mg/Fv_1$  is a constant for this drop, any charge which it may capture will always be proportional to  $(v'_2 - v_2)$ , that is, to the change produced in the velocity in the field  $F$  by the captured ion. The successive values of  $v_2$  and of  $(v'_2 - v_2)$  are shown in Table V.

It will be seen from the last column that within the limits of error of a stop-watch measurement, all the charges captured have exactly the same value save in three cases. In all of these three the captured charges were just twice as large as those appearing in the other changes. Relationships of exactly this sort have been found to hold absolutely without exception, no matter in what gas the drops have been suspended or what sort of droplets were used upon which to catch the ions. In many cases a given drop has been held under observation for five or six hours at a time and has been seen to catch not eight or ten ions, as in the above experiment, but hundreds of them. Indeed, I have observed, all told, the capture of many thousands of ions in this way, and in no case

TABLE V<sup>a</sup>

v <sub>2</sub>	(v' <sub>2</sub> - v <sub>2</sub> )
$\frac{.5222}{12.45} = .04196$	}
$\frac{.5222}{[21.85]} = .02390$	
$\frac{.5222}{34.7} = .01505$	
$\frac{.5222}{85.0} = .006144$	
$\frac{.5222}{34.7} = .01505$	
$\frac{.5222}{16.0} = .02364$	
$\frac{.5222}{34.7} = .01505$	
$\frac{.5222}{21.85} = .02390$	

$.01806 \div 2 = .00903$
$.00885 \div 1 = .00885$
$.00891 \div 1 = .00891$
$.00891 \div 1 = .00891$
$.01759 \div 2 = .00880$
$.01759 \div 2 = .00880$
$[.00885 \div 1 = .00885]$

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<sup>a</sup>[The bracketed numbers are our corrections of typos in Millikan's original table.]

have I ever found one the charge of which, when tested as above, did not have either exactly the value of the smallest charge ever captured or else a very small multiple of that value. *Here, then, is direct, unimpeachable proof that the electron is not a "statistical mean," but that rather the electrical charges found on ions all have either exactly the same value or else small exact multiples of that value.*

## II. Proof That All Static Charges Both on Conductors and Insulators Are Built Up of Electrons

The foregoing experiment leads, however, to results of much more fundamental importance than that mentioned in the preceding section. The charge which the droplet had when it first came under observation had been acquired, not by the capture of ions from the air, but by the ordinary frictional process involved in blowing the spray. If then ordinary static charges are built up of electrons, this charge should be found to be an exact multiple of the ionic charge which had been found from the most reliable measurement shown in Table V to be proportional to the velocity .00891. This initial charge  $e_n$  on the drop is seen from equations (9) and (10) to bear the same relation to  $(v_1 + v_2)$  which the ionic charge  $e_{n'} - e_n$  bears to  $(v'_2 - v_2)$ . Now,  $v_1 = .5222 \div 13.595 = .03842$ , hence  $v_1 + v_2 = .03842 + .04196 = .08038$ . Dividing this by 9 we obtain .008931, which is within about one-fifth of 1 per cent of the value found in the last column of Table V as the smallest charge carried by an ion. *Our experiment has then given us for the first time a means of comparing a frictional charge with the ionic charge, and the frictional charge has in this instance been found to contain exactly 9 electrons.* A more exact means of making this comparison will be given presently, but suffice it to say here that experiments like the foregoing have now been tried on thousands of drops in different media, some of the drops being made of non-conductors like oil, some of semi-conductors like glycerin, some of excellent metallic conductors like mercury. In every case, without a single ex-

ception, the initial charge placed upon the drop by the frictional process, and all of the dozen or more charges which have resulted from the capture by the drop of a larger or smaller number of ions, have been found to be exact multiples of the smallest charge caught from the air. Some of these drops have started with no charge at all, and one, two, three, four, five, and six elementary charges or electrons have been picked up. Others have started with seven or eight units, others with twenty, others with fifty, others with a hundred, others with a hundred and fifty elementary units, and have picked up in each case a dozen or two of elementary charges on either side of the starting point, so that in all, drops containing every possible number of electrons between one and one hundred and fifty have been observed and the number of electrons which each drop carried has been accurately counted by the method described. When the number is less than fifty there is not a whit more uncertainty about this count than there is in counting one's own fingers and toes. It is not found possible to determine with certainty the number of electrons in a charge containing more than one hundred or two hundred of them, for the simple reason that the method of measurement used fails to detect the difference between 200 and 201, that is, we cannot measure  $v'_2 - v_2$  with an accuracy greater than one-half of 1 per cent. But it is quite inconceivable that large charges such as are dealt with in commercial applications of electricity can be built up in an essentially different way from that in which the small charges whose electrons we can count are found to be. Furthermore, since it has definitely been proved that an electrical current is nothing but the motion of an electrical charge over or through a conductor, it is evident that the experiments under consideration furnish not only the most direct and convincing of evidence that all electrical charges are built up out of these very units which we have been dealing with as individuals in these experiments, but that all electrical currents consist merely in the transport of these electrons through the conducting bodies.

In order to show the beauty and precision with which these multiple relationships stand out in all experiments of this kind, a table corresponding to much more precise measurements than those given heretofore is here introduced (Table VI). The times of fall and rise shown in the first and second columns were taken with a Hipp chronoscope reading to one-thousandths of a second. The third column gives the reciprocals of these times. These are used in place of the velocities  $v_2$  in the field, since distance of fall and rise is always the same. The fourth column gives the successive changes in speed due to the capture of ions. These also are expressed merely as time reciprocals.

For reasons which will be explained in the next section, each one of these changes may correspond to the capture of not merely one but of several distinct ions. The numbers in the fifth column represent simply the small integer by which it is found that the numbers in the fourth column must be divided in order to obtain the numbers in the sixth column. These [numbers in the sixth column] will be seen to be exactly alike within the limits of error of the experiment. The mean value at the bottom of the sixth column represents, then, the smallest charge ever caught from the air, that is, it is the elementary *ionic* charge. The seventh column gives the successive values of  $v_1 + v_2$  expressed as reciprocal times. These numbers, then, represent the successive values of the *total* charge carried by the droplet. The eighth column gives the integers by which

<sup>7</sup>[The table entries are given as published; but two values are erroneous. In the fourth column, .03874 should be .03794. On the same line in the sixth column, .005401 should be .005420. These errors do not significantly affect the results.]

<sup>8</sup>[The value presently accepted is  $4.802 \times 10^{-10}$  statcoulomb.]

TABLE VI<sup>7</sup>

$t_g$ Sec.	$t_F$ Sec.	$\frac{1}{t_F}$	$\frac{1}{t'_F} - \frac{1}{t_F}$	$n'$	$\frac{1}{n'} \left( \frac{1}{t'_F} - \frac{1}{t_F} \right)$	$\frac{1}{t_g} + \frac{1}{t_F}$	$n$	$\frac{1}{n} \left( \frac{1}{t_g} + \frac{1}{t_F} \right)$
11.848	80.708	.01236					.09655	18.005366
11.890	22.366				.03234	6.005390		
11.908	22.390	.04470					.12887	24.005371
11.904	22.368				.03751	7.005358		
11.882	140.565	.007192					.09138	17.005375
11.906	79.600	.01254					.09673	18.005374
11.838	34.748				.01616	3.005387		
11.816	34.762	.02870					.11289	21.005376
11.776	34.846							
11.840	29.286						.11833	22.005379
11.904	29.236	.03414						
11.870	137.308	.007268			.026872	5.005375		
11.952	34.638	.02884			.021572	4.005393		
11.860					.01623	3.005410		
11.846	22.104	.04507					.11303	21.005382
11.912	22.268				.04307	8.005384		
11.910	500.1	.002000			.04879	9.005421		
11.918	19.704						.08619	16.005387
11.870	19.668	.05079					.13498	25.005399
11.888	77.630				.03874	7.005401		
11.894	77.806	.01285					.09704	18.005390
11.878	42.302	.02364			.01079	2.005395		
11.880				Means	.005386			.005384

Duration of exp. = 45 min.  
 Plate distance = 16 mm.  
 Fall distance = 10.21 mm.  
 Initial volts = 5,088.8  
 Final volts = 5,081.2  
 Temperature = 22.82°C.

Pressure = 75.62 cm.  
 Oil density = .9199  
 Air viscosity =  $1,824 \times 10^{-7}$  [poise]  
 Radius ( $a$ ) = .000276 cm.  
 $l/a$  [mean free path  $\div a$ ] = .034  
 Speed of fall = .08584 cm./sec.

$$e_i = 4.991 \times 10^{-10} [\text{statcoulomb}]^8$$

the numbers in the seventh column must be divided to obtain the numbers in the last column. These [numbers in the last column] also will be seen to be invariable. The mean at the bottom of the last column represents, then, *the electrical unit out of which the frictional charge on the droplet was built up, and it is seen to be identical with the ionic charge represented by the number at the bottom of the sixth column.*

It may be of interest to introduce one further table (Table VII) arranged in a slightly different way to show how infallibly the atomic structure of electricity follows from experiments like those under consideration.

TABLE VII

$n$	$4.917 \times n$	Observed Charge	$n$	$4.917 \times n$	Observed Charge
1	4.917	...	10	49.17	49.41
2	9.834	...	11	54.09	53.91
3	14.75	...	12	59.00	59.12
4	19.66	19.66	13	63.92	63.68
5	24.59	24.60	14	68.84	68.65
6	29.50	29.62	15	73.75	...
7	34.42	34.47	16	78.67	78.34
8	39.34	39.38	17	83.59	83.22
9	44.25	44.42	18	88.51	...

In this table  $4.917$  is merely a number obtained precisely as above from the change in speed due to the capture of ions and one which is proportional in this experiment to the ionic charge. The column headed  $4.917 \times n$  contains simply the whole series of exact multiples of this number from 1 to 18. The column headed "Observed Charge" gives the successive observed values of  $(v_1 + v_2)$ . It will be seen that during the time of observation, about four hours, this drop carried all possible multiples of the elementary charge from 4 to 18, save only 15. *No more exact or more consistent multiple relationship is found in the data which chemists have amassed on the combining powers of the elements and on which the atomic theory of matter rests than is found in the foregoing numbers.*

Such tables as these—and scores of them could be given—place beyond all question the view that an electrical charge wherever it is found, whether on an insulator or a conductor, whether in electrolytes or in metals, has a definite granular structure, that it consists of an exact number of specks of electricity (electrons) all exactly alike, which in static phenomena are scattered over the surface of the charged body and in current phenomena are drifting along the conductor. Instead of giving up, as Maxwell thought we should some day do, the "provisional hypothesis of molecular charges," we find ourselves obliged to make all our interpretations of electrical phenomena, *metallic as well as electrolytic*, in terms of it.

### III. Mechanism of Change of Charge of a Drop

All of the changes of charge shown in Table IV were spontaneous changes, and it has been assumed that all of these changes were produced by the capture of ions from the air. When a negative drop suddenly increases its speed in the field, that is, takes on a larger charge of its own kind than it has been carrying, there seems to be no other conceivable way in which the change can be produced. But when the charge suddenly decreases there is no a priori reason for thinking that the change may not be due as well to the direct loss of a portion of the charge as to the neutralization of this same amount of electricity by the capture of a charge of opposite sign. That, however, the changes do actually occur, when no X-rays or radioactive rays are passing between the plates,<sup>9</sup> only by the capture of ions from the air, was rendered probable by the fact that drops not too

<sup>9</sup>[As he elsewhere explains, Millikan repeatedly directed x-rays through the chamber or brought radioactive material into proximity with it. These measures would greatly accelerate the formation of ions in the air and so increase the chances of capturing one. But since they might also, by the same token, directly affect the charge carried by a droplet, Millikan considers only those changes that occur in the absence of such external influences.]

heavily charged showed the same tendency on the whole to increase as to decrease in charge. This should not have been the case if there were two causes tending to decrease the charge, namely, direct loss and the capture of opposite ions, as against one tending to increase it, namely, capture of like ions. The matter was very convincingly settled, however, by making observations when the gas pressures were as low as 2 or 3 mm. of mercury. Since the number of ions present in a gas is in general proportional to the pressure,<sup>10</sup> spontaneous changes in charge should almost never occur at these low pressures; in fact, it was found that drops could be held for hours at a time without changing. The frequency with which the changes occur decreases regularly with the pressure, as it should if the changes are due to the capture of ions. For the number of ions formed by a given ionizing agent must vary directly as the pressure.

Again, the changes do not, in general, occur when the electrical field is on, for then the ions are driven instantly to the plates as soon as formed, at a speed of, say, 10,000 cm per second, and so do not have any opportunity to accumulate in the space between them. When the field is off, however, they do so accumulate until, in ordinary air, they reach the number of, say, 20,000 per cubic centimeter. These ions, being endowed with the kinetic energy of agitation characteristic of the temperature, wander rapidly through the gas and become a part of the drop as soon as they impinge upon it. It was thus that all the changes recorded in Table IV took place.

\* \* \*

### COMMENT "WEIGHING" THE OIL DROP

As Millikan shows in his Table V, the two equations

$$\frac{v_1}{v_2} = \frac{mg}{F e_n - mg} \quad \text{or} \quad e_n = \frac{mg}{F v_1} (v_1 + v_2) \quad (9)$$

and

$$e_i = e_{n'} - e_n = \frac{mg}{F v_1} (v'_2 - v_2) \quad (10)$$

suffice to determine *relative* values for  $e_n$  (total charge on an oil drop) and  $e_i$  (charge of a captured ion), using nothing more than stopwatch measurements on the motion of the drop. The equations will determine *exact* values for those charges as well; but only if he can evaluate  $mg$ , the "effective" weight of the drop in a buoyant medium, which we have already expressed above as

$$mg = V(\sigma - \rho)g$$

or, assuming the drop to be a sphere of radius  $a$ ,

$$mg = \frac{4\pi a^3}{3} (\sigma - \rho)g. \quad (3.6)$$

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<sup>10</sup>[That the number of molecules present in a gas is strictly proportional to the pressure, is an element in Avogadro's hypothesis. A relatively constant fraction of these molecules will become ionized under given conditions independent of pressure; hence the proportionality cited.]

Millikan has no way to measure this quantity directly; but reasoning from the viscous (resistive) properties of the medium, air, he is able to devise an indirect measurement.

We have already derived in equation (3.3) an expression for the limiting velocity attained by a body that falls through a viscous medium:

$$v_1 = \frac{mg}{R} \quad (3.3)$$

where  $R$  is a so far unspecified proportionality constant. This constant is different for every different-sized oil drop. However, Millikan was able to relate it to a general, measurable quantity. The *viscosity* of a fluid is its resistance to being passed through, as we mentioned, or to flowing past something. This property can be more precisely defined and measured by various procedures.<sup>11</sup> Accurate tables of the viscosity of air were available to Millikan. In addition, *Stokes's Law* (derived by George Stokes in 1845) applies this property to the case of a smooth sphere moving through a fluid. Millikan assumed that his oil drops were spheres; with air viscosity  $\eta$  and drop radius  $a$ , Stokes's Law gives  $R = 6\pi\eta a$ .<sup>12</sup> Substituting into Eq. 3.3) gave Millikan

$$v_1 = \frac{mg}{6\pi\eta a}. \quad (3.7)$$

He then eliminated  $a$  between equations (3.6) and (3.7) to obtain

$$m = \frac{4\pi}{3}(\sigma - \rho) \left( \frac{mg}{6\pi\eta v_1} \right)^3,$$

from which

$$\left( \frac{mg}{v_1} \right)^2 = \frac{3 \cdot 6^3 \pi^2 \eta^3 v_1}{4g(\sigma - \rho)}.$$

Hence for the coefficient  $mg/Fv_1$  in Millikan's equations (9) and (10) we have

$$\frac{mg}{Fv_1} = \left( \frac{9\pi}{F} \sqrt{\frac{2\eta^3}{g(\sigma - \rho)}} \right) \cdot \sqrt{v_1} \quad (3.8)$$

which is sufficient to evaluate  $e_n$  and  $e_i$ .

## EXPERIMENT: MEASUREMENT OF THE “ATOM OF CHARGE”

We use the Pasco oil-drop apparatus, which is similar to Millikan's, only far smaller. In addition, the viewing telescope and associated illumination are integrally mounted. Make sure that the apparatus is level, the telescope illumination *on*, and the high voltage *off*. If the following preliminary adjustments have not already been made by the laboratory assistant, perform them now:

*Focus the telescope:* Remove the chamber housing, lid, and droplet hole mask, as illustrated in the drawing. Unscrew the focusing wire from its storage position and carefully insert it into the droplet hole in the center of the upper plate. Adjust the Reticle Focusing Ring on the telescope to bring the viewing reticle into focus. Adjust

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<sup>11</sup>The details are beyond our scope.

<sup>12</sup>Again, we cannot follow the details.

the Droplet Focusing Ring to bring the wire image into sharp focus. When the telescope is focused, each minor reticle division corresponds to a droplet fall distance of .01 cm; each major division to .05 cm.

*Focus the lamp:* Turn the lamp's Horizontal Adjustment to bring the right edge of the wire into highest contrast compared to the center of the wire. Turn the Vertical Adjustment to direct the brightest light onto the part of the wire that is within the reticle. Remove and return the focusing wire to its storage position and reassemble the chamber.

*Adjust the plate voltage:* Connect the high-voltage supply. Turn the cable-mounted plate switch to the GROUNDED position. Adjust the supply to deliver between 400 and 500 volts, and record the voltage. The apparatus is now ready for use.

Begin by introducing oil droplets into the chamber. Move the vent lever to the Spray Droplets position; this will permit air to escape from the chamber as the oil spray enters. The atomizer nozzle should be turned vertically downward. After one or two test squeezes to make sure oil sprays correctly, point the nozzle into the spray hole in the lid of the chamber.

While looking through the telescope, give the atomizer *one quick squeeze*, followed immediately by *one slow squeeze* to create a vertical downdraft. When you see a shower of drops through the telescope, move the vent lever to the OFF position.<sup>13</sup>

With a number of drops in view, observe that different drops fall with noticeably different speeds. This illustrates the relation expressed in equation (3.3)—heavier drops fall proportionately faster than lighter ones. Pay attention to those droplets that fall *slowly*—about 10–25 seconds to travel the distance between major reticle lines (.05 cm).

Energizing the plates will reveal which drops bear a charge, and whether the applied voltage is in the right direction to *reverse* a drop's falling motion (which is desired) or not. Repeatedly move the cable-mounted plate switch to its + or – positions. When a droplet is found that can be driven back towards the upper plate by applying the voltage, try to keep it in capture by alternately applying and removing that voltage.



### Measurements on a single drop

Execution of the experiment will require two people, one to observe the drop and operate the stopwatch, the other to read the watch and record the timed intervals. It is usually best to time successive rising and falling transits of the droplet over any *major* (.05 cm) division on the telescope's viewing reticle—ten to twenty measurements in each direction are desirable. Do not raise or lower the plate voltage adjustment once

<sup>13</sup>Avoid immoderate use of the atomizer. The object is to introduce a small number of drops, from which a single drop can be chosen. If a large, bright cloud appears in the viewing area, spraying has been excessive. You can try waiting a few minutes to see if the drops settle out of view, but most likely the chamber will have to be disassembled and cleaned.

you begin timing a drop. Record the fall times and rise times in separate columns. A series of measurements of these times, *all performed on the same drop*, will enable you to construct a table like Millikan's Table VI. Here is an example (figures are from 1997):

	$d = 0.5\text{cm}$		$d = 0.5\text{cm}$	Charge on ion			Frictional charge		
$t_g$	$v_1 (= d/t_g)$ (cm/sec)	$t_F$	$v_2 (= d/t_F)$ (cm/sec)	$(v'_2 - v_2)$	$n'$	$\frac{v'_2 - v_2}{n'}$	$v_1 + v_2$	$n$	$\frac{v_1 + v_2}{n}$
18.2	.00286	3.8	0.01316				0.01602	3	.00534
18.6	<i>avr</i>			.00470	1	.00470			
19.2		2.8	.01786						
18.0				.01561	3	.00520			
17.2		22.2	.00225						
15.4				.00544	1	.00544			
16.7		6.5	.00769						
18.0				.00541	1	.00541			
15.4		21.9	.00228						
17.3				.01123	2	.00562			
<u>18.4</u>		3.7	.01351						
17.5							.00527		
<i>avr</i>							<i>avr</i>		.00534

### Measurements on Multiple Drops

Although it would be convenient to make all measurements on a single droplet, it is seldom possible to do so; for it proves extremely difficult to hold any one drop in play for long periods of time. But droplets of the same material differ from one another only in mass. Therefore—see Equation 3.8 above—if the electric field intensity  $F$  is not changed, the coefficient in Millikan's equations (9) and (10) will vary, from drop to drop, only in proportion to  $\sqrt{v_1}$ . You may therefore combine data from different drops by tabulating and comparing

$$\sqrt{v_1}(v_1 + v_2) \quad \text{and} \quad \sqrt{v_1}(v'_2 - v_2)$$

instead of  $(v_1 + v_2)$  and  $(v'_2 - v_2)$  directly. Here is an example of such a table (the figures are from 1983):

Obsvd. $t_g$	$v_1$ (i.e., $1/t_g$ )	Obsvd. $t_F$	$v_2$ (i.e., $1/t_F$ )	$(v'_2 - v_2)$	$\sqrt{v_1}(v'_2 - v_2)$
7.2 sec	.1389	2.1 sec	.4762	.1984	.0739
		3.6	.2778	.1978	.0737
		12.5	0.0800		
5.8 sec	.1724	1.9	.5263	.3792	.1575
		6.8	.1471	.8529	.3541
		1.0	1.000	.7059	.2931
		3.4	.2941		

The table entries reflect measurements on two different droplets. In the sixth column the observed changes in rise speed are multiplied by  $\sqrt{v_1}$  as explained above. The resulting quantities are very nearly integral multiples of about .076. This trial, therefore, would indicate the existence of a fundamental ionic charge, with a relative value of about .076.

### Enhancing Ionization

It is hoped that the droplet will acquire an ion during one of its falls, as is indeed illustrated in the foregoing chart. Capture of an ion does not change the drop's falling velocity, but it will change the drop's rising velocity when the plate voltage is next applied. However, should you find that your droplet has not caught an ion after 10–20 successive rises, move the vent lever to the IONIZATION ON position for a few seconds during the next fall period. That will expose the air in the chamber to a low-level radioactive thorium source, thus increasing the number of ionized particles in the air and multiplying the chances for the falling drop to encounter an ion. Repeat the exposure if again the drop fails to capture an ion after 10-20 measurements, and continue for as long as the droplet can be held in play. It is desirable to measure as many different charges on a single drop as possible.

### Frictional Charge and Ionic Charge

As Millikan explains, the *initial* charge on a droplet, prior to the capture of an ion, must have been acquired by friction during the spraying process. In the foregoing chart it is assumed that the first measurement made on the drop reflects this initial frictional charge. While that may be a reasonable assumption provided the first measurement was made *soon* after spraying, and the observed frequency of ion capture by a drop is not high, remember that it is *only* an assumption—the drop may have already picked up an ion by the time we first measure it. That is especially to be suspected when, as in this example, the apparent number  $n$  of unit charges on the drop is only 3—a number so small it could as easily reflect ion capture as frictional electrification.

If it is desired to measure *frictional charges specifically*, do not use the ionization source—we want to minimize the chances of capturing an ion. As soon after spraying as possible, try to select a drop whose rising velocity is noticeably *faster* than others. Rapid rising indicates a high charge, which is more likely to have been frictionally acquired. As before, time the drop for 10–20 transits, or until it appears to have encountered an ion. Let the drop escape; spray again, and repeat the measurements on another drop.

### Calculation of the Fundamental Charge

The stopwatch measurements illustrated in the previous chart suffice to determine values of and which, as Millikan's equations (9) and (10) make clear, are proportional to the *initial frictional charge on a drop* and the *charge on a captured ion*, respectively. But in order to calculate exact values of these charges, not just relative ones, we must evaluate the coefficient that appears in those equations. By our equation 3.8 above, the coefficient can be calculated from the following quantities:

- (a) the velocity  $v_1$  of the falling drop. This you have already measured; just remember to cite the correct value for each different drop. (Remember to average and to take the square root.)
- (b) the electric field intensity  $F$  between the plates. To compare our results numerically with Millikan's we will calculate this in e.s.u., so we must express the potential difference between the plates in e.s.u., i.e. in *statvolts*. Our meters give volts and 1 volt = 1/300 statvolts, so *the voltmeter reading*

must be divided by 300. The plate separation is 0.76 cm, unless a different value is labeled on the side of your apparatus. Then the voltage in stat-volts divided by the plate separation in cm will give electric field intensity in e.s.u.<sup>14</sup>

- (c) the density of the oil,  $\sigma$ . We use Squibb #5597 non-volatile mineral oil, for which  $\sigma = .886 \text{ g/cm}^3$ .
- (d) the density of the air,  $\rho$ , obtained from the graph below. You will have to note the temperature of the air in the chamber and the barometric pressure in the room. Typical values for  $\rho$  are about  $.0012 \text{ g/cm}^3$ .
- (e) the viscosity of the air,  $\eta$ , obtained from the graph below. Typical values for  $\eta$  are around  $1825 \times 10^{-7}$  poise (gm/cm-sec).
- (f) the acceleration of gravity,  $g = 980 \text{ cm/sec}^2$ .



### Remarks on Avogadro's Number

As Millikan himself pointed out, mere *measurement* of the fundamental charge is not necessarily, in itself, the most important fruit of this experiment. Of far greater consequence, perhaps, is the demonstration that the same "electron" lies at the root of both *static electricity* (the frictional charge on the drop) and *chemical activity* (the ionic charge). This is strong, even conclusive evidence, for the interpretation of chemical power as being fundamentally electrical, for Millikan's results indicate that the *fundamental unit of charge* corresponds also to the *fundamental unit of chemical combining power*. If the electron has indeed this dual significance, then Millikan's measurement of the electron charge will at last permit accurate calculation of that theoretically pivotal but experi-

<sup>14</sup>See Appendix for an explanation of the units and for the relation between  $F$  and the potential difference.

mentally elusive quantity, *Avogadro's number*—the number of atoms in a gram-atomic weight of any element.<sup>15</sup>

Recall that the “equivalent weight” of an element is that much of it, measured on the scale of atomic weights with Hydrogen = 1, which exercises *one unit* of chemical combining power. But the combining power of one hydrogen atom is taken as the unit for chemical combining power generally; thus for hydrogen and all atoms equal to hydrogen in their combining power, the atomic weight and the equivalent weight are the same.<sup>16</sup>

Now if one unit of chemical combining power actually means *one electron of electric charge*, then one gram-atomic weight of hydrogen will exercise the cumulative charge of Avogadro's number of electrons, which is

$$N_0 \times e,$$

where  $N_0$  denotes Avogadro's number and  $e$  is the electron charge. Now the above is also the total charge associated with a gram-equivalent weight of hydrogen, since for it the gram-atomic weight is equal to the gram-equivalent weight. But we found in electrolysis that the total charge associated with liberation or transfer of one gram-equivalent weight of *any* element is 96,500 coulombs, which equals  $2.895 \times 10^{14}$  statcoulombs; hence we may write

$$2.895 \times 10^{14} \text{ statC} = N_0 \times e$$

While Millikan has shown that (modern value):

$$e = 4.802 \times 10^{-10} \text{ statC}$$

Thus we have

$$N_0 = \text{Avogrado's number} = \frac{2.895 \times 10^{14}}{4.802 \times 10^{-10}} = 6.028 \times 10^{23}.$$

(Other, more recent, determinations yield  $6.023 \times 10^{23}$ .)

### Weighing and Sizing Elementary Particles

Determination of Avogadro's number puts us in a position to “weigh all the atoms”; for if there are  $N_0$  atoms in a gram-atomic weight of an element, then each atom must weigh  $1/N_0$  of the gram-atomic weight. For example, a gram-atomic weight of hydrogen weighs 1.008 grams. Then a single hydrogen atom, for example, must weigh

$$1.008 \div (6.023 \times 10^{23}) = 1.674 \times 10^{-24} \text{ g}$$

and similarly for all the other atoms.

In Chapter II of *The Electron* Millikan pointed out that the term “electron” had been first introduced in 1891 as a name for the supposed “natural unit of electricity,” namely,

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<sup>15</sup>There had been earlier efforts to estimate Avogadro's number, predating Millikan's oil-drop measurements; Einstein cites one of his own in his paper that appears in Chapter VI below. But the most reliable determinations of Avogadro's number and many other constants all depend on accurate knowledge of the electron charge (cf. *The Electron*, Chapter X).

<sup>16</sup>Chemical combining power is commonly expressed in units of “valence”; hydrogen and all atoms equivalent to it are said to be *univalent* atoms.

that quantity of electricity exhibited by a hydrogen ion or any other univalent ion. Thus it denoted simply a *definite quantity of electricity* without reference to any mass or inertia which might be associated with it. It is clear that Millikan's oil-drop experiment has proved the existence of "electron" in this original sense.

But measurements by Thomson and others of the charge-to-mass ratio of ions in both gases and liquids strongly implicated Thomson's *cathode-ray corpuscle* as the essential constituent whereby atoms acquire either an excess or deficiency of negative charge to become ions.<sup>17</sup> This implies that *the charge borne by each cathode ray corpuscle must be the very quantity of charge that had been termed "electron."* As a result, Millikan explains, the word "electron" gradually changed its meaning to become synonymous with the cathode-ray corpuscle: a particle having definite mass as well as charge, a constituent not only of cathode rays but of atoms themselves.<sup>18</sup> Since the electron (in the new sense of *particle*) has the charge-to-mass ratio that was determined for cathode-rays, and has, on the other hand, the quantity of charge that is disclosed in Millikan's experiment, we are able to calculate its mass, to "weigh" the electron itself.

We have, from the cathode rays,

$$m/e = .5685 \times 10^{-7} \text{ g}/\text{abC} = 1.895 \times 10^{-18} \text{ g}/\text{statC}.$$

Then, since the electron charge is

$$e = 4.802 \times 10^{-10} \text{ statC},$$

we may calculate

$$m = 1.895 \times 10^{-18} \times 4.802 \times 10^{-10} = .9099 \times 10^{-27} \text{ g}.$$

Hence the electron will be almost 1840 times lighter than the hydrogen atom. That an electron weighs such a slight fraction of even the lightest atom will prove important in formulating a conception of the atom's structure, as discussed in Rutherford's paper which follows.

### "Sizing" an Atom

Another magnitude interesting in itself and also important in Rutherford's paper is the approximate *size* of an atom. Using Avogadro's Number this is easy to calculate for elemental solids.

Take gold, which is what Rutherford will be dealing with. The density of gold is 19.3 g/cm<sup>3</sup>, while its gram-atomic weight is 197. Therefore there are .098 gram equivalents in a cubic centimeter of gold. But since there are  $N_0$  atoms in a gram-atomic weight of an element, we can now say that there are  $.098 \times (6.023 \times 10^{23})$ , or  $5.90 \times 10^{22}$ , atoms in a cubic centimeter of gold. Each atom thus occupies a volume of  $1/(5.90 \times 10^{22}) = 1.69 \times 10^{-23}$  cubic centimeters. The cube root of this,  $2.57 \times 10^{-8}$  cm, will give the side

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<sup>17</sup>See note 5 above; Millikan devotes the whole of his Chapter II to this very interesting story.

<sup>18</sup>Millikan views this alteration of usage with real distress: "It is unfortunate that modern writers have not been more careful to retain the original significance of ['electron'], for it is obvious that a word is needed which denotes merely the elementary unit of electricity and has no implication as to where that unit is found, to what it is attached, with what inertia it is associated, or whether it is positive or negative in sign."

of a cube of this volume. Let us assume that gold atoms are spherical and that in solid gold they fit together in a more or less cubical pattern. Then half of  $2.57 \times 10^{-8}$  cm, i.e.

$$1.285 \times 10^{-8} \text{ cm},$$

is a reasonable rough estimate for the radius of a gold atom. Rutherford implicitly adopts this size estimate as he analyses how particles that are *much smaller* than this interact with gold atoms.



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# THE SCATTERING OF $\alpha$ AND $\beta$ PARTICLES BY MATTER AND THE STRUCTURE OF THE ATOM

ERNEST RUTHERFORD

## REMARKS

We have seen how the “electron” may be understood as a charged particle, bearing the fundamental quantity of negative charge, with a fixed mass that is far smaller than the lightest of atoms. The chemical or atomic analysis of matter is thus extended to disclose the prospect of subatomic constituents having both mass and charge.

Accordingly, physics is challenged to interpret the chemical elements as more or less complex systems of the primordial constituents. How then, in the atom, are these constituents distributed with respect to one another? In 1902 Lord Kelvin proposed a model of an electrically neutral atom containing both positive and negative charge. The positive charge, and most of the atom’s mass, were in this view distributed continuously throughout the spherical volume of the atom; while the electrons, which carry negative charge, were embedded in the sphere of positive charge. Thomson proceeded to investigate this arrangement both mathematically and experimentally, and it was eventually named after him. The strongest argument in favor of the Thomson model was that it seemed to explain the permanence and stability of atoms: Because the electrons were everywhere surrounded by equal quantities of positive charge the atom would be electrically neutral in all its parts. A great deal of energy would then be required to disturb its equilibrium.

Rutherford initially accepted the essential correctness of Thomson’s scheme and set out to verify it experimentally. He and his associates Geiger and Marsden proposed to bombard individual gold atoms (in fine gold foils only about 2000 atoms in thickness) with streams of a radioactive by-product called *alpha particles*. Two kinds of particles, distinguished as *alpha* and *beta*, are emitted spontaneously at very high speeds by radium and other radioactive materials; beta particles were subsequently identified as high-speed electrons, while the alpha particles proved to be doubly-charged Helium ions.<sup>1</sup> Because of their speed and mass alpha-particles made suitable “probes” with which to explore the interior structure of atoms. By studying the deflections such particles suffered in passing through gold atoms, Rutherford expected to obtain a more detailed picture consistent with the Thomson model.

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<sup>1</sup>That is, Helium atoms bearing a charge of  $+2e$ . A Helium *ion* is very anomalous from the viewpoint of chemistry, for on the electro-chemical interpretation an ion is a *chemically active atom*. But Helium is never chemically active! The process that produces alpha-particles, then, must involve aspects of the atomic structure that chemistry never touches. Furthermore, from measurements of their mean free path it looked as though  $\alpha$ -particles were *far smaller* than neutral Helium atoms. It takes Rutherford’s theory itself to give an explanation for this.

The experiments yielded results that were wholly unexpected. Since the highest concentrations of mass in the Thomson model are the *electrons*; and since these are far lighter than alpha particles and moreover relatively free to move, it was not to be imagined that a gold atom should be capable of disturbing the path of an alpha particle by more than a fraction of a degree. But in fact, prodigious deviations were observed, some greater than  $90^\circ$ . And these deflections occurred, moreover, with a frequency some 104596 times greater than the probability as calculated according to Thomson's arrangement. Rutherford, later in life, expressed his astonishment as follows:

It was quite the most incredible event that ever happened to me in my whole life. It was as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you. On consideration I realized that the scattering backwards must be the result of a single collision, and when I made the calculation I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a single nucleus. It was then that I had the idea of an atom with a minute massive center carrying a charge.

### A Note on Probability<sup>2</sup>

A reader of Ernest Rutherford's famous paper *The Scattering of  $\alpha$  and  $\beta$  Particles by Matter and the Structure of the Atom*, which reports the discovery of the atomic nucleus, may be perplexed by a couple of expressions at the beginning of §3. An explanation follows.



*An alpha particle and its presumptive path through a section of gold foil. You should imagine the atomic centers as being more randomly arrayed.*

We are playing a game of shooting tiny particles at a thin screen of large spherical atoms, in the direction normal (perpendicular) to its surface. With very few exceptions, the particles pass straight through the screen; for our present purpose we assume that all do. Having chosen a distance  $d$ , we say that a particle *hits* an atom if it comes within that distance of the center of the atom. For a given shot, our *score* is the number of atoms hit by the particle. Each shot is taken in the same way, and the shots are independent of one another—the score for one shot has no influence on the score for another.

When we take a number of shots, our *average score* means the result of dividing the total of our scores by the number of shots. For example, if we score successively 2, 0, 5, 2, 0, 2, 3, our total score is 14 and the number of shots is 7, so our average score is 2. If

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<sup>2</sup>Note by Michael Comenetz

we score successively 1, 0, 0, 0, 1, 0, 1, 0, our total score is 3 and the number of shots is 8, so our average score is 0.375.

Since the shots are alike and independent, it is reasonable to suppose that as we take more and more of them, our average score will approach some definite value as a limit. The limiting value can be called our *expected score*, or *expectation*, because when we play the game, we expect our scores to cluster around that value, and our average score to tend towards it. The expectation, which we call  $e$ , will be well approximated by the average score we get when we take a large number of shots.

In order to estimate the expectation, let us call the thickness of the screen  $t$ , and the density of atoms within it  $N$ . The latter quantity means the average number of atoms per unit volume; that is the same as the average number of centers of atoms per unit volume.

The question, "On average, how many atoms does a particle hit?" is equivalent to the question, "On average, how many atom-centers lie within distance  $d$  of the path of the particle?" and therefore also to the question, "On average, how many atom-centers lie within the right circular cylinder of radius  $d$  whose axis is the path of the particle through the screen, and whose height is the thickness  $t$  of the screen?"

The volume of such a cylinder—that is, the number of unit volumes it contains—is the area of its base, which is  $\pi d^2$ , times its height  $t$ , or  $\pi d^2 t$ . It follows that the average number of atom-centers in such a cylinder is  $n \times \pi d^2 t = \pi d^2 n t$ . This is then our expectation:  $E = \pi d^2 n t$

We now apply this result to two special cases.

**Case 1.** Let  $d$  be the radius  $R$  of an atom. In this case, *hitting* an atom has the ordinary sense of coming into contact with it. The expectation  $e$  is  $\pi R^2 n t$ . This is what Rutherford means by saying that "the number of collisions of the particle with the atom of radius  $R$  is  $\pi R^2 n t$ ." The value of  $e$  is of the order of the number of atoms spanning the thickness  $t$ —a few thousand, for a gold-foil screen.

**Case 2.** Let  $d$  be a distance  $p$  much smaller than  $R$ , a thousand or ten thousand times smaller. In this case it is very difficult to *hit* an atom—so difficult, that we may assume that no particle hits more than one. Then for each shot our score is 0 or 1, and the expectation  $E = \pi p^2 n t$  has a value between 0 and 1.

Since in this case there are only two possibilities for each shot, either it hits or it doesn't, we can speak of the *probability*  $p$  that a given shot will hit an atom, understanding by this the proportion of hits, or average score, obtained when a great many shots are taken (more precisely, its limiting value as the number of shots increases)—that is, the expectation:  $p = e$ . If we assert, for example, that  $p = 0.20$ , or 20%, we expect that out of, say, 1000 shots, there will be about 200 hits—that the average score for those 1000 shots will be about  $200/1000 = 0.20$ , that about 20% of them will be hits. Hence Rutherford writes, "The probability ... of entering an atom within distance  $p$  of its centre is given by ...  $\pi p^2 n t$ ."<sup>3</sup>

## Final Thoughts

1. The assumption in the first paragraph of the explanation is justified as follows. A particle deviates appreciably from a straight path only if it hits an atom for very small  $d$ , as in Case 2. Even if so deflected, it is very unlikely to hit another atom, because  $d$

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<sup>3</sup>See page 67.

is much less than  $R$  and  $t$  is very small. Thus only the possibility of a first encounter along a straight path need be admitted.

2. One may wonder why probability enters the picture only with Case 2. Shouldn't the general case somehow involve probability? It does. Let  $N$  be the greatest number of atoms the particle can possibly hit. Let  $p_0$  be the probability that it hits no atoms,  $p_1$  the probability that it hits exactly one,  $p_2$  the probability that it hits exactly two,  $\dots$ ,  $P_N$  the probability that it hits exactly  $N$ . Then  $p_0 + p_1 + p_2 + \dots + P_N = 1$  and  $p_0 \cdot 0 + p_1 \cdot 1 + p_2 \cdot 2 + \dots + P_N \cdot N = e$ . In Case 2, the only non-zero probabilities are  $p_0$  and  $p_1$ , hence  $p_1 = e$ .

3. The intuitive understanding of expectation as the limit of the average score rests on the assumption stated in the third paragraph, that the limit exists. In the mathematical theory of probability a different approach is taken, and the limit assertion becomes a theorem, or rather a class of theorems (*laws of large numbers*).

## THE SCATTERING OF $\alpha$ AND $\beta$ PARTICLES BY MATTER AND THE STRUCTURE OF THE ATOM<sup>4</sup>

ERNEST RUTHERFORD

§1. It is well known that the  $\alpha$  and  $\beta$  particles suffer deflexions from their rectilinear paths by encounters with atoms of matter. This scattering is far more marked for the  $\beta$  than for the  $\alpha$  particle on account of the much smaller momentum and energy of the former particle. There seems to be no doubt that such swiftly moving particles pass through the atoms in their path, and that the deflexions observed are due to the strong electric field traversed within the atomic system. It has generally been supposed that the scattering of a pencil of  $\alpha$  or  $\beta$  rays in passing through a thin plate of matter is the result of a multitude of small scatterings by the atoms of matter traversed. The observations, however, of Geiger and Marsden on the scattering of  $\alpha$  rays indicate that some of the  $\alpha$  particles must suffer a deflection of more than a right angle in a single encounter. They found, for example, that a small fraction of the incident  $\alpha$  particles, about 1 in 20,000, were turned through an average angle of  $90^\circ$  in passing through a layer of gold-foil about .00004 cm. thick, which was equivalent in stopping-power of the  $\alpha$  particle to 1.6 millimetres of air. Geiger showed later that the most probable angle of deflection for a pencil of  $\alpha$  particles traversing a gold-foil of this thickness was about  $0^\circ.87$ .<sup>5</sup> A simple calculation based on the theory of probabilities shows that the chance of an  $\alpha$  particle being deflected through  $90^\circ$  [as the cumulative result of multiple encounters] is vanishingly small.<sup>6</sup> In addition, it will be seen later that the distribution of the  $\alpha$  particles for various angles of large deflection does not follow the probability law to be expected if such large deflexions are made up of a large number of small deviations. It seems reasonable to suppose that the deflection through a large angle is due to a single atomic encounter, for the chance of a second encounter of a kind to produce a large deflection must in most cases be exceedingly small. A simple

<sup>4</sup>[*Philosophical Magazine* 211 (1911), 669–688.]

<sup>5</sup>[That is, particles passing through the foil were deflected within, say,  $.1^\circ$  of  $0.87^\circ$  more often than within  $.1^\circ$  of any other angle.]

<sup>6</sup>[If  $\theta_0$  is the most probable angle of deflection resulting from many atomic encounters, a general theorem holds that the probability of obtaining a deflection angle of any other value  $\theta$  or greater is  $e^{-(\theta/\theta_0)^2}$ . Since Geiger has shown that  $\theta_0 = .87^\circ$ , the probability of obtaining  $\theta = 90^\circ$  will be or about  $10^{-4600}$ .]

calculation shows that the atom must be the seat of an intense electric field in order to produce such a large deflexion at a single encounter.

Recently Sir J. J. Thomson has put forward a theory to explain the scattering of electrified particles in passing through small thicknesses of matter. The atom is supposed to consist of a number  $N$  of negatively charged corpuscles, accompanied by an equal quantity of positive electricity uniformly distributed throughout a sphere. The deflexion of a negatively electrified particle in passing through the atom is ascribed to two causes—(1) the repulsion of the corpuscles distributed through the atom, and (2) the attraction of the positive electricity in the atom. The deflexion of the particle in passing through the atom is supposed to be small, while the average deflexion after a large number  $m$  of encounters was taken as  $\sqrt{m} \cdot \theta$ , where  $\theta$  is the average deflexion due to a single atom. It was shown that the number  $N$  of the electrons within the atom could be deduced from observations of the scattering of electrified particles. The accuracy of this theory of compound scattering was examined experimentally by Crowther in a later paper. His results apparently confirmed the main conclusions of the theory, and he deduced, on the assumption that the positive electricity was continuous, that the number of electrons in an atom was about three times its atomic weight.

The theory of Sir J. J. Thomson is based on the assumption that the scattering due to a single atomic encounter is small, and the particular structure assumed for the atom does not admit of a very large deflexion of an  $\alpha$  particle in traversing a single atom, unless it be supposed that the diameter of the sphere of positive electricity is minute compared with the diameter of the sphere of influence of the atom.

Since the  $\alpha$  and  $\beta$  particles traverse the atom, it should be possible from a close study of the nature of the deflexion to form some idea of the constitution of the atom to produce the effects observed. In fact, the scattering of high-speed charged particles by the atoms of matter is one of the most promising methods of attack of this problem. The development of the scintillation method<sup>7</sup> of counting single  $\alpha$  particles affords unusual advantages of investigation, and the researches of H. Geiger by this method have already added much to our knowledge of the scattering of  $\alpha$  rays by matter.

§2. We shall first examine theoretically single encounters<sup>8</sup> with an atom of simple structure, which is able to produce large deflexions of an  $\alpha$  particle, and then compare the deductions from the theory with the experimental data available.

Consider an atom which contains a charge  $\pm Ne$  at its centre surrounded by a sphere of electrification containing a charge  $\mp Ne$  supposed uniformly distributed throughout a sphere of radius  $R$ .  $e$  is the fundamental unit of charge, which in this paper is taken as  $4.65 \times 10^{-10}$  E.S. unit. We shall suppose that for distances [greater]<sup>9</sup> than  $10^{-12}$  cm. the central charge and also the charge on the  $\alpha$  particle may be supposed to be concentrated at a point. It will be shown that the main deductions from the theory are independent of whether the central charge is supposed to be positive or negative. For convenience, the sign will be assumed to be positive. The question of the stability of the atom proposed need not be considered at this stage, for this will obviously depend

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<sup>7</sup>[The *scintillation method*: an alpha-particle is made to strike a zinc sulphide screen, which then gives off a tiny flash of light. The flash is observed with a microscope, and the number of particles incident on any given area in a given time interval are thus counted.]

<sup>8</sup>The deviation of a particle through a considerable angle from an encounter with a single atom will in this paper be called "single" scattering. The deviation of a particle resulting from a multitude of small deviations will be termed "compound" scattering.

<sup>9</sup>[We here correct a typographical error in the original.]

upon the minute structure of the atom, and on the motion of the constituent charged parts.

In order to form some idea of the forces required to deflect an  $\alpha$  particle through a large angle, consider an atom containing a positive charge  $Ne$  at its centre, and surrounded by a distribution of negative electricity  $Ne$  uniformly distributed within a sphere of radius  $R$ . The electric [field]  $X$  and the potential  $V$  at a distance  $R$  from the centre of an atom, for a point inside the atom, are given by<sup>10</sup>

$$X = Ne \left( \frac{1}{r^2} - \frac{r}{R^3} \right)$$

[and]<sup>11</sup>

$$V = Ne \left( \frac{1}{r} - \frac{3}{2R} + \frac{r^2}{2R^3} \right).$$

Suppose an  $\alpha$  particle of mass  $m$  and velocity  $u$  and charge  $e$  shot directly towards the centre of the atom. It will be brought to rest at a distance  $b$  from the centre given by<sup>12</sup>

$$\frac{1}{2}mu^2 = NeE \left( \frac{1}{b} - \frac{3}{2R} + \frac{b^2}{2R^3} \right).$$

It will be seen that  $b$  is an important quantity in later calculations. Assuming that the central charge is  $100e$ , it can be calculated that the value of  $b$  for an  $\alpha$  particle of velocity  $2.09 \times 10^9$  cm. per second is about  $3.4 \times 10^{-12}$  cm. In this calculation  $b$  is supposed to be very small compared with  $R$ . Since  $R$  is supposed to be of the order of the radius of the atom, viz.  $10^{-8}$  cm., it is obvious that the  $\alpha$  particle before being turned back

<sup>10</sup>[Rutherford's actual expression is "electric force  $X$ ." But what he is actually calculating is the *intensity* of the force—the force per unit charge—and thus  $X$  really represents *electric field strength*. See App. II B below.]

The atom is assumed to contain  $N$  negative electrons evenly distributed throughout its volume and  $N$  positive charges concentrated in the nucleus. Thus the electric field within the atom at a distance  $r$  from the nucleus has two sources: (a) the nucleus, and (b) those electrons that are contained *within* radius  $r$ . (Electrons lying *beyond* radius  $r$  make no contribution to the field at  $r$ , for the electric field within any closed, charged surface is zero; compare the analogous case for gravitation, Newton's *Principia*, Book I, Prop. 70.)

Now (a) the electric field intensity due to the positive nucleus is  $Ne/r^2$ . And the negative charge contained within radius  $r$  is to  $Ne$  as the volume of the sphere of radius  $r$  is to the whole atom; hence that charge is  $-Ne(r^3/R^3)$ . It acts as though it were concentrated at the center (see *Principia*, Book I, Prop. 71); therefore (b) its contribution to the electric field intensity is  $-Ne(r^3/R^3)/r^2$  or  $-Ne(r/R^3)$ . The total electric field intensity  $X$  is the sum of (a) and (b), as in Rutherford's expression.]

<sup>11</sup>[To determine the electric potential we *integrate* the field strength  $X$  over distance (see Appendix II B, 269-71 below for a discussion of this), from  $s = r$  to  $s = R$  (it is not necessary to consider radii greater than  $R$  because, the atom as a whole being electrically neutral, there is no field beyond  $R$ ). Thus Rutherford's expression for  $V$  is the result of having evaluated the integral  $\int_r^R Ne(1/s^2 - s/R^3) ds$ .]

<sup>12</sup>[The work required to bring a positive charge  $e$  from infinity to a distance  $r$  from the center of the atom is given by the product  $VE$  of the charge and the electric potential at the distance  $r$ —again see Appendix II B. If this work is done at the expense of the incident particle's kinetic energy, the particle will be brought to rest (at distance  $b$  from the center) when the initial kinetic energy of the particle equals  $VE$ , that is, when

$$\frac{1}{2}mu^2 = VE = NeE \left( \frac{1}{b} - \frac{3}{2R} + \frac{b^2}{2R^3} \right).$$

penetrates so close to the central charge, that the field due to the uniform distribution of negative electricity may be neglected. In general, a simple calculation shows that for all deflexions greater than a degree, we may without sensible error suppose the deflexion due to the field of the central charge alone.<sup>13</sup> Possible single deviations due to the negative electricity, if distributed in the form of corpuscles, are not taken into account at this stage of the theory. It will be shown later that its effect is in general small compared with that due to the central field.



Figure 1

Consider the passage of a positive electrified particle close to the centre of an atom. Supposing that the velocity of the particle is not appreciably changed by its passage through the atom, the path of the particle under the influence of a repulsive force varying inversely as the square of the distance will be an hyperbola<sup>14</sup> with the centre of the atom S as the external focus. Suppose the particle to enter the atom in the direction PO [Fig. 1],<sup>15</sup> and that the direction of motion on escaping the atom is OP'. OP and OP'

<sup>13</sup>[Since Rutherford has concluded that  $b$  ( $\approx 10^{-12}$  cm.) is very small in comparison with  $R$  ( $\approx 10^{-8}$  cm.), he ignores the last two terms in parentheses in the equation above; thus

$$b = 2NeE/mu^2$$

This is equivalent to assuming that the electric potential  $V$  at  $b$  was equal to  $Ne/b$  and thus that it was due to the field of the central charge alone. Rutherford will make use of this expression for  $b$  below.]

<sup>14</sup>[Newton, *Principia*, Bk. I, Cor. I, Prop. 13. Note also that the force being repulsive ("centrifugal"), Newton's Scholium after Prop. 10 applies to determine the conic as a hyperbola.]

<sup>15</sup>[In Figure 1 we have added auxiliary elements in order to apply propositions from Apollonius' *Conics*. Rutherford himself argues trigonometrically.]

We show that B, C, and S lie on the circumference of a circle as follows: By Apollonius III.45 and II.1, rect. DB, BA and sq. AC are each equal to 1/4 "the figure" and therefore are equal to each other. But DB = OB + OA and BA = OB - OA; hence

make equal angles with the line SA, where A is the apse [vertex] of the hyperbola.  $p = SN$  = perpendicular distance from centre on direction of initial motion of particle.

Let angle POA =  $\theta$ .

Let  $u$  = velocity of particle on entering the atom,<sup>16</sup>  $v$  its velocity at A, then from consideration of angular momentum

$$pu = SA \cdot v.<sup>17</sup>$$

From conservation of energy<sup>18</sup>

$$\frac{1}{2}mu^2 = \frac{1}{2}mv^2 + \frac{NeE}{SA}.$$

[Now, since  $NeE = (1/2)mu^2b$ ,]<sup>19</sup>

$$v^2 = u^2 \left(1 - \frac{b}{SA}\right).$$

\* \* \*

[Therefore also]

$$p^2 = SA \cdot (SA - b).<sup>20</sup>$$

$$(AC)^2 = DB \cdot BA = (OB + OA)(OB - OA) = (OB)^2 - (OA)^2.$$

But in rt. triangle OAC,

$$(AC)^2 = (OC)^2 - (OA)^2.$$

Then  $(OC)^2 = (OB)^2$  and  $OC = OB$ . Similarly  $OC = OS$  also. Thus  $OC = OB = OS$ , so that a circle about O will pass through the points K, B, C, F, S as shown in the drawing. Q.E.D.]

<sup>16</sup>[Rutherford actually writes  $V$  at this point, not  $u$ , to represent the initial velocity of the alpha particle! But since he used  $u$  to denote that velocity on p. 50 above, and  $V$  to represent the *electric potential*, we will retain his original meanings for  $u$  and  $V$  throughout.]

<sup>17</sup>[Newton, *Principia*, Bk. I, Cor. I, Prop. I states that if a body is acted on by a central force, its velocity at different points along its path varies inversely as the perpendiculars dropped from the center of force to the tangents to the body's path at those points. Here SA is the perpendicular dropped from S to the tangent at A; SN ( $= p$ ) is the perpendicular dropped from S to the asymptote, which is nearly the same as the tangent at some extremely distant point. Thus  $u : v :: SA : SN$  or  $u : v :: SA : p$ . Rutherford's equation follows by equating the products of means and extremes. These products are said to express the *angular momentum* of the body at the points in question.]

<sup>18</sup>[The alpha-particle, starting its trajectory far from the atomic center, is considered to have initial potential energy zero. When it reaches vertex A it will have potential energy  $NeE/SA$ , equal to its loss of kinetic energy,  $(1/2)mu^2 = (1/2)mv^2$ ]

<sup>19</sup>[In note 13 above we found

$$b = 2NeE/mu^2; \quad \text{that is, } NeE = bmu^2.$$

Hence, substituting into the previous equation,

$$(1/2)mu^2 - (1/2)mv^2 = bmu^2/2 \cdot SA, \quad \text{or} \quad v^2 = u^2(1 - b/SA).$$

]

<sup>20</sup>[In  $pu = SA \cdot v$  from above, square both sides to obtain

$$p^2u^2 = (SA)^2v^2.$$

But

$$v^2 = u^2(1 - b/SA),$$

\* \* \*

The angle of deviation  $\phi$  of the particle is  $\pi - 2\theta$  and

$$\cot \phi/2 = 2p/b.^{2122} \quad (1)$$

This gives the angle of deviation of the particle in terms of  $b$ , and the perpendicular distance of the direction of projection from the centre of the atom.

For illustration, the angles of deviation  $\phi$  for different values of  $p/b$  are shown in the following table:—

$p/b$	10	5	2	1	.5	.25	.125
$\phi$	5°.7	11°.4	28°	53°	90°	127°	152°

### §3. Probability of Single Deflection Through Any Angle

Suppose a pencil of electrified particles to fall normally on a thin screen of matter of thickness  $t$ . With the exception of the few particles which are scattered through a large angle, the particles are supposed to pass nearly normally through the plate with only a small change of velocity. Let  $n$  = number of atoms in unit volume of material. Then the number of collisions of the particle with the atom of radius  $R$  is  $\pi R^2 nt$  in the thickness  $t$ .

The probability  $m$  of entering an atom within distance  $p$  of its centre is given by

$$m = \pi p^2 nt.^{23}$$

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as was just derived. Therefore,

$$p^2 u^2 = (\text{SA})^2 \cdot u^2 (1 - b/\text{SA})$$

or

$$p^2 = \text{SA} \cdot (\text{SA} - b).$$

] <sup>21</sup>[In Figure 1,  $\triangle OAC \cong \triangle ONS$ ; therefore  $SN = AC$ . But  $AC$  is a mean proportional between segments  $SA, AB$  since it is perpendicular to the circle diameter  $SB$ . Hence  $SN$ , that is  $p$ , is likewise a mean proportional between the same two segments, or

$$p^2 = \text{SA} \cdot AB.$$

But we just saw, above,

$$p^2 = \text{SA} \cdot (\text{SA} - b)$$

so it must be the case that

$$AB = \text{SA} - b,$$

that is,

$$b = \text{SA} - AB = \text{SA} - SD = DA.$$

Now since  $p = AC$  and  $b = DA$ ,

$$2p/b = 2 \cdot AC/DA = KC/CF = \tan \angle CKF = \cot \angle CKF = \cot \phi/2.]$$

<sup>22</sup>A simple consideration shows that the deflexion is unaltered if the forces are attractive instead of repulsive. [Compare Newton, *Principia*, Book I, Prop. 12, "The Same Otherwise": "And the same way it may be demonstrated, that the body having its centripetal changed into a centrifugal force, will move in the opposite branch of the hyperbola."]

<sup>23</sup>[This was our "note on probability" that preceded Rutherford's paper. As was there implied, Rutherford here assumes that  $m$  is much less than 1.]

Chance  $dm$  of [an alpha-particle's] striking within radii  $p$  and  $p + dp$  [and, correlatively, of its emerging from the gold foil at an angle of deviation between  $\phi$  and  $\phi + d\phi$ ] is given by

$$dm = 2\pi p \cdot n \cdot t \, dp = \frac{\pi}{4} ntb^2 \cot\left(\frac{\phi}{2}\right) \csc^2\left(\frac{\phi}{2}\right) \, d\phi.^{24} \quad (2)$$

\* \* \*

It is convenient to express the equation (2) in another form for comparison with experiment. In the case of the  $\alpha$  rays, the number of scintillation[s] appearing on a *constant* area of a zinc sulphide screen are counted for different angles with the direction of incidence of the particles. Let  $r$  = distance from point of incidence of  $\alpha$  rays on scattering material, then if  $Q$  be the total number of  $\alpha$  particles falling on the scattering material, then number  $y$  of  $\alpha$  particles falling on a unit area which are deflected through an angle  $\phi$  is given by

$$y = \frac{Q \cdot dm}{2\pi r^2 \sin(\phi) \, d\phi} = \frac{ntb^2 \cdot Q \cdot \csc^4(\phi/2)}{16r^2} \quad ^{25} \quad (5)$$

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<sup>24</sup>[Beginning with the prior equation, Rutherford lets  $p$  vary by the small amount  $dp$ ;  $m$  then varies by  $dm$ . As a result,  $dm \approx 2\pi ptn \, dp$  may be said to represent the probability that a particle will strike between distances  $p$  and  $p + dp$  of an atomic center. Now since  $\cot \phi/2 = 2p/b$ ,

$$p = \frac{b}{2} \cot \phi/2.$$

Hence, differentiating  $p$  with respect to  $\phi$ ,

$$dp = d\left(\frac{b}{2} \cot(\phi/2)\right) = \frac{b}{2} d\left(\frac{\cos(\phi/2)}{\sin(\phi/2)}\right),$$

and first by the quotient rule and then by the trigonometric identity,  $\sin^2 \phi + \cos^2 \phi = 1$ ,

$$dp = \frac{b}{2} \left( \frac{-(1/2) \sin^2(\phi/2) - (1/2) \cos^2(\phi/2)}{\sin^2 \phi/2} \right) d\phi = -\frac{b}{4} \csc^2(\phi/2) d\phi.$$

If we substitute the equations for both  $p$  and  $dp$  into the equation found above for  $dm$  (i.e.,  $dm \approx 2\pi ptn \, dp$ ), then

$$dm \approx 2\pi nt \left( \frac{b}{2} \cot(\phi/2) \right) \left( -\frac{b}{4} \csc^2(\phi/2) d\phi \right)$$

$$dm \approx -\frac{\pi ntb^2}{4} \cot(\phi/2) \csc^2(\phi/2) d\phi.$$

Rutherford ignores the minus sign since  $\phi$  may be considered either positive or negative.]

<sup>25</sup>[Rutherford's detector is a tiny zinc sulphide screen which emits a microscopic flash of light when struck by an alpha particle. It can "view" only a small portion of each ring-shaped zone which its diameter defines. Plainly, then, the particles that strike it do not indicate the total number that fall upon each zone, but rather the number that fall *per unit area*. This quantity is obtained by dividing  $Q \, dm$  by the area of each zone. The area is approximately equal to the zone's circumference times its width. The latter is  $r \, d\phi$  (when  $\phi$  is expressed in radians) and the former is  $2\pi R$ , that is,  $2\pi r \sin \phi$ .

Since

$$b = 2NeE/mu^2,$$
<sup>26</sup>

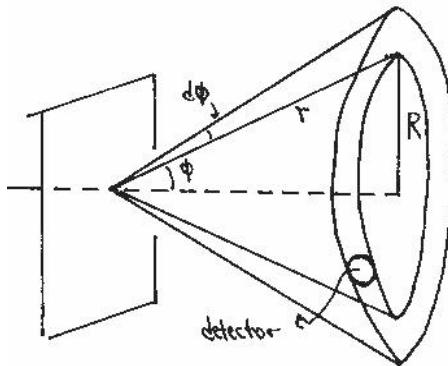
we see from this equation that a number of  $\alpha$  particles (scintillations) per unit area of zinc sulphide screen at a given distance  $r$  from the point of incidence of the rays is proportional to

- (1)  $\text{cosec}^4(\phi/2)$  or  $1/\phi^4$  if  $\phi$  be small;
- (2) thickness of scattering material  $t$  provided this is small
- (3) magnitude of central charge  $Ne$  [squared]
- (4) and is inversely proportional to  $(mu^2)^2$ , or to the fourth power of the velocity if  $m$  be constant.

In these calculations, it is assumed that the  $\alpha$  particles scattered through a large angle suffer only one large deflection. For this to hold, it is essential that the thickness of the scattering material should be so small that the chance of a second encounter involving another large deflection is very small. If, for example, the probability of a single deflection  $\phi$  in passing through a thickness  $t$  is  $1/1000$ , the probability of two successive deflexions each of value  $\phi$  is  $1/10^6$ , and is negligibly small.

The angular distribution of the  $\alpha$  particles scattered from a thin metal sheet affords one of the simplest methods of testing the general correctness of this theory of single scattering. This has been done recently for  $\alpha$  rays by Dr. Geiger, who found that the distribution for particles deflected between  $30^\circ$  and  $150^\circ$  from a thin gold-foil was in substantial agreement with the theory. A more detailed account of these and other experiments to test the validity of the theory will be published later.

\* \* \*



Therefore, by substituting for  $dm$  the equation found above,

$$y = \frac{Q \cdot dm}{2\pi r^2 \sin(\phi) d\phi} = \frac{Q\pi ntb^2 \cot(\phi/2) \csc^2(\phi/2) d\phi}{8\pi r^2 \sin(\phi) d\phi}$$

Apply the trigonometric identity  $\sin 2a = 2 \sin a \cos a$ , where  $\phi/2 = a$  (n.b.: the identity is a simpler form of the identity,  $\sin(a + b) = \sin a \cos b + \cos a \sin b$ ), and it follows that,

$$y = \frac{Qntb^2 \cot(\phi/2) \csc^2(\phi/2)}{16r^2 \sin(\phi/2) \cos(\phi/2)} = \frac{Qntb^2 \cos(\phi/2) \csc^2(\phi/2)}{16r^2 \sin^2(\phi/2) \cos(\phi/2)}$$

which reduces to Rutherford's formula (5).]

<sup>26</sup>[Derived in note 13 above.]

## §6. Comparison of Theory with Experiments

\* \* \*

Geiger['s experiments] showed that the most probable angle of deflection for an atom was nearly proportional to its atomic weight. It consequently follows that the value of  $N$  for different atoms should be nearly proportional to their atomic weights, at any rate for atomic weights between gold and aluminum.

Since the atomic weight of platinum is nearly equal to that of gold, it follows from these considerations that the magnitude of the diffuse deflexion of  $\alpha$  particles through more than  $90^\circ$  from gold and the magnitude of the average small angle scattering of a pencil of rays in passing through gold-foil are both explained on the hypothesis of single scattering by supposing the atom of gold has a central charge of about  $100e$ .

\* \* \*

## §7. General Considerations

In comparing the theory outlined in this paper with the experimental results, it has been supposed that the atom consists of a central charge supposed concentrated at a point, and that the large single deflexions of the  $\alpha$  and  $\beta$  particles are mainly due to their passage through the strong central field. The effect of the equal and opposite compensating charge supposed distributed uniformly throughout a sphere has been neglected. Some evidence in support of these assumptions will now be briefly considered. For concreteness, consider the passage of a high speed  $\alpha$  particle through an atom having a positive central charge  $Ne$ , and surrounded by a compensating charge of  $N$  electrons. Remembering that the mass, momentum, and kinetic energy of the  $\alpha$  particle are very large compared to the corresponding values for an electron in rapid motion, it does not seem possible from dynamic considerations that an  $\alpha$  particle can be deflected through a large angle by a close approach to an electron, even if the latter be in rapid motion and constrained by strong electrical forces. It seems reasonable to suppose that the chance of single deflexions through a large angle due to this cause, if not zero, must be exceedingly small compared with that due to the central charge.

It is of interest to examine how far the experimental evidence throws light on the question of the extent of the distribution of the central charge. Suppose, for example, the central charge to be composed of  $N$  unit charges distributed over such a volume that the large single deflexions are mainly due to the constituent charges and not to the external field produced by the distribution. It has been shown that the fraction of the  $\alpha$  particles scattered through a large angle is proportional to  $(NeE)^2$ , where  $Ne$  is the central charge concentrated at a point and  $E$  the charge on the deflected particle. If, however, this charge is distributed in single units, the fraction of the  $\alpha$  particles scattered through a given angle is proportional to  $Ne^2$  instead of  $N^2e^2$ .<sup>27</sup> In this calculation, the influence of mass of the constituent particle has been neglected, and account has only been taken of its electric field. Since it has been shown that the value of the central point charge for gold must be about 100, the value of the distributed charge required to produce the same proportion of single deflexions through a large angle should be at least 10,000. Under these conditions the mass of the constituent particle would be small compared with that of the  $\alpha$  particle, and the difficulty arises of the production of large single deflections at all. In addition, with such a large distributed charge, the effect of

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<sup>27</sup>[Proportionality to  $Ne^2$  had been derived by Thomson for his atom-model.]

compound scattering is relatively more important than that of single scattering. For example, the probable small angle of deflexion of a pencil of  $\alpha$  particles passing through a thin gold-foil would be much greater than that experimentally observed by Geiger. The large and small angle scattering could not then be explained by the assumption of a central charge of the same value. Considering the evidence as a whole, it seems simplest to suppose that the atom contains a central charge distributed through a very small volume, and that the large single deflexions are due to the central charge as a whole, and not to its constituents. At the same time, the experimental evidence is not precise enough to negative the possibility that a small fraction of the positive charge may be carried by satellites extending some distance from the centre. Evidence on this point could be obtained by examining whether the same central charge is required to explain the large single deflexions of  $\alpha$  and  $\beta$  particles; for the  $\alpha$  particle must approach much closer to the centre of the atom than the  $\beta$  particle of average speed to suffer the same large deflection.

The general data available indicate that the value of this central charge for different atoms is approximately proportional to their atomic weights, at any rate for atoms heavier than aluminum. It will be of great interest to examine experimentally whether such a simple relation holds also for the lighter atoms. In cases where the mass of the deflecting atom (for example, hydrogen, helium, lithium) is not very different from that of the  $\alpha$  particle, the general theory of single scattering will require modification, for it is necessary to take into account the movements of the atom itself<sup>28</sup>...

The deductions from the theory so far considered are independent of the sign of the central charge, and it has not so far been found possible to obtain definite evidence to determine whether it be positive or negative. It may be possible to settle the question of sign by consideration of the difference of the laws of absorption of the  $\beta$  particle to be expected on the two hypotheses, for the effect of radiation in reducing the velocity of the  $\beta$  particle should be far more marked with a positive than with a negative centre. If the central charge be positive, it is easily seen that a positively charged mass, if released from the centre of a heavy atom, would acquire a great velocity in moving through the electric field. It may be possible to account in this way for the high velocity of  $\alpha$  particles without supposing that they are initially in rapid motion within the atom.<sup>29</sup>

Further consideration of the application of this theory to these and other questions will be reserved for a later paper, when the main deductions of the theory have been tested experimentally. Experiments in this direction are already in progress by Geiger and Marsden.

## GEIGER AND MARDSEN'S EXPERIMENTS

The most decisive experimental work corroborating the theory Rutherford developed was reported by Geiger and Marsden in 1913. We quote from the introduction to their

<sup>28</sup>[Compare Newton, *Principia*, Book I, Props. 57-60, in which corrections are made for the motion of the central body.]

<sup>29</sup>[The conjecture of a positive central charge was confirmed in later work, lending credence to the hypothesis that the alpha particles ejected by radium and other radioactive materials originate in the atomic *nuclei* of those materials. The  $\alpha$ -particle itself could now be understood to be the "bare" *nucleus*, *without the surrounding electrons*, of a helium atom. This accounted both for its +2 charge and for its extremely small size.]

report in *Philosophical Magazine* 25 (1913), 604–623; reprinted in *The World of The Atom*, vol. I, 722–733:

At the suggestion of Prof. Rutherford, we have carried out experiments to test the main conclusions of the above theory. The following points were investigated:—

- (1) Variation with angle.
- (2) Variation with thickness of scattering material.
- (3) Variation with atomic weight of scattering material.
- (4) Variation with velocity of incident  $\alpha$  particles.
- (5) The fraction of particles scattered through a definite angle.

The main difficulty of the experiments has arisen from the necessity of using a very intense and narrow source of  $\alpha$  particles owing to the smallness of the scattering effect. All the measurements have been carried out by observing the scintillations due to the scattered  $\alpha$  particles on a zinc-sulphide screen, and during the course of the experiments over 100,000 scintillations have been counted. It may be mentioned in anticipation that all the results of our investigation are in good agreement with the theoretical deductions of Prof. Rutherford, and afford strong evidence of the correctness of the underlying assumption that an atom contains a strong charge at the centre, of dimensions small compared with the diameter of the atom.

### EXPERIMENT: RUTHERFORD SCATTERING OF $\alpha$ PARTICLES

The College has built a scattering apparatus which can provide a rough test of the hypothesis of the concentration of positive charge in the atom. Our apparatus includes an alpha particle source that is directed toward a piece of gold foil; on the far side of the foil is placed a detector. Our object is to measure how frequently alpha particles are deflected at high angles, from 30 to 70 degrees. In our apparatus, however, rather than moving the detector, the alpha particle source and the foil sit on an arm that swivels, and we jointly move the particle source and foil in order to adjust the angle between the far surface of the foil and the detector (which remains fixed). The College's apparatus is not as precise as Geiger and Marsden's, primarily because our alpha particle source is weak compared to theirs.<sup>30</sup> In addition, the beam of alpha particles is relatively wide, about thirty degrees (in measurements taken without the gold foil in place, the detector records about 200 counts per second at the center of the beam, and 100 counts per second up to six or seven degrees to each side of the center). Nevertheless, the apparatus is sufficiently precise to test Rutherford's statement that, at a given angle  $\phi$ , the number of alpha particles detected per unit area and per unit time will be proportional to  $\text{cosec}^4(\phi / 2)$ .

Although long angle deflections are more probable than Thomson's model of the atom would suggest, they are still relatively rare, so that measurements need to be taken over a long period of time. In the late afternoon lab assistants will set the angle

<sup>30</sup>Theirs was “hot enough to cook a chicken,” according to a knowledgeable commentator.

of the detector and reset the counter to zero, and then read the counter the following morning. Readings will be taken between 30 and 70 degrees at intervals of 10 degrees.

During class, one may take readings at short angles, between 0 and 30 degrees, for short periods of time (between 20 and 200 seconds, using longer periods for longer angles). These readings cannot be used to confirm Rutherford's mathematical prediction of the probability of deflections, but they can be compared to readings previously taken *without the gold foil in place* in order to observe, in general terms, the effect of the foil on the alpha particle beam.



## CHAPTER 5

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# THE QUANTUM HYPOTHESIS

MAX PLANCK<sup>1</sup>

The mathematical analysis in Einstein's paper in Chapter VI is connected to something called "Planck's quantum hypothesis," and Einstein emphasizes the strength the connection lends to his own argument. Planck's quantum hypothesis states that microscopic light-emitting bodies only absorb and emit energy in indivisible units or "quanta." As we shall see in his paper, Einstein adopts this hypothesis and indeed argues for a radical extension of it. Unfortunately, the work leading up to this hypothesis involves a great deal of probability theory which we cannot go into here. But at least the phenomena and the ways of thinking about them that led to the quantum hypothesis can be sketched.

### A. BLACK BODY RADIATION: THE PHENOMENA, FIRST ATTEMPTS TO UNDERSTAND THEM, AND PLANCK'S *Empirical DETERMINATION OF A FORMULA TO FIT THEM.*

Being hot enough will make any solid body glow visibly. The filament in an incandescent light bulb is not undergoing any chemical reaction: it is glowing because it is hot. Furthermore, such a glowing body will glow in a characteristic color and will change color, up or down the spectrum in order, if it gets hotter or cooler.

For instance, what happens when an iron bar is heated? If its temperature gets high enough, it starts to glow. Some of the energy absorbed as heat is given off as light. This emitted light first becomes visible when it is red-hot. (In fact at lower temperatures a body "glows" in the infra-red range, that is, at frequencies too low for human eyes to see. This is what makes infrared photography possible.) As the temperature rises the bar changes to other colors, up through the spectrum, and eventually becomes blue-hot.

Why does it have distinct colors along the way? If the frequencies at which it can emit light were all equally entitled to an equal share of the energy, like the piano strings or the air molecules, we'd expect that the blend of colors given off by the bar would always be the same and that only the intensity of its glow would increase with increasing temperature. But, instead, as we heat the bar, it goes through a phase of intense red, a later phase of intense yellow, etc. For some reason, at a certain range of temperatures, the bulk of the light-energy is emitted at the red frequency, but at a higher temperature range yellow is preferred.

Well before 1900, it was known that electromagnetic waves were absorbed and emitted by bodies. These waves could be in the form of infrared radiation (also known as thermal radiation or heat), visible light, ultraviolet light, or x-rays. Anything that is at a temperature above absolute zero will emit some kind of light in the infrared.

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<sup>1</sup>Indented sections of this chapter describing Planck's research are drawn from Robert Resnick, *Basic Concepts in Relativity and Early Quantum Theory* (New York: John Wiley and Sons, Inc., 1972), 113–116 and 119–123.

Nothing can emit for very long unless it is also absorbing light at some frequency. In general, the more the body absorbs, the more it will emit. Once a body absorbs light, assuming the body is dense enough, the energy of the light will come to some kind of equilibrium within the body and the emitted light will be in a range of frequencies, with a peak at some frequency that depends on the temperature and, to some extent, on the make-up of the body. The dependence on the make-up of the body gets less and less as the body becomes more uniformly dense (so that equilibrium of frequencies is achieved and conduction and convection do not carry off some of the heat) and blacker (so that more and more light is absorbed in order to be emitted).

The radiation emitted by a body as a result of its temperature is called *thermal radiation*. All bodies emit such radiation to their surroundings and absorb such radiation from it. If a body is at first hotter than the surroundings it will cool off because its rate of emitting energy exceeds its rate of absorbing energy. When *thermal equilibrium* is reached, the rates of emission and absorption are equal.

Matter in a condensed state (i.e., solid or liquid) emits a continuous spectrum of radiation. The details of the spectrum depend strongly on the temperature. At ordinary temperatures most bodies are visible to us not by their emitted light but by the light they reflect. If no light shines on them we cannot see them. At very high temperatures, however, bodies are self-luminous. We can see them glow in a darkened room (hot coals, e.g.). But even at temperatures as high as several thousand degrees Kelvin, well over 90% of the emitted thermal radiation is invisible to us, being in the infrared part of the electromagnetic spectrum. Self-luminous bodies are quite hot, therefore.

If we were to steadily raise the temperature of a hot body, we would observe two principal effects: (1) the higher the temperature, the more the thermal radiation emitted—at first the body appears dim, then it glows intensely; and (2) the higher the temperature, the higher the frequency of that part of the spectrum radiating most intensely—the predominant color of the hot body shifts from “red heat” to “white heat” to “blue heat.” Since the quality of its spectrum depends on the temperature, we can estimate the temperature of a hot body, such as a star or a glowing chunk of steel, by analyzing the radiation it emits. There is a continuous spectrum of radiation emitted, the eye seeing chiefly the color corresponding to the most intense emission in the visible region.

The detailed form of the spectrum of the thermal radiation emitted by a hot body at a given temperature depends somewhat upon the composition of the body. There is one class of hot bodies, however, called *black bodies*, which emit thermal radiation with the same spectrum at a given temperature, regardless of the details of their composition. Such bodies have surfaces that absorb all the thermal radiation incident upon them and, because they do not reflect light, appear black. An object coated with a diffuse layer of black pigment, such as lamp black or bismuth black, is (nearly) a black body. A cavity in a body, open to the outside by a small hole, is also a black body, as we shall soon explain. A theoretical understanding of black body,

or cavity, radiation was a major goal of physicists before the turn of the [twentieth] century.

Consider first the experimental observations. The spectral distribution of black-body radiation is described by a quantity  $\mathfrak{R}_T(\nu)$  called the *spectral radiancy*, which is defined so that the quantity  $\mathfrak{R}_T(\nu) d\nu$  is the [time] rate at which energy is radiated per unit area of a surface at absolute temperature  $T$  for frequencies in the interval  $\nu$  to  $\nu + d\nu$ . In Fig. 1, we show the experimentally observed dependence of  $\mathfrak{R}_T(\nu)$  on  $\nu$  and  $T$ . For a given value of the



**Figure 1.** The observed spectral radiancy of a black body  $\mathfrak{R}_T$ , as a function of frequency  $\nu$  of radiation, shown for black body temperatures of 1000°, 1500°, and 2000° Kelvin. The total energy emitted per unit time per unit area (radiancy  $R_T$ , or area under the curve) increases rapidly with temperature. Note that the frequency of maximum spectral radiancy (dashed line) increases linearly with temperature (Wien's displacement law). The visible region of the spectrum is off scale to the right, yellow being at about  $5 \times 10^{14}$  Hz. Most of the radiation is in the infrared at these temperatures.

frequency  $\nu$ , we see that the spectral radiancy  $\mathfrak{R}_T(\nu)$  increases with increasing temperature  $T$ . If we integrate the quantity  $\mathfrak{R}_T(\nu)$  over all frequencies  $\nu$  we obtain the total energy emitted per unit time per unit area from a black body at temperature  $T$ . This quantity

$$R_T = \int_0^\infty \mathfrak{R}_T(\nu) d\nu \quad (1)$$

is called the *radiancy*, appropriate units for it being watts/m<sup>2</sup>. It can be interpreted as the area under a curve in Fig. 1, from which we see that it increases rapidly as the temperature increases. The exact dependence of radiancy on temperature is given by *Stefan's law*,

$$R_T = \sigma T^4, \quad (2)$$

in which  $\sigma = 5.67 \times 10^{-8}$  watt/(m<sup>2</sup> °K<sup>4</sup>) is a universal constant called the Stefan-Boltzman constant. We also see from Fig. 1 that as the temperature  $T$  increases, the spectral distribution of frequencies shifts to higher values. If the frequency  $\nu$  at which  $\mathfrak{R}_T(\nu)$  reaches its maximum value is called  $\nu_{max}$ , then as  $T$  increases  $\nu_{max}$  is displaced toward higher frequencies. This relation,

$$\nu_{max} \propto T \quad (3a)$$

is called *Wien's displacement law* [discovered in 1894]. These experimental results are consistent with the observations we discussed earlier, namely that the quantity of thermal radiation increases rapidly with temperature (a hot body radiates much more heat energy at higher temperatures) and that the principal frequency of the radiation becomes higher with increasing temperature (the color of a hot body changes from red to white to blue).

Most black bodies used in laboratory experiments are cavities (ovens) having a very small opening. Let's explain why such a cavity, shown schematically in Fig. 2, is a black body. Radiation outside the cavity can enter it through the hole. It then strikes the inner wall, where it is partially absorbed and partially reflected. The reflected part then strikes another part of the inner wall where it, too, is partially absorbed and partially reflected. Eventually, therefore, after many successive reflections, the incident radiation is totally absorbed by the wall. Because the area cut out by the hole is such a very small part of the total area of the cavity wall, we can safely neglect the (very small) amount of the incoming radiation that can be reflected back out through the hole. For practical purposes we can say that all the radiation incident on the hole from the outside is absorbed by it. Therefore, the hole behaves just as the surface of a black body behaves, i.e., it absorbs all the radiation incident on it. Indeed, at low temperatures the hole appears black. If we raise the temperature by heating the cavity walls uniformly, the hole will become self-luminous. The inner walls emit thermal radiation into the cavity and some very small part of this radiation will emerge from the interior through the hole. Since the hole acts like a black surface, the spectrum of radiation emitted by it will be characteristic of a black body.

Of course, the thermal radiation emitted by the hole is just a specimen of the radiation filling the cavity. Therefore, the radiation inside the cavity also has a spectrum characteristic of a black body. Since the hole acts as a black surface, the spectrum emitted by the hole in the cavity whose walls are at a temperature  $T$  can be described, as before, by the spectral radiancy  $\mathfrak{R}_T(\nu)$ . But the spectrum of radiation *inside* the cavity, called *cavity radiation*, is more conveniently described by the *energy density*  $\rho_T(\nu)$ , which gives the energy in the frequency interval  $\nu$  to  $\nu + d\nu$  per unit volume of the cavity at



**Figure 2.** A cavity in a body connected by a small hole to the outside. Radiation incident upon the hole is partly absorbed on each reflection and completely absorbed after many successive reflections on the inner surface of the cavity. (Note the diminution in intensity of the successive reflections.) The hole absorbs like a black body. . . . The hole emits like a black body.

temperature  $T$ . These quantities are proportional to one another; that is,

$$\rho_T(\nu) = (8\pi/c)\Re_T(\nu) \text{ [equation modified]} \quad (4)$$

. . . Suppose that we uniformly heat to a temperature  $T$  a piece of metal containing a cavity. The electrons in the metallic walls are thermally agitated and emit electromagnetic radiation into the cavity. Thermal equilibrium is established and maintained in the cavity by the absorption and re-radiation of energy by the walls.

One attempt to understand the phenomenon of black body radiation was that of Lord Rayleigh and Sir James Jeans. By 1905 their combined efforts had led to the derivation of a formula for  $\rho_T(\nu)$ .

Rayleigh and Jeans showed that the radiation inside such a cavity of volume  $V$  consists of standing waves with nodes at the walls. They computed the number of standing waves in the frequency interval  $\nu$  to  $\nu + d\nu$  to be

$$N(\nu) d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu \quad (5)$$

in which  $c$  is the velocity of electromagnetic waves. Now, each such standing wave contains energy. The average energy per wave, when the system is in thermal equilibrium, can be determined from the **classical law of equipartition of energy**.... This states that the average energy [per wave] is the same for each standing wave in the cavity, independent of its frequency, i.e., the energy is partitioned equally over all frequencies; the value of the average energy  $\bar{\epsilon}$  depends only on the temperature  $T$  and is given by

$$\bar{\epsilon}(\nu, T) = \bar{\epsilon}(T) = kT \quad (6)$$

where  $k (= 1.37 \times 10^{-23} \text{ joule}/\text{°K})$  is the Boltzmann constant. To get the average energy content per unit volume of cavity in the frequency interval  $\nu$  to  $\nu + d\nu$ , we simply multiply the number of standing waves in the frequency interval by the average energy of a wave and divide by the volume of the cavity. In this way [based on the classical law of equipartition], Rayleigh and Jeans found the energy density  $\rho_T(\nu)d\nu$  to be

$$\rho_T(\nu)d\nu = \frac{8\pi\nu^2}{c^3}kT d\nu, \quad (7)$$

which is called *the Rayleigh-Jeans formula for black-body radiation*.<sup>2</sup>

We compare the Rayleigh-Jeans formula, in Fig. 4, with the experimental result for a cavity radiator at  $1500^\circ\text{K}$ . As the frequency is reduced to zero, the spectrum predicted by the Rayleigh-Jeans classical formula does come closer and closer to the experimentally observed spectrum. However, as the frequency is increased to large values (ultraviolet region of the spectrum), the classical theoretical result diverges enormously from experiment. Indeed, the classical formula predicts an infinite energy density whereas experiment shows that the energy density goes to zero at very high frequencies. This completely erroneous prediction of classical physics was regarded as such a serious shortcoming that it came to be called "the ultraviolet catastrophe."



**Figure 4.** The Rayleigh-Jeans prediction (dashed line) compared with the experimental result (solid line) for the energy density of a black body, showing the ultraviolet catastrophe.

In 1900 Max Planck made an independent attempt to understand black body radiation. He began by letting  $\bar{\varepsilon}(\nu, T)$  stand for the average energy of an electromagnetic wave of frequency  $\nu$  at temperature  $T$ , and then was able to demonstrate theoretically that when the walls and the radiation within the cavity are in equilibrium, the energy

<sup>2</sup>Rayleigh realized in 1900 that Equation 7 contradicted Wien's displacement law (Eq. 3a). In 1911 Paul Ehrenfest pointed out that it also implied what was called "the ultra-violet catastrophe."

density,  $\rho_T(\nu)$ , is related to the average energy per wave at  $\nu$  and  $T$ ,  $\bar{\varepsilon}(\nu, T)$ , as follows:

$$\rho_T(\nu) d\nu = \frac{8\pi\nu^2}{c^3} \bar{\varepsilon}(\nu, T) d\nu. \quad (10)$$

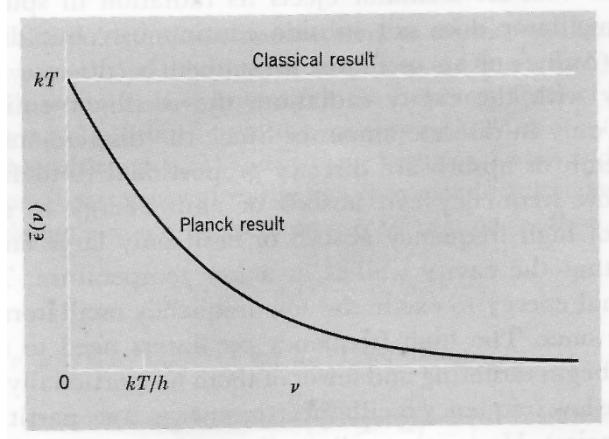
In an effort to arrive at an expression for  $\rho_T(\nu)$  which would not predict an ultraviolet catastrophe, Planck sought to determine a formula for  $\bar{\varepsilon}$  by trying to fit the graphs of experimental results. He arrived at the following empirical formula:

$$\bar{\varepsilon}(\nu) = \frac{h\nu}{e^{h\nu/kT} - 1}, \quad (11)$$

where  $h$  is a constant.<sup>3</sup> In particular, it turned out that the value of this constant  $h$  that would give the best fit between his formula and the experimental data was:  $h = 6.63 \times 10^{-34}$  joule-sec =  $4.14 \times 10^{-15}$  eV-sec, which is very nearly the same as the modern value for what has come to be known as *Planck's constant*.

In Figure 5 we compare Equation 11 with Equation 6, the classical law of equipartition:

$$\bar{\varepsilon}(\nu, T) = \bar{\varepsilon}(T) = kT \quad (6)$$



**Figure 5.** Planck's formula for the average value of the energy, as a function of frequency, compared with the classical result.

[N]ote that  $\bar{\varepsilon}(\nu)$  drops from  $kT$  to zero in a continuous way with increasing frequency, at first rapidly and then slowly.

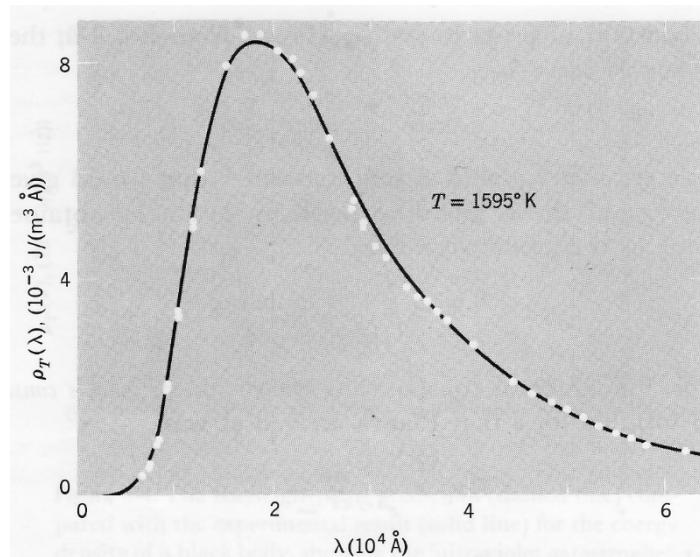
When Planck used his result (Eq. 11) for  $\bar{\varepsilon}$  rather than the classical value  $\bar{\varepsilon} = kT$  (Eq. 6) in the calculation of the energy density in the cavity radiation spectrum, he found

$$\rho_T(\nu) d\nu = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} d\nu. \quad (12)$$

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<sup>3</sup>The constant  $e$  in eq. 11 is the number  $2.718\dots$  providing the base of natural logarithms. This is different from the "e" in the unit "eV" in the next sentence, an abbreviation for electronvolts.

This is *the Planck formula for black body radiation*. Figure 6 shows a comparison of this result of Planck's [calculations] with experiment for a temperature  $T = 1595^{\circ}\text{K}$ . The experimental results are in complete agreement with Planck's formula at all temperatures.



**Figure 6.** Planck's energy density prediction (solid line) compared to the experimental results (circles) of the energy density of a black body. The data were reported by Coblenz in 1916 and apply to a temperature of  $1595^{\circ}\text{K}$ . The author remarked in his paper that after drawing the spectral energy curves resulting from his measurements, "owing to eye fatigue, it was impossible for months thereafter to give attention to the reduction of the data." The data, when finally reduced, led to a value of Planck's constant of  $6.57 \times 10^{-34} \text{ J-sec}$ .

## B. BLACK BODY RADIATION: PLANCK'S *Theoretical DETERMINATION OF THE FORMULA THAT FIT THE EXPERIMENTAL RESULTS.*

Up to this point Equation 12 is merely an *ad hoc* formula based on Equation 11, which had been constructed to fit the experimental results. Planck was convinced that it was right. Yet, theorist that he was, he wanted more: he wanted a *theoretical* derivation of Equation 11 that would explain why it was so, giving it physical meaning. We shall ignore most of the details and, instead, focus on Planck's fundamental modification of the classical view.

In thinking about the black-body problem, Planck had been guided by Hertz's discovery (which may have been demonstrated in Junior Laboratory) that oscillating charged particles—parts of tiny elastic systems of some sort—presumably parts of atoms—emit electromagnetic waves, which meant that cavity radiation must originate in submicroscopic electric oscillators in the cavity walls. He reasoned that heating a material body ought to set microscopic systems of charged particles vibrating, for

according to Maxwell they should be made to resonate harmonically by incoming light of the proper frequencies, and they would also be jostled by the vibratory heat motions of their neighbors. In turn a vibrating electric charge should generate light of the same frequency as its own vibration, again in accordance with Maxwell's theory.

Furthermore, since the character of cavity radiation had been shown to be independent of the material of the cavity walls, Planck had felt free to make possibly artificial assumptions about the character of the oscillators: He had supposed them all to be *simple harmonic oscillators*. In this analogy, Planck imagined that the cavity walls consisted of tiny 'springs' of force constants  $\beta$ , on the ends of which were charged particles of masses  $m$ . As we saw in Junior Laboratory, this meant that each such oscillator would have a natural frequency given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\beta}{m}}. \quad (13)$$

That is, each of them had its own fixed frequency, determined by the force binding the charge to its equilibrium position, and by the mass of the charge.

Since the range of frequencies in cavity radiation is assumed to be continuous, the assumption must be that the cavity walls contain large numbers of oscillators of all frequencies represented in the radiation. When any oscillator is vibrating at its fixed frequency, it is radiating electromagnetic waves of the same frequency; and it is losing energy. The temperature of the cavity walls will drop unless the lost energy is replaced. It can be replaced by absorption of radiant energy; each oscillator will absorb energy only of its natural frequency. But the energy can also be replaced by heat supplied to the cavity walls: The cavity is kept in a constant-temperature oven. The available energy will be constantly re-distributed among the various oscillators, because of their constant absorption and radiation of energy.

Considering the temperature  $T$  to be fixed, Planck set out to determine how, on the average, the total amount of energy in the cavity at temperature  $T$  would distribute itself on the average among the various oscillators of different natural frequencies,  $\nu$ , of vibration. That is, Planck tried to *derive* the formula for  $\bar{\varepsilon}(\nu)$  (Eq. 11), which he had already arrived at by matching the experimental results. This *equilibrium distribution* of energy among the oscillators will, in turn, determine how the energy density,  $\rho_T(\nu)$ , of the cavity radiation varies with frequency.

So, Planck had to answer the question: If, of the portions of energy given to all the oscillators at a given moment, we consider the subset consisting of those amounts of energy allotted to the oscillators of natural frequency  $\nu$ , how do those amounts of energy distribute themselves among the latter? Planck's first insight was that his question was analogous to a question that had already been answered by Ludwig Boltzmann, namely: How does the energy allotted to a set of gas molecules in a closed container at a constant temperature  $T$  distribute itself among the individual molecules? These molecules have an average kinetic energy, which is the analogue to Planck's  $\bar{\varepsilon}(\nu)$ . Stated as a proportion the analogy is roughly:

$$\text{(all gas molecules in the container) : (all oscillators of natural frequency } \nu \text{ in the cavity walls)} :: \text{(all gas molecules in the container having energy } \varepsilon \text{) : (all oscillators of natural frequency } \nu \text{ having energy } \varepsilon \text{ in the cavity walls).}$$

Because of the large numbers of molecules and because of the fact that they are constantly colliding, Boltzmann assumed that the energy eventually became distributed

among the molecules in a stable way. Using probability theory as well as mechanics, Boltzmann imagined that, at any given time, each of the  $N$  molecules in a given volume of a gas would have one of, say,  $n$  different energy states. His problem was to find the probability of the various possible distributions of particles among these  $n$  energy states. By calculating the total number of ways in which each such distribution could be achieved, Boltzmann was able to determine the most probable distribution of particles among the available energy states. That is, for each of the available energy states,  $\varepsilon$ , he determined the fraction,  $\Delta N_\varepsilon/N$ , of the total number of molecules,  $N$ , that had energy  $\varepsilon$ , in the most probable distribution:

$$\frac{\Delta N_\varepsilon}{N} \propto e^{-\varepsilon/kT} \quad (14)$$

where  $e$  is the base of natural logarithms,  $T$  is the absolute temperature, and  $k$  is Boltzmann's constant, given by the gas constant  $R$  divided by Avogadro's number. The proportionality (14) implies that the fraction  $\Delta N_\varepsilon/N$  decreases as  $\varepsilon$ , the energy state considered, increases.

In order to find the way energy would distribute itself among his hypothetical oscillators, Planck made use of the Boltzmann distribution (14). He proceeded in somewhat the following way.

Consider an oscillator of mass  $m$  and force constant  $\beta$ ; let its displacement be  $x$  and its momentum  $p = m(dx/dt)$ . Its potential energy will be  $(1/2)\beta x^2$  and its kinetic energy  $(1/2)m(dx/dt)^2 = p^2/2m$ . Therefore, its total energy is<sup>4</sup>

$$\varepsilon = \frac{p^2}{2m} + \frac{\beta x^2}{2} \quad (15)$$

Its frequency, which should be regarded as fixed in what follows, is given by Equation 13.

Equation 15 can be viewed as the equation of an ellipse in the  $(p,x)$  plane (this plane is called the *state domain* by Planck), where  $\sqrt{2m\varepsilon}$  and  $\sqrt{2\varepsilon/\beta}$  are the semi-minor and semi-major axes<sup>5</sup> of the inmost ellipse in Figure 7, labeled  $\varepsilon = h\nu$ . The area of the inmost ellipse will be<sup>6</sup>

$$A_1 = \pi p_{max}x_{max} = \pi \sqrt{2m\varepsilon} \sqrt{\frac{2\varepsilon}{\beta}} = 2\pi\varepsilon \sqrt{m/\beta} = \frac{\varepsilon}{\nu}. \quad (16)$$

Let us define a constant  $h$ , such that  $h = A_1 = \varepsilon/\nu$ . Previously Planck had showed that

<sup>4</sup>You may want to review the second semester junior lab manual treatment of the pendulum for what follows. Potential energy should equal the work done against the restoring force in moving the mass  $m$  from zero to displacement  $x$ . The restoring force is  $F = -\beta x$ . Therefore the potential energy is this force integrated from 0 to  $x$ . One must integrate over  $x$  rather than write  $Fx$  because the force varies with  $x$ .

<sup>5</sup>According to the Sophomore Mathematics manual, *A Cartesian Survey of the Conic Sections*, when the equation for an ellipse centered at the origin is put into standard form:

$\frac{x^2}{a^2} + \frac{y^2}{b^2} - 1 = 0$ , according as  $a$  is greater or less than  $b$ , the major axis is of length  $2a$ , along the  $x$ -axis, or of length  $2b$ , along the  $y$ -axis.

<sup>6</sup>Given the equation of the ellipse in the previous note, one-fourth of the ellipse would correspond to  $y = b[1 - (x/a)^2]^{1/2}$ ,  $x \geq 0$ .

Then the area contained by the ellipse would be given by:

$A = 4 \int_0^a b(1 - \frac{x^2}{a^2})^{1/2} dx = \frac{4b}{a} \int_0^a (a^2 - x^2)^{1/2} dx = \frac{4b}{a} [\frac{x}{2}(a^2 - x^2)^{1/2} + \frac{a^2}{2} \sin^{-1}(\frac{x}{a})]_0^a = \pi ab$ , where the indefinite integral is found from a table of integrals.



**Figure 7.** Ellipses in the state domain.

the area integral,  $\int dp dx$ , does not vary over time. One way to think of this is to notice that if each of the points  $(p, x)$  inside the inmost ellipse is given an additional energy of  $h\nu$  (for example, by pushing a pendulum or a spring with an additional force), then each of these points will be displaced to the annular region between the ellipses labeled  $\varepsilon = h\nu$  and  $\varepsilon = 2h\nu$ , respectively (the inmost cross-hatched annulus in the diagram). Thus, this annular region, equal to the area of the second ellipse,  $A_2$ , minus that of the first,  $A_2 - A_1$ , also has area  $h$ , as does every annular region between two consecutive ellipses. The entire state domain (the  $[p, x]$ -plane) is thus naturally divided into non-overlapping areas of size  $h$ , each of which corresponds to an amount of energy  $= h\nu$ . It remains to associate a probability with each annular region and then to take the limit of the sum of these probabilities as the areas of the annular regions shrink to zero. But this is given to us by the Boltzmann distribution, Equation 14.

Identifying  $\varepsilon$  in Equation 14 with  $h\nu$  gives us the result that the probability of an oscillator of frequency  $\nu$  having energy  $\varepsilon = h\nu$ , that is,  $P(\nu, h\nu)$ , or, equivalently, the fraction of the total number of oscillators of frequency  $\nu$  that have energy  $\varepsilon = h\nu$ ,  $\Delta N_\varepsilon / N$ , is

$$P(\nu, h\nu) = Ce^{-h\nu/kT}.$$

( $C$  is the constant of proportionality, to be determined.) Analogously, for any whole number  $n$ , we obtain that the probability of an oscillator of frequency  $\nu$  having energy  $n\varepsilon = nh\nu$  is

$$P(\nu, nh\nu) = Ce^{-nh\nu/kT}. \quad (17)$$

This is the probability associated with the annular region between the ellipses  $\varepsilon = (n - 1)h\nu$  and  $\varepsilon = nh\nu$ .

The constant  $C$  is determined by adding up all the probabilities, which must equal

1;<sup>7</sup>

$$\sum_{n=0}^{\infty} P(\nu, nh\nu) = \sum_{n=0}^{\infty} Ce^{-nh\nu/kT} = C(1 - e^{-h\nu/kT})^{-1} = 1, \quad (18)$$

from which it follows that

$$C = 1 - e^{-h\nu/kT}. \quad (19)$$

If we want to find the average energy,  $\bar{\varepsilon}(\nu, T)$ , of all the oscillators having the frequency  $\nu$  at temperature  $T$ , we multiply each of the energies,  $h\nu, 2h\nu, 3h\nu, \dots$ , by the probability of an oscillator's having that energy, and add up all the terms:

$$\bar{\varepsilon}(\nu, T) \approx Ch\nu \left( e^{-h\nu/KT} + 2e^{-2h\nu/kT} + \dots \right) = Ch\nu e^{-h\nu/kT} \left( 1 - e^{-h\nu/kT} \right)^{-2}. \quad (20)$$

where, be it noted, we have had to include the possibility that an oscillator have zero energy.<sup>8</sup> Substituting our value for  $C$ , (19), into Equation 20, we obtain for the average energy of the oscillators of frequency  $\nu$  at temperature  $T$ :<sup>9</sup>

$$\bar{\varepsilon}(\nu, T) \approx \frac{h\nu e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1}, \quad (21)$$

which would be identical with Equation 11 if the “ $\approx$ ” were replaced by “=.”

We observe that, so far, Planck has been considering finite increments in energy, of amount  $h\nu$ . Equation 21 is thus, according to the notions of all earlier physics, only approximate; to obtain the exact expression, it would normally be necessary to take the limit of Equation 21 as  $h$  goes to zero. If this is done, however, we find that<sup>10</sup>

$$\bar{\varepsilon}(\nu, T) \rightarrow kT \quad \text{as } h \rightarrow 0.$$

Substituting this expression— $\bar{\varepsilon}(\nu, T) = kT$  [Eq. 6]—for the average energy into Equation 10, gives for the energy density the Rayleigh-Jeans formula, Equation 7, which, as we have seen, is in disagreement with experiment and is theoretically unacceptable in that it implies the “ultraviolet catastrophe.”

<sup>7</sup>The last step to the equation relies on an identity that is part of the “toolkit” of physicists and mathematicians, derivable using Taylor’s theorem:

$$(1 - x)^{-1} = 1 + x + x^2 + x^3 + \dots$$

We let  $x = e^{-h\nu/kT}$ , and writing out some of the summation, we find that the identity is applicable.

<sup>8</sup>We have again made use of an identity, derivable from Taylor’s Theorem,

$$(1 - x)^{-2} = 1 + 2x + 3x^2 + 4x^3 + \dots$$

And we again let  $x = e^{-h\nu/kT}$  and factor that out, then use this identity to get the last expression in Equation 20.

<sup>9</sup>The equation gets its right-hand form by multiplication of both numerator and denominator by  $e^{h\nu/kT}$ .

<sup>10</sup>We let  $a = h\nu/kT$ , and we also recall that from junior math,  $e^a$  is expressible in the form

$$e^a = 1 + a + \frac{a^2}{2!} + \frac{a^3}{3!} + \dots + \frac{a^n}{n!} + \dots$$

If we now write

$$\bar{\varepsilon}(\nu, T) = \frac{kTa}{e^a - 1}$$

and expand  $e^a$ , the denominator will go to  $a$  as  $h$  and  $a$  go to zero, which cancels with the  $a$  in the numerator, leaving  $kT$ .

Now, in the classical calculation of the average energy of a large number of things of the same kind in thermal equilibrium with each other at temperature  $T$  (a calculation that leads to the Equipartition Law, Eq. 6), it was assumed that the energy  $\varepsilon$  was a continuous variable. However, as we have seen, Equation 21, *without taking the limit*, implies an equation for the energy density, Equation 12, that accords with experiment (Fig. 6). Thus, in order to derive the equation which fits the experimental results, Planck was forced to say that the correct expression for  $\bar{\varepsilon}(\nu, T)$  must be, not the approximate Equation 21, or the exact equation resulting from allowing the annular regions to shrink, but rather Equation 11. In other words, he had to deny the assumption that the energy  $\varepsilon$  varies continuously. He could not allow  $h$  to approach zero but, instead, had to assume that the amount of energy assigned to an oscillator of frequency  $\nu$  must be an integral number of units  $\Delta\varepsilon = h\nu$  of energy—"energy quanta," as Planck called them—where  $h$  was the non-zero constant whose value he had determined by fitting his Equation 11 to the empirical data. We have then, for nonzero  $h$ , a theoretical formula which describes the empirical results. What does it mean? How is the meaning of  $h$  different now as compared with its meaning when it was first encountered above where it was defined as  $\varepsilon/\nu$ ?

One can understand the results of Planck's assumption physically in this way. The electromagnetic waves in the cavity originate from radiation given off by electrons that are thermally agitated and oscillate in the walls of the cavity. The electronic oscillators in the cavity wall are pictured classically as radiating their energy smoothly as their motion gradually subsides. Planck assumed instead that an oscillator ejects its radiation in spurts. Thus the energy of an oscillator does not subside continuously but discretely. The allowed energy values of an oscillator must then be discrete and, as it exchanges energy with the cavity radiation, the oscillator emits or absorbs radiant energy only in discrete amounts. Since the discrete energies that an oscillator can emit or absorb [ $\Delta\varepsilon = h\nu$ ] are directly proportional to its frequency, the oscillators of low frequency can absorb or emit energy in small packets whereas those of high frequency absorb or emit only large energy packets. Now imagine that the cavity wall is at a low temperature. Then there is sufficient thermal energy to excite the low frequency oscillators, but not the high frequency ones. The high frequency oscillators need to receive much more energy to begin radiating and fewer of them proportionally are activated compared to the low frequency oscillators (the energy is not partitioned equally over all frequencies). Hence the walls radiate principally in the long wavelength region and hardly at all in the ultraviolet. As the temperature of the wall is raised there is sufficient thermal energy to activate a larger number of high frequency oscillators and the resulting radiation shifts its character toward higher frequencies, i.e., toward the ultraviolet. Hence the Planck assumptions quite naturally lead to the experimental observations discussed earlier and avoid the ultraviolet catastrophe of the classical analysis.

Physicists acknowledged the remarkable predictive power of Planck's model. Still, the fact that it relied on the quantum hypothesis was disturbing. It seemed extremely unlikely that actual microscopic oscillators should only absorb and emit energy in

units. Certainly macroscopic oscillators do not seem to act this way: We can (we believe) get a pendulum to absorb energy in any continuously varying amount, just by nudging it right; and an oscillating pendulum seems to give up its energy to its surroundings continuously. Quantization seemed just as unlikely to happen in any plausible microscopic picture of the interactions between atoms and electromagnetic waves in a continuous medium. Thus, as long as the necessity for the quantum hypothesis was not overcome, black-body radiation seemed to stand as a question mark to Maxwell's theory itself.

## CHAPTER 6

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# THE PHOTOELECTRIC EFFECT

ALBERT EINSTEIN

## REMARKS

The *photoelectric effect* was discovered by Heinrich Hertz in 1887. He found that a spark passed more readily across a narrow gap in an electric circuit if the ends of the wires were being illuminated by ultraviolet light—when the wires were not so illuminated, the gap between them had to be reduced in order for the spark to pass. Shortly afterwards Wilhelm Hallwachs found that if a freshly polished zinc plate was insulated and connected to an electroscope, it would lose an initial *negative* charge while illuminated by ultraviolet light, but that there was no effect if the initial charge was *positive*. He concluded that negatively charged particles were being emitted under the action of the light.

In 1900 Philipp Lenard was able to show that the negatively charged particles emitted from metals under the action of light were identical with the “corpuscles” of Thomson’s cathode rays—and therefore, as we will now say, identical with *electrons*. He also showed that when a photosensitive metal was made the cathode in a cathode ray tube and then illuminated, a measurable *photoelectric current*, carried by these emitted electrons, passed from cathode to anode. His measurements disclosed that this current increased steadily with the intensity of the light falling on the cathode.

Furthermore, by opposing this photoelectric current with an oppositely-directed electric field, Lenard was able to determine the potential difference at which the photoelectric current was reduced to zero—that is, the potential difference at which even the most energetic electrons emitted from the cathode were turned back just before they reached the anode, called the *stopping potential difference*,  $\Pi$ . This potential difference was a measure of the kinetic energy with which these electrons were ejected from the cathode.<sup>1</sup> In this way he discovered that this maximum kinetic energy was *not* dependent on the intensity of the illuminating light but, instead, rose with the light *frequency*.

In two major respects the photoelectric effect contradicted classical electromagnetic wave theory:

(1) The *intensity* of any wave is defined as the energy delivered by the wave to each unit area of a surface per second.<sup>2</sup> Maxwell had argued that light is an electromagnetic

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<sup>1</sup> As an emitted electron moves toward the anode against the electric field, its energy increases, and the work done on it by the field is given by the product  $\Delta V e$ , the difference in its potential times the charge. Since this work is done at the expense of the particle’s kinetic energy, the particle will be brought to rest when its initial kinetic energy equals this product. (Compare the similar situation in Rutherford, Chapter 4, n. 13 above.) If this happens *just* before it hits the anode, then its final potential difference with respect to the cathode is practically identical to the *measured* potential difference between the anode and cathode. Assuming that all the electrons carry the same charge  $e$ , this measured  $\Delta V$  is directly proportional to the initial kinetic energy of those emitted electrons.

<sup>2</sup> Thus, for example, if all the energy in light is converted to heat upon its striking a perfectly non-reflecting surface, then doubling the intensity of the light will deliver twice as much heat per second to each square centimeter of the surface.

wave; and he had proven mathematically that if so then the intensity of light must be directly proportional to the square of the *amplitude*<sup>3</sup> of the oscillating electric field which constitutes the electric component of the wave. But the force which an electromagnetic wave applies to an electron in its path will be  $eF$ , where  $e$  is the charge on the electron and  $F$  is the strength of the electric field (at the location of the electron) at any instant. If then the amplitude of the electric field increases, the force applied to the electron at each instant likewise increases. It would seem, then, that a more intense light beam should impart greater kinetic energy to the electrons in its path than a light beam of lesser intensity would. *But it does not.* Increasing the light intensity has no discernible effect on the kinetic energy of the ejected electrons; rather it increases the *number* of electrons emitted per second from the cathode.

(2) In Maxwell's theory, the *frequency* of the incident light may play an indirect role in determining the energy imparted to electrons—for example, the light frequency might agree or disagree with some resonances that characterize the forces binding individual electrons to the solid. Nevertheless such a connection must be highly variable, and it would seem that any relation between the electron energy and light frequency would be correspondingly complicated. *But it is not.* The relation observed between electron energy and light frequency showed no such complexity.

Not surprisingly, in the five years between Planck's work (1900) and the Einstein paper (1905) physicists had tried to come up with another model that did not depend on quantization, with results ranging from partial success to catastrophic failure (see Niels Bohr's comments in Chapter 7). Nobody was inclined to take the quantum hypothesis seriously until Einstein adopted it.

He did more than adopt it, however. He gave a very radical answer to the question of *why* microscopic bodies could only absorb and emit light energy in units. Planck had proposed only that the hypothetical electrons oscillating in the radiating body emit their energy not continuously, as Maxwell's theory would require, but rather in discrete bursts of light, each burst containing an amount of energy,  $hv$ , proportional to the frequency of the individual oscillating electron and thus of the emitted light as well. He did not assume that that energy, once emitted, would continue to travel in a discontinuous distribution, because it would have contradicted the electromagnetic wave theory of light, a theory that had served remarkably well. Einstein's account in the present paper, while it harmonizes with the experimental observations on the photoelectric effect, does contradict the electromagnetic theory:

According to the presently proposed assumption, the energy in a beam of light . . . consists of a finite number of energy quanta, localized at points of space, which move without subdividing and which are absorbed and emitted only as units.

Note Einstein does not call his account a *theory* but rather a “heuristic” point of view (from “*heurisko*,” I discover)—one intended to serve as an aid to learning or discovery.

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<sup>3</sup>The *amplitude* of an oscillating quantity is the peak value which that quantity attains in each cycle, without regard to sign.

## CONCERNING A HEURISTIC POINT OF VIEW ABOUT THE CREATION AND TRANSFORMATION OF LIGHT<sup>4</sup>

ALBERT EINSTEIN

There is a profound formal difference between the theoretical representations of gases and other ponderable bodies which physicists have constructed and Maxwell's theory of electromagnetic processes in so-called empty space. Whereas we may consider the state of a body as being completely determined by the positions and velocities of, to be sure, a very large but finite number of atoms and electrons, we must use continuous spatial functions to specify the electromagnetic state of a region, so that a finite number of parameters cannot be considered as sufficient to describe completely the electromagnetic state of a region of space. According to Maxwell's theory, in all cases of pure electromagnetic phenomena, hence in the case of light, the energy must be considered as a continuous spatial function; whereas the energy of a ponderable body, according to the current concepts of physicists, can be represented by a sum taken over the atoms and electrons. The energy of a ponderable body cannot break up into arbitrarily many, arbitrarily small parts; whereas the energy of a ray of light emitted by a point source of light distributes itself continuously throughout an ever-increasing volume of space according to Maxwell's theory (or, more generally, according to any wave theory).

The wave theory, operating with continuous spatial functions, has proved to be correct in representing purely optical phenomena and will probably not be replaced by any other theory. One must, however, keep in mind that the optical observations are concerned with temporal mean values and not with instantaneous values; and it is possible, in spite of the complete experimental verification of the theory of diffraction, reflection, refraction, dispersion, and so on, that the theory of light that operates with continuous spatial functions may lead to contradictions with observations if we apply it to the phenomena of the generation and transformation of light.

It appears to me, in fact, that the observations of "black-body radiation," photoluminescence, the generating of cathode rays [by] ultraviolet radiation, and other groups of phenomena related to the generation and transformation of light can be understood better on the assumption that the energy in light is distributed discontinuously in space. According to the presently proposed assumption, the energy in a beam of light emanating from a point source is not distributed continuously over larger and larger volumes of space but consists of a finite number of energy quanta, localized at points of space, which move without subdividing and which are absorbed and emitted only as units.

In what follows, I want to present the thinking and indicate the facts that have led me along the present path in the hope that the point of view associated with these ideas may prove useful to some researchers in their investigations.<sup>5</sup>

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<sup>4</sup>[*Annalen der Physik*, 17 (1905), 132-148. Translated by the Editors of *Annalen der Physik*.]

<sup>5</sup>[What follows is section 8 of Einstein's paper, sections 1-7 and 9 being here omitted. The omitted sections treat, among other topics, black-body radiation and Planck's derivation of elementary energy quanta.]

### VIII. On the Production of Cathode Rays by Irradiating Solid Bodies

The traditional view that the energy of light is distributed continuously through the region illuminated runs into great difficulty in trying to explain photoelectric phenomena, as was outlined in a trail-blazing paper by Lenard.<sup>6</sup>

According to the concept that the exciting radiation consists of energy quanta with energy content  $h\nu$ ,<sup>7</sup> the production of cathode rays by light can be understood as follows: Quanta of energy penetrate into the surface layer of the body; and their energy, at least in part, is transformed into kinetic energy of electrons. The simplest explanation is that a quantum transfers all its energy to a single electron; we shall assume that this occurs. However, it ought not to be excluded that electrons take up only part of the energy of light quanta. An interior electron with kinetic energy will have lost some of this kinetic energy by the time it reaches the surface. Besides this we must assume that each electron will have to do some work (an amount characteristic of the body) when it leaves the body.<sup>8</sup> The electrons lying right at the surface of the body will leave the body with the greatest velocity normal [i.e. perpendicular] to the surface. The kinetic energy of such electrons is

$$h\nu - P.$$

If the body is charged to the positive potential  $\Pi$ <sup>9</sup> [...] and if  $\Pi$  is [just]<sup>10</sup> large enough to prevent a discharge of the body, then we must have

$$\Pi e = h\nu - P,<sup>11</sup>$$

where  $e$  is the electric charge of the electron, or

$$\Pi E = N h\nu - P'$$

where  $E$  [=  $Ne$ ] is the charge of a gram equivalent of a single charged ion [i.e., one faraday] and  $P'$  is the potential of this amount of negative charge relative to the body.<sup>12</sup>

If we place  $E = 9.6 \times 10^3$ , then  $\Pi \times 10^{-8}$  is the potential in volts that the body acquires on being irradiated in a vacuum.<sup>13</sup>

<sup>6</sup>[*Annalen der Physik*, 8 (1902), 169–170. We gave a brief summary of Lenard's findings above.]

<sup>7</sup>[Here  $\nu$  is the light frequency and  $h$  is Planck's constant. Einstein actually writes here not  $h$  but rather a quotient of three other constants, introduced in omitted sections of this paper. Since there he shows his own expression to be equal to Planck's we take the liberty of substituting  $h$  throughout this section. However, it is worth noting that his more complicated expression contains *Avogadro's number* in the denominator. In 1905 its size was very conjectural.]

<sup>8</sup>[The necessity for an electron to do work specifically to leave the surface of a body can be compared to the phenomenon of surface tension in a fluid. The work required is called the "work function"; Einstein denotes it by  $P$  in the expression that follows.]

<sup>9</sup>[Thus there is a potential *difference*  $\Pi$  between the body and the surrounding grounded conductors, which opposes the current. This is exactly equivalent to what Lenard did.]

<sup>10</sup>[We here correct an omission in the translation.]

<sup>11</sup> [That is,  $\Pi e$ , potential difference times charge, must equal the initial kinetic energy of the most energetic emitted electrons which are just stopped by this  $\Pi$ .]

<sup>12</sup>[The equation  $\Pi e = N h\nu - P'$  is the previous equation multiplied through by Avogadro's number  $N$ . Einstein does this because in 1905 physicists had much better measurements for the faraday  $E$  than for  $e$  and Einstein was more confident about the size of  $Nh$  than about either  $N$  or  $h$  separately. He's not worried about  $P'$  since he's about to set it to zero.]

<sup>13</sup>[The *faraday* equals 96,500 cou or about 9650 abcou. With  $E$  expressed in abcoulombs and  $h$  in erg-seconds,  $\Pi$  will be given in erg/abcou or *abvolts*. Hence  $\Pi \times 10^{-8}$  will express the potential in volts. See Appendix II.]

In order to see at first if the derived relationship is of the right order of magnitude as obtained empirically we place  $P' = 0$ ,  $\nu = 1.03 \times 10^{15}$  (corresponding to the ultraviolet limit of the solar spectrum<sup>14</sup>) and [ $Nh = 4.01 \times 10^{-3}$ ].<sup>15</sup> We obtain [ $\Pi = 4.3 \times 10^8$  abvolts, so that  $\Pi \times 10^{-8} = 4.3$ ] volts, which agrees in order of magnitude with the results of Lenard.<sup>16</sup>

If the derived formula is correct, then [ $\Pi$ ] must be a linear function of the frequency whose slope [is independent of] the nature of the material being studied.<sup>17</sup>

Our point of view, as far as I can see, does not contradict Lenard's observed properties of the photoelectric phenomena. If each quantum of energy of the exciting light gives up its energy to an electron independently of all the other quanta, then the velocity distribution of the electrons, that is, the characteristic of the produced cathode ray, is independent of the intensity of the exciting radiation; on the other hand the number of electrons leaving the body, all other conditions being the same, will depend on the intensity of the exciting radiation.

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## EXPERIMENT: THE PHOTOELECTRIC EFFECT

### Current is directly proportional to illumination intensity.

If light consists of a stream of discrete quanta of energy, and if each quantum gives up all its energy to a single electron, then the number of electrons released per second from an illuminated photocell cathode should equal the number of energy quanta absorbed per second by the cathode. But the number of electrons released per second is proportional to the *cathode current*, since each electron carries a determinate charge. And the number of energy quanta absorbed per second is proportional to the *illumination intensity*; since the very definition of that quantity is the amount of energy absorbed, per unit time, by unit area of the illuminated surface. Thus the current produced by the photocell should be proportional to the illumination supplied, as Einstein states.

To investigate this effect, a photocell is connected directly to a sensitive picoammeter as indicated in the sketch below; set the meter to the 2 microampere ( $\mu A$ ) range. An ordinary illuminating lamp makes a satisfactory light source. For a rough test of the relation between light intensity and current, observe how the photocurrent rises and falls when the light source is moved toward and away from the cell.

Examine the *variable transmission mask*. This is a strip of transparent material on which computer-generated patterns of dots and lines have been printed so as to block selected percentages of the transparent area and thereby vary the intensity of the transmitted light. The five sections transmit, respectively, 100%, 80%, 60%, 40%, and 20% of the incident light. With the lamp aimed to illuminate the photocell aperture, hold

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<sup>14</sup>[Sunlight comprises wavelengths as small as  $2902 \times 10^{-8}$  cm, corresponding to frequencies as great as  $1.03 \times 10^{15}$  cycles/sec.]

<sup>15</sup>[Einstein actually expresses  $Nh$  here in terms of two other constants. His expression does *not* contain Avogadro's number, since multiplying through by  $N$  removed it from the denominator of the three-constant expression for  $h$  mentioned in n. 8. Note that in the cgs system of measurement, Planck's constant,  $h$ , has the value  $6.6 \times 10^{-27}$  erg-sec.]

<sup>16</sup>[In the experiments mentioned above, Lenard had found that when the cathode is illuminated by direct sunlight, electrons are emitted until the cathode acquires a potential on the order of a few volts.]

<sup>17</sup>[That is, the energy acquired by the electrons will be proportional to the frequency of the exciting light.]



the transmission mask so that light passes through the section labeled "100%," and record the current generated. Repeat the measurement for the remaining sections and compare the currents to the corresponding transmission percentages.

### **Electron energy is directly proportional to light frequency.**

It follows from Einstein's equation  $\Pi e = h\nu - P$  above that the most energetic electrons among those released from the illuminated cathode will have kinetic energy *per unit charge* of amount

$$\Pi = h\nu/e - P/e$$

where  $\nu$  is the frequency of the incident light,  $e$  is the charge on the electron, and  $P$  is a constant characteristic of the material of the cathode. If  $e$  is given in abcoulombs and  $h$  in erg-seconds, then  $\Pi$  will express this energy per unit charge (the potential) in abvolts. As Einstein states, a graph of  $\Pi$  vs.  $\nu$  should yield a straight line; furthermore, it should have a slope equal to  $h/e$ , having a value of  $4.14 \times 10^{-7}$  abvolt/Hz or  $4.14 \times 10^{-15}$  volt/Hz.<sup>18</sup>

When illuminated, the photocell cathode will lose electrons and thus acquire a positive potential which continues to increase so long as electrons continue to flow from it. But, when the cathode potential rises to a value  $\Pi$  that equals the energy per unit charge of the most energetic electron, no additional electrons will be able to reach the anode, the photoelectric current will drop to zero, and the potential will stop rising. An incident light beam will therefore charge the cathode to the potential  $\Pi$ ; and we can investigate  $\Pi$  as a function of  $\nu$  by causing light of various frequencies to charge the cathode to the corresponding potentials.

For a source of illumination, we shall use a spectrometer diffraction grating to separate out individual *spectral lines*<sup>19</sup> from an intense mercury vapor lamp. The principal lines are given in the following table.

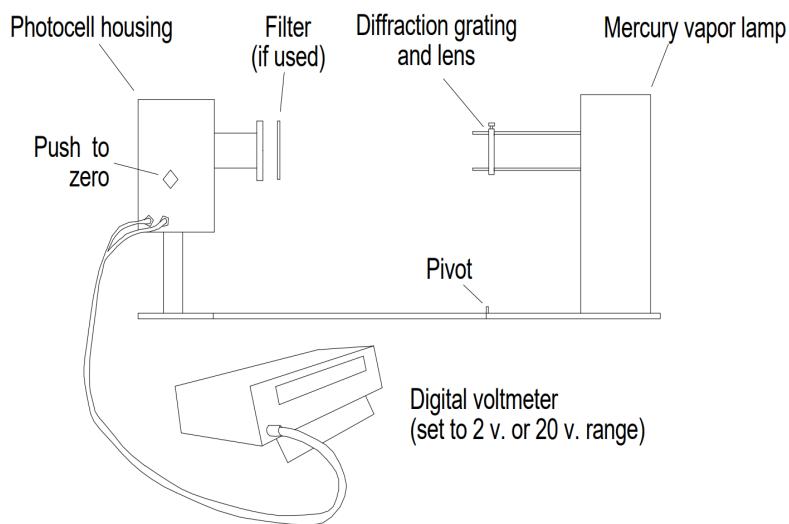
<sup>18</sup>The quotient of presently accepted values  $h = 6.625 \times 10^{-27}$  erg/Hz and  $e = 1.6 \times 10^{-20}$  abcoul is  $4.14 \times 10^{-7}$  abvolt/Hz.

<sup>19</sup>Glowing gases, unlike glowing solid bodies, give off light in pure, isolated, sharply-demarcated colors, which gives a pattern of isolated monochromatic lines separated by wide dark areas when passed

	$\lambda$	$\nu$
Yellow <sup>20</sup>	5780 Å <sup>21</sup>	$5.19 \times 10^{14} \text{ Hz}$
Green	5461	5.49
Blue	4358	6.88
Violet	4047	7.41
Ultraviolet	3655	8.20

Our light source is rich in ultraviolet content and is capable of damaging the eyes. Suitable protective shielding is provided and you should not remove it or attempt to defeat its purpose. Needless to say, *you should avoid looking directly at the beam of light or any reflections*. Note that the mercury vapor lamp requires a warm-up period of about five minutes before measurements are made. Also, frequent on-off operation will reduce the lamp life; once turned on, it is best to leave it burning until all work for that session is completed.

The apparatus for this part of the experiment is diagrammed here.



Light exits through a narrow slit at the front of the lamp and is focused on the photocell aperture by means of an adjustable lens.<sup>22</sup> A diffraction grating is mounted adjacent to the lens and forms a spectrum of lines on either side of the beam axis. The spectrum is significantly brighter on one side than on the other; make your measurements on the brighter spectrum.

The sketch below shows a top view of the apparatus. Each line of the Mercury spectrum can be separately introduced to the photocell by moving the cell to the appropriate position. The spectral lines will be clearly reflected on the white mask surrounding

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through a diffraction grating. *Why* this should be is a question which Neils Bohr addresses in our next reading: it proves to have a profound bearing on atomic structure.

<sup>21</sup>There are really two yellow lines in the mercury spectrum, at 5770 and 5882 Å, respectively; but these are not separable by the grating and so the line of higher frequency will predominate, according to Einstein's treatment.

<sup>22</sup>(One Angstrom (Å) equals  $10^{-8}$  cm.)

<sup>22</sup>The laboratory assistants will have already performed an internal alignment to insure that light falling on the aperture fully enters the photocell. If you wish to check this adjustment, the procedure is described in the final section of this chapter.

the photocell aperture. This mask has been made slightly fluorescent in order to reveal the location of the otherwise invisible ultraviolet band; it will emit a blue glow where it is illuminated by ultraviolet light.



A voltmeter measures the potential difference between the photocell cathode and anode. But ordinary measuring instruments cannot be connected to the photocell directly, since they lack sufficient sensitivity and would actually discharge the photocell in the very process of measuring its potential. For this part of the experiment, therefore, the photocell unit is equipped with a battery-powered amplifier circuit that in effect *reproduces* the cell's potential difference at a pair of auxiliary terminals. The voltmeter connected to these terminals will indicate a potential difference equal to that developed between cathode and anode. Turn the battery switch on at the beginning of each session, and please remember to turn it off again when you conclude your work.<sup>23</sup>

For each measurement, swing the photocell unit until the desired spectral line falls on the aperture in the cell housing. Take care to permit only one line at a time to illuminate the aperture. Also, it is best to confine your measurements to the *first order* of lines produced by the diffraction grating. Even though the grating will furnish two or even three orders of spectral lines, the second- and third-order patterns overlap one another, making some lines unusable.

When measuring the green or yellow spectral lines, be sure to mount the corresponding green or yellow filter over the face of the cell aperture. Otherwise ambient light in the room, or even stray reflections from other spectral lines, might enter the cell housing and cause erroneous readings. The filters attach easily with magnetic strips. Please treat the filters with care, as they are easily scratched.

Notice the switch labeled "push to zero" on the rear of the photocell unit. You should operate this switch prior to each reading in order to discharge any previously accumulated potential difference.

When the photocell is illuminated, and the "zero" switch pressed and released, the voltmeter will gradually rise to a stable value which represents the maximum potential  $\Pi$ , corresponding to the frequency  $\nu$  of the light presently being admitted to the cell.<sup>24</sup>

Our digital voltmeters perform poorly when their batteries run down; *please* turn off the voltmeters at the end of each session. If the readings obtained for bright spectral lines appear to be erratic, try another voltmeter, or replace the battery. But note that

<sup>23</sup>The battery voltage can be tested at the two terminals marked "test." Six volts is the minimum acceptable reading between each test terminal and the chassis.

<sup>24</sup>In some devices, the voltmeter will temporarily read *high* and gradually *decrease* to a stable value. This reflects a variation in the manufacturer's amplifier circuit; but the stable reading nevertheless indicates the actual potential difference in the photocell.

when the photocell is *not* illuminated, it is normal for the voltmeter readings to drift randomly.

#### **INTERNAL ALIGNMENT — Adjust only if necessary**

1. Swing the photocell to the side having the brighter diffraction pattern until the green line, say, falls on the white mask surrounding the photocell aperture.
2. Roll the cylindrical light shield out of the way to reveal a second white mask with a smaller aperture. Loosen the thumbscrew on the photocell housing support rod and rotate the photocell unit until the green line is centered both on the aperture of the external mask *and* the aperture of the internal mask, simultaneously. Tighten the support rod thumbscrew securely.
3. Loosen the thumbscrew on the diffraction grating/lens assembly and slide it back and forth on the support rods to focus the light onto the internal white mask. Roll the cylindrical light shield back into position; tighten the grating/lens thumbscrew to hold the assembly in place.
4. For additional alignment accuracy, repeat steps 2 and 3 again.



## CHAPTER 7

## ON THE SPECTRUM OF HYDROGEN

NIELS BOHR

ON THE SPECTRUM OF HYDROGEN<sup>1</sup>

*Empirical Spectral Laws.* Hydrogen possesses not only the smallest atomic weight of all the elements, but it also occupies a peculiar position both with regard to its physical and its chemical properties. One of the points where this becomes particularly apparent is the hydrogen line spectrum.

The spectrum of hydrogen observed in an ordinary Geissler tube consists of a series of lines,<sup>2</sup> the strongest of which lies at the red end of the spectrum, while the others extend out into the ultra violet, the distance between the various lines, as well as their intensities, constantly decreasing. In the ultra violet the series converges to a limit.

Balmer, as we know, discovered (1885) that it was possible to represent the wave lengths of these lines very accurately by the simple law

$$\frac{1}{\lambda_n} = R \left( \frac{1}{4} - \frac{1}{n^2} \right), \quad (1)$$

where  $R$  is a constant and  $n$  is a whole number. The wave lengths of the five strongest hydrogen lines, corresponding to  $n = 3, 4, 5, 6, 7$ , measured in air at ordinary pressure and temperature, and the values of these wave lengths multiplied by

$$\left( \frac{1}{4} - \frac{1}{n^2} \right)$$

are given in the following table:<sup>3</sup>

$n$	$\lambda \cdot 10^8 [\text{\AA}]$	$\lambda \cdot \left( \frac{1}{4} - \frac{1}{n^2} \right) \cdot 10^{10}$
3	6563.04	91153.3
4	4861.49	91152.9
5	4340.66	91153.9
6	4101.85	91152.2
7	3970.25	91153.7

The table shows that the product is nearly constant, while the deviations are not greater than might be ascribed to experimental errors.

As you already know, Balmer's discovery of the law relating to the hydrogen spectrum led to the discovery of laws applying to the spectra of other elements. The most

<sup>1</sup>[Address delivered before the Physical Society in Copenhagen, Dec. 20, 1913. Essay I from *The Theory of Spectra and Atomic Constitution*, Cambridge, 1922.]

<sup>2</sup>[You saw similar sharp lines in the last practicum.]

<sup>3</sup>[Recall that an Ångstrom unit equals  $10^{-8}$  cm. Thus, for example, 6563.04 in the second column actually equals  $6.563 \times 10^{-5}$  cm. The third column, by Eq. 1, gives  $1/R \times 10^{10}$ .]

important work in this connection was done by Rydberg (1890) and Ritz (1908). Rydberg pointed out that the spectra of many elements contain series of lines whose wave lengths are given approximately by the formula

$$\frac{1}{\lambda_n} = A - \frac{R}{(n + \alpha)^2}$$

where  $A$  and  $\alpha$  are constants having different values for the various series, while  $R$  is a universal constant equal to the constant in the spectrum of hydrogen. If the wave lengths are measured in vacuo Rydberg calculated the value of  $R$  to be 109675.<sup>4</sup> In the spectra of many elements, as opposed to the simple spectrum of hydrogen, there are several series of lines whose wave lengths are to a close approximation given by Rydberg's formula if different values are assigned to the constants  $A$  and  $\alpha$ . Rydberg showed, however, in his earliest work, that certain relations existed between the constants in the various series of the spectrum of one and the same element. These relations were later very successfully generalized by Ritz through establishment of the "combination principle." According to this principle, the wave lengths of the various lines in the spectrum of an element may be expressed by the formula

$$\frac{1}{\lambda} = F_r(n_1) - F_s(n_2). \quad (2)$$

In this formula  $n_1$  and  $n_2$  are whole numbers, and  $F_1(n), F_2(n), \dots$  is a series of functions of  $n$ , which may be written approximately

$$F_r(n) = \frac{R}{(n + \alpha_r)^2}$$

where  $R$  is Rydberg's universal constant and  $\alpha_r$  is a constant which is different for the different functions. A particular spectral line will, according to this principle, correspond to each combination of  $n_1$  and  $n_2$ , as well as to the functions  $F_1, F_2, \dots$ . The establishment of this principle led therefore to the prediction of a great number of lines which were not included in the spectral formulae previously considered, and in a large number of cases the calculations were found to be in close agreement with the experimental observations. In the case of hydrogen Ritz assumed that formula (1) was a special case<sup>5</sup> of the general formula

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad (3)$$

and therefore predicted among other things a series of lines in the infra red given by the formula

$$\frac{1}{\lambda} = R \left( \frac{1}{9} - \frac{1}{n_2^2} \right),$$

In 1909 Paschen succeeded in observing the first two lines of this series corresponding to  $n = 4$  and  $n = 5$ .

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<sup>4</sup>[One over this  $\times 10^{10}$  is 91178.5 (this is for a vacuum, not air as in the previous table).]

<sup>5</sup>["special case": Formula (1) is that special case of equation (3) in which  $n_1^2$  has the value 4. Equation (3) is in turn that special case of equation (2) in which  $F_r(n)$  and  $F_s(n)$  each have the form  $R/n^2$ .]

The discovery of these beautiful and simple laws concerning the line spectra of the elements has naturally resulted in many attempts at a theoretical explanation. Such attempts are very alluring because the simplicity of the spectral laws and the exceptional accuracy with which they apply appear to promise that the correct explanation will be very simple and will give valuable information about the properties of matter. I should like to consider some of these theories somewhat more closely, several of which are extremely interesting and have been developed with the greatest keenness and ingenuity, but unfortunately space does not permit me to do so here. I shall have to limit myself to the statement that not one of the theories so far proposed appears to offer a satisfactory or even a plausible way of explaining the laws of the line spectra. Considering our deficient knowledge of the laws which determine the processes inside atoms it is scarcely possible to give an explanation of the kind attempted in these theories. The inadequacy of our ordinary theoretical conceptions has become especially apparent from the important results which have been obtained in recent years from the theoretical and experimental study of the laws of temperature radiation.<sup>6</sup> You will therefore understand that I shall not attempt to propose an explanation of the spectral laws; on the contrary I shall try to indicate a way in which it appears possible to bring the spectral laws into close connection with other properties of the elements, which appear to be equally inexplicable on the basis of the present state of the science. In these considerations I shall employ the results obtained from the study of temperature radiation as well as the view of atomic structure which has been reached by the study of the radioactive elements.

*Laws of temperature radiation.* I shall commence by mentioning the conclusions which have been drawn from experimental and theoretical work on temperature radiation.

Let us consider an enclosure surrounded by bodies which are in temperature equilibrium. In this space there will be a certain amount of energy contained in the rays emitted by the surrounding substances and crossing each other in every direction. By making the assumption that the temperature equilibrium will not be disturbed by the mutual radiation of the various bodies Kirchoff (1860) showed that the amount of energy per unit volume as well as the distribution of this energy among the various wave lengths is independent of the form and size of the space and of the nature of the surrounding bodies and depends only on the temperature. Kirchoff's result has been confirmed by experiment, and the amount of energy and its distribution among the various wave lengths and the manner in which it depends on the temperature are now fairly well known from a great amount of experimental work; or, as it is usually expressed, we have a fairly accurate experimental knowledge of the "laws of temperature radiation."

Kirchoff's considerations were only capable of predicting the existence of a law of temperature radiation, and many physicists have subsequently attempted to find a more thorough explanation of the experimental results. You will perceive that the electromagnetic theory of light together with the electron theory suggests a method of solving this problem. According to the electron theory of matter<sup>7</sup> a body consists of a

<sup>6</sup>[By "temperature radiation" Bohr refers to what was called "black-body radiation" by Planck and Einstein. In the following section of this paper Bohr offers his own account.]

<sup>7</sup>[“One has been led to the conception of *electrons*, i.e. extremely small particles, charged with electricity, which are present in immense numbers in all ponderable bodies, and by whose distribution and motions we endeavor to explain all electric and optical pheno-mena that are not confined to free ether” (H. A. Lorentz, *The Theory of Electrons*, 1905).]

system of electrons. By making certain definite assumptions concerning the forces acting on the electrons it is possible to calculate their motion and consequently the energy radiated from the body per second in the form of electromagnetic oscillations of various wave lengths. In a similar manner the absorption of rays of a given wave length by a substance can be determined by calculating the effect of electromagnetic oscillations upon the motion of the electrons[...]. As is well known this has been done by Lorentz (1903). He calculated the emissive as well as the absorptive power of a metal for long wave lengths[...]. Lorentz really obtained an expression for the law of temperature radiation which for long wave lengths agrees remarkably well with experimental facts. In spite of this beautiful and promising result, it has nevertheless become apparent that the electromagnetic theory is incapable of explaining the law of temperature radiation. For, it is possible to show, that, if the investigation is not confined to oscillations of long wave lengths, as in Lorentz's work, but is also extended to oscillations corresponding to small wave lengths, results are obtained which are contrary to experiment. This is especially evident from Jeans' investigations (1905) in which he employed a very interesting statistical method first proposed by Lord Rayleigh.

We are therefore compelled to assume, that the classical electrodynamics does not agree with reality, or expressed more carefully, that it cannot be employed in calculating the absorption and emission of radiation by atoms. Fortunately the law of temperature radiation has also successfully indicated the direction in which the necessary changes are to be sought. Even before the appearance of the papers by Lorentz and Jeans, Planck (1900) had derived theoretically a formula for the black body radiation which was in good agreement with the results of experiment. Planck did not limit himself exclusively to the classical electrodynamics, but introduced the further assumption that a system of oscillating electrical particles (elementary resonators) will neither radiate nor absorb energy continuously, as required by the ordinary electrodynamics, but on the contrary will radiate and absorb discontinuously. The energy contained within the system at any moment is always equal to a whole multiple of the so-called quantum of energy the magnitude of which is equal to  $h\nu$ , where  $h$  is Planck's constant and  $\nu$  is the frequency of oscillation of the system per second. In formal respects Planck's theory leaves much to be desired; in certain calculations the ordinary electrodynamics is used, while in others assumptions distinctly at variance with it are introduced without any attempt being made to show that it is possible to give a consistent explanation of the procedure used. Planck's theory would hardly have acquired general recognition merely on the ground of its agreement with experiments on black body radiation, but, as you know, the theory has also contributed quite remarkably to the elucidation of many different physical phenomena, such as specific heats, photoelectric effect, X-rays and the absorption of heat rays by gases. These explanations involve more than the qualitative assumption of a discontinuous transformation of energy, for with the aid of Planck's constant  $h$  it seems possible, at least approximately, to account for a great number of phenomena about which nothing could be said previously. It is therefore hardly too early to express the opinion that, whatever the final explanation will be, the discovery of "energy quanta" must be considered as one of the most important results arrived at in physics, and must be taken into consideration in investigations of the properties of atoms and particularly in connection with any explanation of the spectral laws in which such phenomena as the emission and absorption of electro-magnetic radiation are concerned.

*The nuclear theory of the atom.* We shall now consider the second part of the foun-

dation on which we shall build, namely the conclusions arrived at from experiments with the rays emitted by radioactive substances. I have previously here in the Physical Society had the opportunity of speaking of the scattering of  $\alpha$  rays in passing through thin plates, and to mention how Rutherford (1911) has proposed a theory for the structure of the atom in order to explain the remarkable and unexpected results of these experiments. I shall, therefore, only remind you that the characteristic feature of Rutherford's theory is the assumption of the existence of a positively charged nucleus inside the atom. A number of electrons are supposed to revolve in closed orbits around the nucleus, the number of these electrons being sufficient to neutralize the positive charge of the nucleus. The dimensions of the nucleus are supposed to be very small in comparison with the dimensions of the orbits of the electrons, and almost the entire mass of the atom is supposed to be concentrated in the nucleus.

According to Rutherford's calculations the positive charge of the nucleus [for a given element] corresponds to a number of electrons equal to about half the atomic weight [of that element]. This number coincides approximately with the number of the particular element in the periodic system and it is therefore natural to assume that the number of electrons in the atom is exactly equal to that number. This hypothesis, which was first stated by van den Broek (1912), opens the possibility of obtaining a simple explanation of the periodic system.<sup>8</sup> This assumption is strongly confirmed by experiments on the elements of small atomic weight. In the first place, it is evident that according to Rutherford's theory the  $\alpha$  particle is the same as the nucleus of a helium atom. Since the  $\alpha$  particle has a double positive charge it follows immediately that a neutral helium atom contains two electrons. Further the concordant results obtained from calculations based on experiments as different as the diffuse scattering of X-rays and the decrease in velocity of  $\alpha$  rays in passing through matter render the conclusion extremely likely that a hydrogen atom contains only a single electron. This agrees most beautifully with the fact that J. J. Thomson in his well-known experiments on rays of positive electricity has never observed a hydrogen atom with more than a single positive charge, while all other elements investigated may have several charges.

Let us now assume that a hydrogen atom simply consists of an electron revolving around a nucleus of equal and opposite charge, and of a mass which is very large in comparison with that of the electron. It is evident that this assumption may explain the peculiar position already referred to which hydrogen occupies among the elements, but it appears at the outset completely hopeless to attempt to explain anything at all of the special properties of hydrogen, still less its line spectrum, on the basis of considerations relating to such a simple system.

Let us assume for the sake of brevity that the mass of the nucleus is infinitely large in proportion to that of the electron, and that the velocity of the electron is very small in comparison with that of light.<sup>9</sup> If we now temporarily disregard the energy radiation, which, according to the ordinary electrodynamics, will accompany the accelerated motion of the electron, the latter in accordance with Kepler's first law will describe an

<sup>8</sup>[Recall that Mendeleev (1871) had noticed that some elements appeared to belong at places in his periodic system that would be out of order with their accepted atomic weights. He went so far as to presume to "correct" the atomic weight of tellurium in order to rectify this apparent violation. The hypothesis referred to by Bohr has proved to be a sounder approach: the atoms perfectly display their periodic properties when ordered not by *weight* but by *number of electrons* (or, what is the same, *number of positive charges in the nucleus*).]

<sup>9</sup>[With this simplifying assumption Bohr avoids having to apply Einstein's relativity theory.]

ellipse with the nucleus in one of the foci. Denoting the frequency of revolution by  $\omega$ , and the major axis of the ellipse by  $2a$  we find that

$$\omega^2 = \frac{2W^3}{\pi^2 e^4 m}, \quad 2a = \frac{e^2}{W} \quad (4)$$

where  $e$  is the charge of the electron and  $m$  its mass, while  $W$  is the work which must be added to the system in order to remove the electron to an infinite distance from the nucleus.<sup>10</sup>

These expressions are extremely simple and they show that the magnitude of the frequency of revolution as well as the length of the major axis depend only on  $W$ , and are independent of the eccentricity of the orbit. By varying  $W$  we may obtain all possible values for  $\omega$  and  $2a$ . This condition shows, however, that it is not possible to employ the above formulae directly in calculating the orbit of the electron in a hydrogen atom. For this it will be necessary to assume that the orbit of the electron can not take on all values, and in any event, the line spectrum clearly indicates that the oscillations of the electron cannot vary continuously between wide limits.<sup>11</sup> The impossibility of making any progress with a simple system like the one considered here might have been foretold from a consideration of the dimensions involved; for with the aid of  $e$  and  $m$  alone

<sup>10</sup>[ $W$  therefore is the *ionization energy*, the work required to remove the electron completely and thereby form a hydrogen *ion*. Let us derive equations (4) for the case of a circular orbit.

(a) By Coulomb's Law, the electrostatic force exerted on the orbiting electron is  $f = -e^2/r^2$  (negative because attractive, that is, opposite to the direction of increasing  $r$ ). Integrate this to obtain the potential energy at radius  $a$ :

$$\text{p.e.} = \int_{\infty}^a (-e^2/r^2) dr = -e^2/a.$$

Now the centripetal force associated with a circular orbit of radius  $a$  is  $mv^2/a$  (*Principia* Book I, Prop. 4, Cor. 1). Setting this equal to the electrostatic attractive force,

$$mv^2/a = e^2/a^2; \quad \text{or} \quad mv^2 = e^2/a. \quad (i)$$

This gives the kinetic energy k.e.  $= mv^2/2 = e^2/2a$  and the total energy  $e$  will be the sum of p.e. and k.e., so that  $E = -e^2/2a$ .

Now to "remove" the electron is to make radius  $a$  increase without limit, and hence to change the energy  $e$  from its present negative value to zero. To do so we must *add* energy in the amount  $e^2/2a$ , and hence

$$W = e^2/2a, \quad (ii)$$

which is the righthand member of Bohr's equations (4). Note that in general, if energy must be *added* to the un-ionized atom in order to bring it to an energy level of *zero*, then  $e + W = 0$ , and therefore  $e = -W$ . Bohr will make this relation explicit later on; see note 17 below.

(b) If the electron has tangential velocity  $v$  and the circumference of its orbit is  $2\pi a$ , then the number of revolutions it accomplishes per second will be  $\omega = v/2\pi a$ , from which

$$\omega^2 = v^2/4\pi^2 a^2.$$

But from (i) above,  $v^2 = e^2/ma$ ,

while from (ii),  $a = e^2/2W$ .

Substituting for  $v^2$  and  $a$  then yields

$$\omega^2 = e^2/4\pi^2 ma^3 = 2W^3/\pi^2 me^4,$$

the lefthand member of equations (4). Note that Bohr uses the symbol  $\omega$  to denote *simple frequency* (revolutions per second) and not *angular velocity* (radians per second).

One may prove that equations (4) hold also for an *elliptical* orbit of the same diameter  $2a$ ; use the Corollary to Prop. 15 and Corollary IV to Prop. 16 of Newton's *Principia*, Book I.]

<sup>11</sup>[Otherwise we should expect the spectroscopy pattern to show not sharp monochromatic lines but broad blurs covering the range of frequencies in question.]

it is impossible to obtain a quantity which can be interpreted as a diameter of an atom or as a frequency.<sup>12</sup>

If we attempt to account for the radiation of energy in the manner required by the ordinary electrodynamics it will only make matters worse. As a result of the radiation of energy,  $W$  would continually increase, and the above expressions (4) show that at the same time the frequency of revolution of the system would increase, and the dimensions of the orbit decrease.<sup>13</sup> This process would not stop until the particles had approached so closely to one another that they no longer attracted each other.<sup>14</sup> The quantity of energy which would be radiated away before this happened would be very great. If we were to treat these particles as geometrical points this energy would be infinitely great, and with the dimensions of the electrons as calculated from their mass (about  $10^{-13}$  cm), and of the nucleus as calculated by Rutherford (about  $10^{-12}$  cm), this energy would be many times greater than the energy changes with which we are familiar in ordinary atomic processes.

It can be seen that it is impossible to employ Rutherford's atomic model so long as we confine ourselves exclusively to the ordinary electrodynamics. But this is nothing more than might have been expected. As I have mentioned we may consider it to be an established fact that it is impossible to obtain a satisfactory explanation of the experiments on temperature radiation with the aid of electrodynamics, no matter what atomic model be employed. The fact that the deficiencies of the atomic model we are considering stand out so plainly is therefore perhaps no serious drawback; even though the defects of other atomic models are much better concealed they must nevertheless be present and will be just as serious.

*Quantum theory of spectra.* Let us now try to overcome these difficulties by applying Planck's theory to the problem.

It is readily seen that there can be no question of a direct application of Planck's theory. This theory is concerned with the emission and absorption of energy in a system of electrical particles, which oscillate with a given frequency per second, dependent only on the nature of the system and independent of the amount of energy contained in the system. In a system consisting of an electron and a nucleus the period of oscillation corresponds to the period of revolution of the electron. But the formula (4) for  $\omega$  shows that the frequency of revolution depends upon  $W$ , i.e. on the energy of the system. Still the fact that we can not immediately apply Planck's theory to our problem is not as serious as it might seem to be, for in assuming Planck's theory we have manifestly acknowledged the inadequacy of the ordinary electrodynamics and have definitely parted with the coherent group of ideas on which the latter theory is based. In fact in taking such a step we cannot expect that all cases of disagreement between the theoretical conceptions hitherto employed and experiment will be removed by the use of Planck's assumption regarding the quantum of the energy momentarily present in an oscillating system. We stand here almost entirely on virgin ground, and upon introducing new assumptions we need only take care not to get into contradiction with

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<sup>12</sup>[For example, the electrostatic unit of charge is expressed in  $gm^{1/2} - cm^{3/2} - sec^{-1}$ , while the unit of mass is  $gm$ . No combination of these units alone can yield either  $cm$  ("the diameter of an atom") or  $sec^{-1}$  ("a frequency") exclusively.]

<sup>13</sup>[The electron, like any satellite which lost energy, would fall toward the center and thus, by Kepler's law of periods or by Newton IV, 6, would revolve with a decreased period or increased frequency. If  $W$  is the work required to remove the electron, then clearly  $W$  increases as the electron loses energy.]

<sup>14</sup>[That is, until the particles had reached the limit, if there is one, of their approach to one another.]

experiment. Time will have to show to what extent this can be avoided; but the safest way is, of course, to make as few assumptions as possible.

With this in mind let us first examine the experiments on temperature radiation. The subject of direct observation is the distribution of radiant energy over oscillations of the various wave lengths. Even though we may assume that this energy comes from systems of oscillating particles, we know little or nothing about these systems. No one has ever seen a Planck's resonator, nor indeed even measured its frequency of oscillation; we can observe only the period of oscillation of the radiation which is emitted. It is therefore very convenient that it is possible to show that to obtain the laws of temperature radiation it is not necessary to make any assumptions about the systems which emit the radiation except that the amount of energy emitted each time shall be equal to  $h\nu$ , where  $h$  is Planck's constant and  $\nu$  is the frequency of the radiation. Indeed, it is possible to derive Planck's law of radiation from this assumption alone, as shown by Debye, who employed a method which is a combination of that of Planck and Jeans. Before considering any further the nature of the oscillating systems let us see whether it is possible to bring this assumption about the emission of radiation into agreement with the spectral laws.

If the spectrum of some element contains a spectral line corresponding to the frequency  $\nu$  it will be assumed that one of the atoms of the element (or some other elementary system) can emit an amount of energy  $h\nu$ . Denoting the energy of the atom before and after the emission of the radiation by  $E_1$  and  $E_2$  we have<sup>15</sup>

$$h\nu = E_1 - E_2 \quad \text{or} \quad \nu = \frac{E_1}{h} - \frac{E_2}{h}. \quad (5)$$

During the emission of the radiation the system may be regarded as passing from one state to another; in order to introduce a name for these states, we shall call them "stationary" states, simply indicating thereby that they form some kind of waiting places between which occurs the emission of the energy corresponding to the various spectral lines. As previously mentioned the spectrum of an element consists of a series of lines whose wave lengths may be expressed by the formula (2). By comparing this expression with the relation given above it is seen that—since  $\nu = c/\lambda$ , where  $c$  is the velocity of light—each of the spectral lines may be regarded as being emitted by the transition of a system between two stationary states in which the energy apart from an arbitrary additive constant is given by  $-chF_r(n_1)$  and  $-chF_s(n_2)$  respectively.<sup>16</sup> Using

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<sup>15</sup>[The subscripts <sub>1</sub> and <sub>2</sub> here mean simply *before* and *after* emission. It will be helpful to think of equation (5) as if it were written

$$\nu = E_{bef}/h - E_{aft}/h.$$

Note that since  $\nu$  must be positive,  $E_{bef}$  must exceed  $E_{aft}$ .]

<sup>16</sup>[We saw earlier that the most general form of the empirical spectral laws is Eq. (2):

$$1/\lambda = F_r(n_1) - F_s(n_2);$$

therefore since  $1/\lambda$  is also equal to  $\nu/c$ , we can write

$$\nu = cF_r(n_1) - cF_s(n_2).$$

But from equation (5) we also have

$$\nu = E_{bef}/h - E_{aft}/h$$

(cf. our previous note). When the two expressions for  $\nu$  are equated, it is attractive to try to associate them term by term. *One way* of doing so (there are others) is to set

$$E_{bef} = -chF_s(n_2) \quad \text{and} \quad E_{aft} = -chF_r(n_1).$$

this interpretation the combination principle asserts that a series of stationary states exists for the given system, and that it can pass from one to any other of these states with the emission of a monochromatic radiation. We see, therefore, that with a simple extension of our first assumption it is possible to give a formal explanation of the most general law of line spectra.

*Hydrogen spectrum.* This result encourages us to make an attempt to obtain a clear conception of the stationary states which have so far only been regarded as formal. With this end in view, we naturally turn to the spectrum of hydrogen. The formula applying to this spectrum is given by the expression [from equation (3) above]

$$\frac{1}{\lambda} = \frac{R}{n_1^2} - \frac{R}{n_2^2}.$$

According to our assumption this spectrum is produced by transitions between a series of stationary states of a system, concerning which we can for the present only say that the energy of the system in the  $n$ th state, apart from an additive constant, is given by  $-Rhc/n^2$ .<sup>17</sup> Let us now try to find a connection between this and the model of the hydrogen atom. We assume that in the calculation of the frequency of revolution of the electron in the stationary states of the atom it will be possible to employ the above formula for  $\omega$ . It is quite natural to make this assumption; since, in trying to form a reasonable conception of the stationary states, there is, for the present at least, no other means available besides the ordinary mechanics.

Corresponding to the  $n$ th stationary state in formula (4) for  $\omega$ , let us by way of experiment put  $W = Rhc/n^2$ .<sup>18</sup> This gives us

$$\omega_n^2 = \frac{2}{\pi^2} \frac{R^3 h^3 c^3}{e^4 m n^6}. \quad (6)$$

The radiation of light corresponding to a particular spectral line is according to our assumption emitted by a transition between two stationary states, corresponding to two different frequencies of revolution, and we are not justified in expecting any simple relation between these frequencies of revolution of the electron and the frequency of the emitted radiation.<sup>19</sup> You understand, of course, that I am by no means trying to give what might ordinarily be described as an explanation; nothing has been said here about how or why the radiation is emitted. On one point, however, we may expect a connection with the ordinary conceptions; namely that it will be possible to calculate

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To some extent, it is the aim of the rest of Bohr's paper to give us reasons for adopting these equalities as a theoretical hypothesis.

Note also that since integers  $n_1$  and  $n_2$  appear in the denominators for functions  $F_r$  and  $F_s$  (note 5 above), then must  $n_2 > n_1$  since  $E_{bef} > E_{aft}$ . But *any* stationary state can be regarded either as a "before" or an "after" state. Hence all stationary states of the atom, without exception, are expressible in either of the forms

$$E_n = -chF_r(n) \quad \text{or} \quad E_n = -chF_s(n),$$

where the greater energy (that is, less negative) corresponds in each case to the larger value of  $n$ . For hydrogen,  $F_r(n)$  and  $F_s(n)$  prove to be identical functions, each equal to  $R/n^2$  as indicated in equation (3). So Bohr will express the stationary states for hydrogen in the general form  $E_n = -Rhc/n^2$ .

<sup>17</sup>[See the last paragraph of the previous note.]

<sup>18</sup>[We saw in note 10 above that  $W$  is numerically equal to the energy of the system but opposite in sign. Since now the energy of any stationary state has been taken to be  $-Rhc/n^2$ ,  $W$  must be  $Rhc/n^2$ .]

<sup>19</sup>[By sharp contrast, under Maxwell's theory a charged body orbiting with any frequency  $\omega$  must generate electromagnetic waves having the same frequency  $\omega$ .]

the emission of slow electromagnetic oscillations on the basis of the classical electrodynamics. This assumption is very strongly supported by the result of Lorentz's calculations which have already been described. From the formula for  $\omega$  it is seen that the frequency of revolution decreases as  $n$  increases, and that the expression  $\omega_n/\omega_{n+1}$  approaches the value 1.<sup>20</sup>

According to what has been said above, the frequency of the radiation corresponding to the transition between the  $(n + 1)$ th and the  $n$ th stationary state is given by

$$\nu = Rc \left( \frac{1}{n^2} - \frac{1}{(n+1)^2} \right).$$

If  $n$  is very large this expression is approximately equal to

$$\nu = 2Rc/n^3.$$
<sup>21</sup>

In order to obtain a connection with the ordinary electrodynamics let us now place this frequency equal to the frequency of revolution, that is

$$\omega_n = 2Rc/n^3.$$

Introducing this value of  $\omega_n$  in (6) we see that  $n$  disappears from the equation, and further that the equation will be satisfied only if

$$R = \frac{2\pi^2 e^4 m}{ch^3} \quad (7)$$

The constant  $R$  is very accurately known, and is, as I have said before, equal to 109675. By introducing the most recent values of  $e$ ,  $m$  and  $h$  the expression on the right-hand side of the equation becomes equal to  $1.09 \times 10^5$ . The agreement is as good as could be expected, considering the uncertainty in experimental determination of the constants  $e$ ,  $m$  and  $h$ . The agreement between our calculations and the classical electrodynamics is, therefore, fully as good as we are justified in expecting.

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Let us continue with the elucidation of the calculations, and in the expression for  $2a$  introduce the value of  $W$  which corresponds to the  $n$ th stationary state. This gives us

$$2a = n^2 \cdot \frac{e^2}{chR} = n^2 \cdot \frac{h^2}{2\pi^2 me^2} = n^2 \cdot 1.1 \times 10^{-8}. \quad (8)$$

It is seen that for small values of  $n$ , we obtain values for the major axis of the orbit of the electron which are of the same order of magnitude as the values of the diameters of the atoms calculated from the kinetic theory of gases. For large values of  $n$ ,  $2a$  becomes very large in proportion to the calculated dimensions of the atoms. This, however, does not necessarily disagree with experiment. Under ordinary circumstances a

<sup>20</sup>[From equation (6) it follows algebraically that  $\omega_n/\omega_{n+1} = (n+1)^3/n^3$ ; and the latter approaches 1 as  $n \rightarrow \infty$ .]

<sup>21</sup>[For,

$$\frac{1}{n^2} - \frac{1}{(n+1)^2} = \frac{(n+1)^2 - n^2}{n^2(n+1)^2} = \frac{2n+1}{n^2(n+1)^2}.$$

In the rightmost expression, as  $n$  grows large 1 becomes negligible in comparison to it and the expression  $2n/n^4 = 2/n^3$  becomes a better and better approximation for it. (Put more strictly, as the ratio between the two expressions goes to 1:1, as you may be able to establish by dividing one by the other.)]

hydrogen atom will probably exist only in the state corresponding to  $n = 1$ . For this state  $W$  will have its greatest value and, consequently, the atom will have emitted the largest amount of energy possible; this will therefore represent the most stable state of the atom from which the system can not be transferred except by adding energy to it from without. The large values for  $2a$  corresponding to large  $n$  need not, therefore, be contrary to experiment; indeed, we may in these large values seek an explanation of the fact, that in the laboratory it has hitherto not been possible to observe the hydrogen lines corresponding to large values of  $n$  in Balmer's formula, while they have been observed in the spectra of certain stars. In order that the large orbits of the electrons may not be disturbed by electrical forces from the neighboring atoms the pressure will have to be very low, so low, indeed, that it is impossible to obtain sufficient light from a Geissler tube of ordinary dimensions. In the stars, however, we may assume that we have to do with hydrogen which is exceedingly attenuated and distributed throughout an enormously large region of space.

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*Other spectra.* For the spectra of other elements the problem becomes more complicated, since the atoms contain a larger number of electrons. It has not yet been possible on the basis of this theory to explain any other spectra besides those which I have already mentioned.<sup>22</sup> On the other hand it ought to be mentioned that the general laws applying to the spectra are very simply interpreted on the basis of our assumptions[...].

I shall not tire you any further with more details; I hope to return to these questions here in the Physical Society, and to show how, on the basis of the underlying ideas, it is possible to develop a theory for the structure of atoms and molecules. Before closing I only wish to say that I hope I have expressed myself sufficiently clearly so that you have appreciated the extent to which these considerations conflict with the admirably coherent group of conceptions which have been rightly termed the classical theory of electrodynamics. On the other hand, by emphasizing this conflict, I have tried to convey to you the impression that it may also be possible in the course of time to discover a certain coherence in the new ideas.

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## EXPERIMENT: THE BALMER SERIES FOR HYDROGEN

Using a spectrometer and diffraction grating, we will measure the wavelengths of light that make up the visible spectrum of hydrogen gas, comparing these wavelengths to the series formulated by Balmer.

The spectrometer is in effect a high-precision optical protractor. Light from the hydrogen source is "collimated" to produce a parallel beam that falls squarely on the diffraction grating. A telescope focused to parallel rays (to "infinity") gathers the diffracted light into an image for the eye.

Recall from the Junior Laboratory the spectrometer relation

$$k\lambda = d \sin \theta$$

where  $d$  is the line spacing of the grating,  $\theta$  is the angle of diffraction of a given image, and  $k$  is the order number of that image ( $k = 1, 2, 3, \dots$ ); it will enable measurement of  $\lambda$ .

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<sup>22</sup>[Namely, hydrogen and helium, the latter having been discussed in a section here omitted.]

Unless they are permanently aligned by the builder (ours are not), spectrometers need to be adjusted according to a rather elaborate routine before each use. In most cases the assistants will have done this work beforehand; but if you wish, or are requested, to perform your own alignment, a separate set of instructions is available.

The light source for this experiment is a sealed glass tube containing hydrogen gas and two electrodes. High voltage applied to the electrodes excites the hydrogen atoms, which then emit light as excited electrons lose energy again. Most of our sources contain, in addition to hydrogen, certain impurities which suppress the emission of light frequencies that are due to diatomic combinations of the hydrogen atoms, for Bohr's treatment is of a single atom, not a diatomic molecule. Tubes are available which emit the natural diatomic spectrum if desired for comparison.

Determine, for the wavelengths cited by Bohr in his first table, which ones fall in the visible spectrum and what their expected colors would be. Then use the spectrometer to identify as many of these lines as possible; calculate the wavelengths of these observed lines carefully, using the relation  $k\lambda = d \sin \theta$  cited above. (Given the way the spacing of our equipment is arranged, we will only see first-order images, so  $k$  will always be equal to 1.) Finally, use these measured wavelengths to determine an average value for  $R$  according to the Balmer series (Bohr's equation 1):

$$\frac{1}{\lambda_n} = R \left( \frac{1}{4} - \frac{1}{n^2} \right),^{23} \quad (1)$$

Compare this spectroscopically-determined constant  $R$  to the theoretically-determined value of  $R$  according to Bohr's equation (7):

$$R = \frac{2\pi^2 e^4 m}{ch^3}. \quad (7)$$

In the calculation, use presently-accepted values for the various quantities:

$$\begin{aligned} e &= 4.802 \cdot 10^{-10} \text{ esu} \\ m &= 0.910 \cdot 10^{-27} \text{ gm} \\ c &= 2.999 \cdot 10^{10} \text{ cm/sec} \\ h &= 6.625 \cdot 10^{-27} \text{ erg-sec} \end{aligned}$$

### Additional Exercises

Here are some exercises that may be helpful for visualizing Bohr's model of the hydrogen atom more clearly. They have no direct connection with our experiments.

1. Calculate the electron energies of the first seven stationary states ( $n = 1$  to  $n = 7$ ) according to Bohr's hypothesis (see note 16 to Bohr's text above) that the energies are given by

$$E_n = -Rhc/n^2$$

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<sup>23</sup>We leave it to you to solve for  $R$ .

or

$$E_n = -\frac{2\pi^2 me^4}{h^2 n^2}, \quad (8)$$

substituting for  $R$  from Equation 7.

2. Show that the quantum energy  $h\nu$  or  $hc/\lambda$  for each spectral line equals the difference between two stationary states. For example: between what two states must the electron fall in order to emit a quantum of light corresponding to the *red* Balmer line? to the *blue-green* line? (Note: do not confuse the number  $n$  in the Balmer series with  $n$  the number of a stationary state. The  $n$ th stationary state does not radiate; but the Balmer line  $\lambda_\nu$  is a radiation of light. Therefore the two  $n$ 's cannot mean the same thing.)
3. Using Bohr's equation (4), calculate the radii of the first seven stationary states; then construct a scale drawing of the Bohr atom, assuming that the orbits are circular.
4. Try calculating the *angular momentum*  $L_n$  of the electron orbit for a given value of  $n$ . Hints:
  - a. Assume, for simplicity, that the orbits are circles of radius  $a$  rather than ellipses with semi-major axis  $a_n$ .
  - b. The angular momentum of a body of mass  $m$  moving with velocity  $v$  in a circle of radius  $a_n$  is  $L_n = mva_n$ .
  - c. As shown in footnote 10, the kinetic energy of an electron in a circular orbit of radius  $a_n$  is  $mv^2/2 = e^2/2a_n$ . Show from this that  $m^2v^2a_n^2 = ma_n e^2$ .
  - d. According to Bohr's equation (8), each allowable elliptical orbit has a semi-major axis  $a_n$  given by  $2a_n = n^2 h^2 / 2\pi^2 m e^2$ . This formula applies also to circular orbits of radius  $a_n$ . Show from this that  $ma_n e^2 = n^2 h^2 / 4\pi^2$ .

Answer: You should be able to prove that  $L_n = nh/2\pi$ . In fact, Bohr himself derived this result in another paper he published in 1913. What might be the significance of the fact that, on Bohr's theory, the allowable electron orbits in the hydrogen atom are, apparently, just those in which the electron's angular momentum is an integral multiple  $n$  of the common unit  $h/2\pi$ ?



## CHAPTER 8

# MATTER WAVES

LOUIS DE BROGLIE

### A. PHASE WAVES GUIDING PARTICLES

In order to elucidate spectral phenomena, Bohr found himself forced to relinquish, on the atomic scale, at least, a classical law of electromagnetism: that a revolving, and hence continuously accelerating, charge must radiate energy continuously. But Newton's laws still functioned within Bohr's system, just as they had in Rutherford's nuclear model of the atom. Nevertheless, a failure of electrodynamics in the atomic microcosm laid open the question how far other macrocosmic principles could be trusted to apply at scales of magnitude beneath the reach of our senses. Moreover, Bohr's theory ran into ever greater difficulties in describing the atoms of elements other than hydrogen—atoms which must contain several electrons to remain electrically neutral.

In contrast to mechanics, the science of optics was early forced to acknowledge the importance of size in determining the validity of its laws. Under ordinary conditions light travels in straight lines, or rays, just as do particles in free space; but when it is confined to narrow openings light spreads out into the peculiar pattern of diffraction that indicates the presence of waves. Such waves which had been predicted for light by Huygens and Young, were predicted also for *matter* by Louis de Broglie<sup>1</sup> in 1923. He reasoned that there could not be one physics for light and another physics for matter; and that in order for the two domains to be brought into relation with one another there had to be a wave-particle duality for matter such as was by then already acknowledged in the case of light. Here is de Broglie's account of the point of departure for his hypothesis:

### THE UNDULATORY ASPECTS OF THE ELECTRON<sup>2</sup>

Prince Louis V. de Broglie

When, in 1920, I resumed my investigations in theoretical Physics after a long interruption through circumstances out of my own control, I was far from imagining that this research would within a few years be rewarded by the lofty and coveted distinction given each year by the Swedish Academy of Sciences: the Nobel Prize in Physics. At that time what drew me towards theoretical Physics was not the hope that so high a distinction would ever crown my labors: what attracted me was the mystery which was coming to envelop more and more deeply the structure of Matter and of radiation

<sup>1</sup>The pronunciation "de Broy" was attested to by Br. Robert Smith, who knew one of de Broglie's students.

<sup>2</sup>[Nobel Prize Address, Stockholm, 1929, from *The World of the Atom*, Vol. II (New York: Basic Books, 1966). For the sake of consistency throughout this and the following chapters, the letters used by de Broglie in his equations have occasionally been changed.]

in proportion as the strange concept of the quantum, introduced by Planck about 1900 during his researches on black body radiation, came to extend over the entire field of Physics.

But to explain the way in which my research came to develop I must first outline the critical period through which Physics had for the last twenty years been passing.

Physicists had for long been wondering whether Light did not consist of minute corpuscles in rapid motion, an idea going back to the philosophers of antiquity, and sustained in the eighteenth century by Newton. After interference phenomena had been discovered by Thomas Young, however, and Augustin Fresnel had completed his important investigation, the assumption that Light had a granular structure was entirely disregarded, and the Wave Theory was unanimously adopted. In this way physicists of last century came to abandon completely the idea that Light had an atomic structure. But the Atomic Theory, being thus banished from optics, began to achieve great success, not only in Chemistry, where it provided a simple explanation of the laws of definite proportions, but also in pure Physics, where it enabled a fair number of the properties of solids, liquids and gases to be interpreted. Among other things it allowed the great kinetic theory of gases to be formulated, which, in the generalized form of statistical Mechanics, has enabled clear significance to be given to the abstract concepts of thermodynamics. We have seen how decisive evidence in favor of the atomic structure of electricity was also provided by experiments. Thanks to Sir J. J. Thomson, the notion of the corpuscle of electricity was introduced; and the way in which H. A. Lorentz has exploited this idea in his electron Theory is well known.

Some thirty years ago, then, Physics was divided into two camps. On the one hand there was the Physics of Matter, based on the concepts of corpuscles and atoms which were assumed to obey the classical laws of Newtonian Mechanics; on the other hand there was the Physics of radiation, based on the idea of wave propagation in a hypothetical continuous medium: the ether of Light and of electromagnetism. But these two systems of Physics could not remain alien to each other: an amalgamation had to be effected; and this was done by means of a theory of the exchange of energy between Matter and radiation. It was at this point, however, that the difficulties began; for in the attempt to render the two systems of Physics compatible with each other, incorrect and even impossible conclusions were reached with regard to the energy equilibrium between Matter and radiation in an enclosed and thermally isolated region: some investigators even going so far as to say that Matter would transfer all its energy to radiation, and hence tend towards the temperature of absolute zero. This absurd conclusion had to be avoided at all costs; and by a brilliant piece of intuition Planck succeeded in doing so. Instead of assuming, as did the classical Wave Theory, that a light-source emits its radiation continuously, he assumed that it emits it in equal and finite quantities—in quanta. The energy of each quantum, still further, was supposed to be proportional to the frequency of the radiation,  $\nu$ , and to be equal to  $h\nu$ , where  $h$  is the universal constant since known as Planck's Constant.

The success of Planck's ideas brought with it some serious consequences. For if Light is emitted in quanta, then surely, once radiated, it ought to have a granular structure. Consequently the existence of quanta of radiation brings us back to the corpuscular conception of Light. On the other hand, it can be shown—as has in fact been done by Jeans and H. Poincaré—that if the motion of the material particles in a light-source obeyed the laws of classical Mechanics, we could never obtain the correct Law of black body radiation—Planck's Law. It must therefore be admitted that the older dynamics, even as modified by Einstein's Theory of Relativity, cannot explain motion on a very minute scale.

The existence of a corpuscular structure of Light and of other types of radiation has been confirmed by the discovery of the photo-electric effect which, as I have already observed, is easily explained by the assumption that the radiation consists of quanta— $h\nu$ —capable of transferring their entire energy to an electron in the irradiated substance; and in this way we are brought to the theory of light-quanta which, as we have seen, was advanced in 1905 by Einstein—a theory which amounts to a return to Newton's corpuscular hypothesis, supplemented by the proportionality subsisting between the energy of the corpuscles and the frequency. A number of arguments were adduced by Einstein in support of his view, which was confirmed by Compton's discovery in 1922 of the scattering of X-rays, a phenomenon named after him.<sup>3</sup> At the same time it still remained necessary to retain the Wave Theory to explain the phenomena of diffraction and interference, and no means was apparent to reconcile this Theory with the existence of light-corpuscles.

I have pointed out that in the course of investigation some doubt had been thrown on the validity of small-scale Mechanics. Let us imagine a material point describing a small closed orbit—an orbit returning on itself; then according to classical dynamics there is an infinity of possible movements of this type in accordance with the initial conditions, and the possible values of the energy of the moving material point form a continuous series. Planck, on the other hand, was compelled to assume that only certain privileged movements—quantized motion—are possible, or at any rate stable, so that the available values of the energy form a discontinuous series. At first this seemed a very strange idea; soon, however, its truth had to be admitted, because it was by its means that Planck arrived at the correct Law of black body radiation and because its usefulness has since been proved in many other spheres. Finally, Bohr founded his famous atomic Theory on this idea of the quantization of atomic motion—a theory so familiar to scientists that I will refrain from summing it up here.

Thus we see once again it had become necessary to assume two contradictory theories of Light, in terms of waves, and of corpuscles, respectively; while it was impossible to understand why, among the infinite number of

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<sup>3</sup>[In 1922, Arthur Compton had demonstrated experimentally that, with de Broglie's assumptions, the interaction of x-rays with electrons can be understood as *particle-like collisions* between electrons and photons, in which the x-ray photon transfers some of its energy to the electron and thus changes its own wavelength and momentum. His measurements showed that then both energy and momentum were conserved in these interactions.]

paths which an electron ought to be able to follow in the atom according to classical ideas, there was only a restricted number which it could pursue in fact. Such were the problems facing physicists at the time when I returned to my studies. When I began to consider these difficulties I was chiefly struck by two facts. On the one hand the Quantum Theory of Light cannot be considered satisfactory, since it defines the energy of a light-corpuscle by the equation  $E = h\nu$ , containing the frequency  $\nu$ . Now a purely corpuscular theory contains nothing that enables us to define a frequency; for this reason alone, therefore, we are compelled, in the case of Light, to introduce the idea of a corpuscle and that of periodicity simultaneously. On the other hand, determination of the stable motion of electrons in the atom introduces integers; and up to this point the only phenomena involving integers in Physics were those of interference and of normal modes of vibration. This fact suggested to me the idea that electrons too could not be regarded simply as corpuscles, but that periodicity must be assigned to them also. In this way, then, I obtained the following general idea, in accordance with which I pursued my investigations:—that it is necessary in the case of Matter, as well as of radiation generally and of Light in particular, to introduce the idea of the corpuscle and of the wave simultaneously: or in other words, in the one case as well as in the other, we must assume the existence of corpuscles accompanied by waves. But corpuscles and waves cannot be independent of each other [...]. It must consequently be possible to establish a certain parallelism between the motion of a corpuscle and the propagation of its associated wave. The first object at which to aim, therefore, was to establish the existence of this parallelism.

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De Broglie went on to “establish the existence of this parallelism” by outlining an idea of “matter waves” complementary to Planck’s light quanta. If the quantum treatment of light gives to the classical light wave an accompanying *particle* (the photon), so also de Broglie will give the classical Newtonian particle of matter an accompanying *matter wave*. Since the Planck-Einstein hypothesis makes the photon’s energy proportional to the frequency of its associated light wave, so too will de Broglie ascribe a frequency  $\nu$  to the wave that accompanies a material particle—a frequency related to the particle’s total energy  $E$  according to the very same equation as Planck’s,  $E = h\nu$ . Thus to every material body endowed with total energy  $E$  de Broglie associates a corresponding wave and ascribes to that wave a frequency given by:

$$\nu \text{ (of matter wave)} = \frac{E \text{ (of material body)}}{h}$$

For the wavelength of the proposed matter wave, de Broglie similarly carries over a relation previously established for light. Maxwell had demonstrated that a light wave conveys momentum to the surface that absorbs it, in the amount

$$p = \frac{E}{c}$$

where  $p$  is the momentum and  $E$  is the energy delivered, over any period of time, to the absorbing surface. By Planck’s hypothesis, each quantum of light energy  $E$  may be

expressed as  $E = h\nu$ , so that, substituting,

$$p = \frac{h\nu}{c} = \frac{h}{\lambda};$$

which implies that *a light quantum possesses momentum inversely proportional to its wavelength*. De Broglie extends this same relation to the proposed matter wave; thus, if the material body has momentum  $p$ , de Broglie ascribes to the corresponding wave a *wavelength* given by:

$$\lambda(\text{of matter wave}) = \frac{h}{p(\text{of material body})}.$$

Finally, de Broglie assumes that the postulated matter wave obeys the usual relation  $u = \nu\lambda$  between frequency, wavelength, and wave velocity, so that the matter wave corresponding to a body endowed with energy  $E$  and momentum  $p$  will propagate with a *velocity* given by:

$$u(\text{of matter wave}) = \nu\lambda = \frac{E}{h} \cdot \frac{h}{p} = \frac{E(\text{of material body})}{p(\text{of material body})}.$$

At first sight, this result would not appear to tell us anything plausible about the wave speed, since for a body moving with speed  $w$  and so having kinetic energy in the amount  $\frac{1}{2}mw^2$  and momentum equal to  $mw$ ,  $u$  is equal to  $\frac{1}{2}w$ : the wave travels with half the speed of the particle! But de Broglie points out that the energy  $E$  in the above expressions is the *total* energy of the body—and according to relativity theory, a body's kinetic energy represents only a tiny part of its total energy, unless that body moves with speeds comparable to that of light! We will derive this astonishing result in the second-semester senior mathematics tutorial. De Broglie accepts it as given, and on that basis assumes—remember, he *only* assumes—that the wave velocity  $u$  is inversely proportional to the particle speed  $w$ :  $wu = c^2$ , where  $c$  is the speed of light in empty space.<sup>4</sup>

De Broglie's new, postulated, wave is not a wave in the electromagnetic field and does not itself carry energy; nevertheless it is conceived as governing the motion of the particle. At this stage of trying to conceive of ways in which the matter waves and the material particle might be related, de Broglie proposes the metaphor of guiding; the waves might “guide” the particle. If a body's motion corresponds to this *guiding wave* in the same way that a ray of light is determined by the self-coherent interference pattern of light waves spreading throughout all space, then—de Broglie argues—there is a possibility of explaining why the electron in the hydrogen atom is able to move only in those discrete orbits, discontinuous from one another, that Bohr discovered.

But how *could* such a wave guide a particle? In a later article, in which he reflects on his papers of 1923 and his dissertation of 1924, de Broglie writes:

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<sup>4</sup>Here are the grounds for the assumption. The relativistic *mass-energy equivalence theorem* holds that a body's mass  $m$  represents a contribution, called the body's *rest energy*, of  $E_{\text{rest}} = mc^2$  to its total energy ( $c$  being the speed of light); thus, since  $c$  is very large, it is clear that for any realistic speeds, a body's total energy will scarcely exceed this rest energy. Then, in the earlier expression for the velocity of the matter wave, we have  $u = E_{\text{total}}/p \approx mc^2/mw$  or  $uw \approx c^2$ .

Note that henceforth we shall continue to use  $w$ , instead of  $v$ , to refer to the speed of a particle. This is done in order that the reader not mistake the speed for the frequency  $\nu$ .

I was seeking to picture to myself a real physical wave carrying a very small localized object in space through the passage of time. Two ways of doing so then presented themselves to my mind. The first, [...] which I now consider to be much more profound, was [...] developed in the first chapter of my dissertation. It consisted in beginning with the difference in the relativistic transformations of the frequency of a wave and of the frequency of a clock. Admitting that the particle possesses an internal vibration which permits its being likened to a little clock, I supposed that this clock displaced itself in its wave in such a way that its internal vibration remains constantly in phase with that of the wave: this is the postulate of "the agreement of phases." These hypotheses appeared to me to be made necessary by the fact that the relation  $E = h\nu$ , applied to the particle, implies the existence of a frequency  $\nu$  internal to the particle, whereas, since the works of Planck and Einstein, it is known that  $\nu$  is *also* the frequency of the wave that carries the particle. The particle appears then as incorporated into the wave in which it constitutes a very small region where the amplitude is very large. From this one can deduce the [...] formula  $p = h/\lambda$ .<sup>5</sup>

If every portion of matter is thought of as containing some sort of internal vibration or oscillation,<sup>6</sup> then the particle and its associated wave may be brought into connection through their common property of frequency. This, he states, implies a criterion by which the associated wave can *distinguish one path from another*, and so play a guiding role for the particle. "Agreement of phases" seems to mean that, when the "hand" on the body's internal clock has swept out some part of a complete revolution, it will be at that instant at a point in space at which its guiding wave is in exactly the same phase of its cycle. This leads de Broglie to call the wave associated with the particle its *phase wave*. The particle carries energy, but the wave "carries" the particle, *guiding it through the only trajectory that keeps the two in phase*. Thus agreement of phases between particle and associated wave is the sought-for criterion that distinguishes the particle's actual path from other, hypothetical, paths.

A second consequence of de Broglie's assumptions is to secure formal agreement between optical laws governing motion of light rays and dynamical laws that determine the motion of particles—and ultimately, the "synthesis" of waves and particles:

[I.] We propose to base the dynamics of material particles on the following postulate: In each point of its trajectory, a freely moving particle follows

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<sup>5</sup>"Sur les véritables idées de base de la mécanique ondulatoire" in *Recherches d'un demi-siècle* (Paris: Albin Michel, 1976), 64.

De Broglie went on to develop the second way: "In the second chapter of my dissertation, I then had shown that, *in the case where the wave propagation takes place approximately as in geometrical optics*, we are led to identify Fermat's principle [of least time in optics] with Maupertuis's principle of least action [in mechanics]" (italics added). His reasons for preferring the first way were that, of the two, only it is "essentially relativistic" in the sense of special relativity and holds even for wave propagations that are *not* approximately the same as those in geometrical optics. In Section C we shall return to the approximate character of geometrical optics in de Broglie's view.

In spite of the possible advantages of the first way, it was by pursuing the second way that Schrödinger was able to determine the differential equation for the matter waves. For a discussion of the principles of Fermat and Maupertuis, see the introduction to Schrödinger's paper in Chapter 10.

<sup>6</sup>Whereas here the frequency of oscillation varies as the energy of the particle, in Planck's analogy the frequency of each oscillator was fixed and determined the size of the packets of energy that an oscillator could hold, absorb, or radiate.

with a uniform motion the *ray* of its phase wave, that is, (in an isotropic medium) the normal to the surfaces of equal phase [...].

This new principle on which dynamics is to be based would explain the diffraction of light quanta, *however small their number*. Moreover, *any* moving particle would be subject to diffraction given the appropriate circumstances. A flow of electrons, for example, passing through a sufficiently small slit, would be expected to show diffraction phenomena. It is from this direction that experimental confirmation of our ideas will perhaps have to be sought.<sup>7</sup>

Hence we conceive the phase wave as guiding the displacements of energy, and this is what enables the synthesis of waves and quanta. The wave theory went too far when it denied the discontinuous structure of radiant energy and not far enough when it refused to intervene in dynamics. *The new dynamics of the free material particle is to the old dynamics [...] what wave optics is to geometrical optics.*<sup>8</sup> In reflecting on it one will see that the proposed synthesis of waves and quanta is the logical coronation of the comparative development of dynamics and optics since the 17th century.

[II.] Let us come now to the explanation of interference bands. Let us suppose that a material atom has a probability of absorbing or emitting an atom of light that is determined by [the square of the amplitude] of one of the phase waves that cross each other in passing over it. Of course, emission is possible only if the [material] atom is excited, while absorption is possible only if a light atom is present nearby. The preceding hypothesis is completely analogous to that of the electromagnetic theory when that theory connects the *detectable* intensity of light [...] with the intensity of the electric field vector.<sup>9</sup>

When any cause whatever has triggered the emission of a light quantum in a “point” source, its phase wave, in traversing the neighboring atoms, will trigger other emissions of light quanta, the internal vibration of which

<sup>7</sup>[Diffraction of electrons was observed experimentally only four years after de Broglie’s proposal.]

<sup>8</sup>[Or what Young’s optics (*Mechanics*, 159ff.) is to Newton’s optics (*ibid.*, 149ff.).]

<sup>9</sup>[At the end of Junior Laboratory, Maxwell’s argument that light is an electromagnetic wave was studied. Earlier the energy density (energy per unit volume) in an electromagnetic field had been shown to be proportional to the square of the field strength, here represented by  $F$ :  $E/V \propto F^2$ . The *intensity* of a wave ( $I$ ) is defined as the amount of energy ( $E$ ) that flows per second ( $t$ ) across unit area perpendicular to the direction of travel ( $A$ ). Hence, if  $s$  represents distance in the direction of travel, then

$$I \equiv \frac{E}{tA} = \frac{Es}{tAs} = \frac{E}{As} \frac{s}{t} = \frac{E}{Vol} c \propto F^2,$$

where  $c$  is the speed of light. Or since both  $I$  and  $F$  are different at different places and times:  $I(x, y, z, t) \propto F(x, y, z, t)^2$ . Thus, the intensity of light is proportional to the square of the amplitude of the electric field vector.

On the other hand, the Einstein reading in Chapter 6 showed that the intensity of light is proportional to the number of photons ( $N$ ) passing per second through a unit area perpendicular to the direction of travel. If the time interval is small enough, then  $N$  will be less than one. Since a photon is not divisible, we could regard  $N$  as a measure of the probability ( $P$ ) that a photon will pass through  $A$  as was done with alpha particles in the introduction to the chapter on Rutherford. Thus,  $P(x, y, z, t) \propto N \propto I \propto F(x, y, z, t)^2$ . Hence, the probability that an electric field will manifest itself as a particle, a photon, in a given area is also proportional to the square of the amplitude of the electric field vector. De Broglie refers to this in the second sentence of the paragraph.]

we shall suppose in phase with the wave itself.<sup>10</sup> Therefore, all the emitted light quanta will have the same phase wave as the first quantum. We shall say that they are 'phase-coupled'. Thus, a single phase wave [of light] carries along with itself a throng [*une foule*] of little bits of energy [...].

Let us consider then Young's double-slit experiment.<sup>11</sup> Some light quanta pass through the slits; and they will be diffracted because [according to our theory] they must follow the *ray* of the phase wave in their vicinity. In the spaces beyond the double slit, their capacity to act photoelectrically [i.e., to be absorbed by an electron] will vary at each point, according to the state of interference of the phase waves which have been diffracted by the two slits. Hence, *however weak the intensity of the incident light may be*, there will be bright and dark bands such as had been predicted by the wave theories.

This mode of explanation, which borrows its essential points from wave theory in the very act of introducing quanta, is to be generalized so as to deal with all interference and diffraction phenomena.<sup>12</sup>

*Light Waves and Einstein's Photons.* As we have seen, de Broglie's discussion of light above supplements Einstein's quantum hypothesis by interpreting the Maxwellian wave as guiding photons analogously to the way in which matter waves guide electrons.

Consider monochromatic diffracted light falling on a screen. De Broglie postulates that at any point on the screen the probability of a photon interacting with an atom (or an electron) there is directly proportional to the square of the amplitude of the Maxwellian wave there. This implies that *the number of such interactions per second* at different regions on the screen is proportional to the squared amplitude of the waves hitting those points. And each interaction delivers one quantum of energy, so that the measurable intensities, that is, the energy delivered per second per unit area, are naturally proportional to the same thing.

Furthermore, consider *one photon* going through a slit. The relative probability that it will eventually interact with an atom at one point on the screen compared with another is in this hypothesis proportional to the squared amplitude of the Maxwellian wave at those points.

## B. REFRACTION OF MATTER WAVES: APPLICATION TO THE ORBITING ELECTRON

De Broglie applied the mode of explanation outlined in the previous quotation to the phenomenon of refraction that would have to be involved in the case of the orbital electron of the hydrogen atom.

The most interesting application is the study of the atom of hydrogen as conceived by Bohr. We now regard the atom of hydrogen as a refracting

<sup>10</sup>[De Broglie has thus interpreted Maxwell's electromagnetic waves as being guiding waves, which guide light quanta in the same way as de Broglie's matter waves guide material particles.]

<sup>11</sup>[*Mechanics*, 167ff.]

<sup>12</sup>"Quanta de Lumière, Diffraction et Interférences," *Comptes rendus* 177 (1923), 548, in *Recherches d'un demi-siècle* (Paris: Albin Michel, 1976).

sphere, which, for the waves accompanying the motion of an electron of charge,  $e$ , possesses a refractive index<sup>13</sup> which varies [from point to point...]. The rays which return into themselves coincide with the possible trajectories of the electron, and some of them possess the very remarkable property of being in resonance with the wave: it is just these rays which are the "stable" trajectories of Bohr.<sup>14</sup>

In two different ways the refraction involved here is more complicated than that discussed in the *Mechanics* manual. First, whereas Huygens studied refraction at the boundary of two surfaces of noticeably different indices of refraction, the refraction of the matter waves around the hydrogen orbits would be analogous to light waves' being bent in a *gradual curve* due to the medium's being made of non-uniform glass such that the glass's index of refraction varied continuously from point to point. Then the index of refraction  $n$  would depend on the location within the glass:  $n = n(x, y, z)$ . For the case of a spherical orbit, de Broglie considers "a medium with spherical symmetry in which the refractive index varies [inversely] with the distance  $r$  from the centre,"<sup>15</sup> so that  $n \propto 1/r$ .

Second, Newton had shown that the "Analogy between colors and refrangibility is very strict, the Rays always either exactly agreeing in both or proportionally disagreeing in both" (*Mechanics*, 154). In the wave theory of light, the property of the wave that is constant when the wave passes from one medium to another is its frequency, while its speed and wavelength both change. Thus, light of different frequencies is refracted in different amounts in the same medium, that is, the index of refraction of light depends on its frequency.

Whenever the separate colors in white light spread out into a spectrum upon passing through a prism, it is because waves of different frequencies are being propagated at different speeds, causing their rays to bend along different paths. For example, when red light of wavelength 6563 Å shines on the flat surface of a piece of crown glass at an angle of incidence of 30°, it will be refracted within the glass at an angle of 19.15° (Fig. 1). By Snell's law, the sines



Figure 1: Light beams of different wavelengths refract at different angles in a dispersive medium. (The angular difference is exaggerated in this drawing.)

<sup>13</sup>[Huygens had shown that his wave theory of light implied that the ratio of the sine of the angle of incidence to the sine of the angle of refraction was the same as the ratio of the speeds of the waves in the two media (*Treatise on Light, Mechanics*, 123ff.), or, written in terms of fractions:  $\sin \theta_i / \sin \theta_r = c_i / c_r$ , where  $c_i$  and  $c_r$  refer to the speeds of light in the incident and refracting media, respectively. The number  $n = \sin \theta_i / \sin \theta_r = c_i / c_r$  is the *index of refraction* of medium  $r$  with respect to medium  $i$ , and this equation is known as *Snell's Law*. The index of refraction of a vacuum, where the speed of light is  $c$ , is taken to be 1. If the vacuum is taken as a standard, an index of refraction,  $n_{med}$ , can be assigned to any medium:  $n_{med} = c / c_{med}$ .]

<sup>14</sup>[L. de Broglie, "On the Parallelism between the Dynamics of a Material Particle and Geometrical Optics," 14 in *Selected Papers on Wave Mechanics* (London: Blackie & Sons, 1928), originally published in *Journal de Physique* 7 (1926).]

<sup>15</sup>*Ibid.*, 13-14.

of these angles will be in the same ratio as the speeds of the light in the air and in the glass, respectively. The frequency remains the same, so the wavelength must diminish in the glass, in the same ratio in which the speed is reduced. Thus,

$$n^{red} = c_{air}^{red}/c_{glass}^{red} = \sin 30^\circ / \sin 19.15^\circ = \lambda_{air}^{red}/\lambda_{glass}^{red}.$$

The speed of light in air, virtually the same as in vacuum, is about 186,000 miles/sec or  $3 \times 10^8$  m/sec—denoted by the letter  $c$ . Then, knowing the wavelength of this red light in air, we may calculate its speed and wavelength in the glass. Similarly, blue light of wavelength 4861 Å entering the same glass at the same angle will refract at  $19.04^\circ$ . At what speed then does this blue light travel in the glass and what is its index of refraction?

In describing “the manner how colors are produced by the Prism,” Newton wrote that “the Rays [...] by their unequal refractions must be severed and *dispersed* into an oblong form in an orderly succession from the least refracted Scarlet to the most refracted Violet” (*Mechanics*, 156; italics added). The prism is said to be a *dispersive medium*, and the phenomenon of spreading-out is called *dispersion*.

So, in dispersive media for matter waves, the index of refraction would have to depend on the frequency of the waves, in addition to the location:  $n = n(x, y, z, \nu)$ . In the particular case of spherical symmetry:  $n \propto f(\nu)/r$ , where  $f$  is some function of  $\nu$ .

De Broglie first proved the general theorem enunciated below and then applied it to an electron orbiting the hydrogen nucleus, understood as analogous to light waves moving in a spherically symmetrical, dispersive medium:

Now let us suppose that at time  $t = 0$  the moving particle coincides in space with a wave of frequency  $\nu$ , which propagates with speed  $u = c^2/w$  in the same direction as the particle. This wave of speed greater than  $c$  cannot correspond to a propagation of energy;<sup>16</sup> we consider it only as a fictional wave associated with the motion of the moving particle.

I say that, if at time  $t = 0$  there is agreement of phase between the [guiding] wave and the internal [vibrational] phenomenon of the moving particle this agreement of phase will continue [...].

Let us now pass to the case of an electron describing a closed trajectory at a uniform speed considerably less than  $c$ . At time  $t = 0$  the moving particle is at a point P. The associated fictive wave, departing then from P and describing the complete closed trajectory at [a constant speed much greater than that of the electron], catches up with the electron at time  $\tau$  and at point P'.<sup>17</sup>

After calculating the period of revolution of the electron around its orbit and the internal phase of the electron upon reaching point P', de Broglie concluded:

<sup>16</sup>[The product of wave and particle speeds has been supposed equal to the speed of light squared. Therefore, since the particle speed is certainly less than the speed of light, the wave speed must be supposed greater than the speed of light. But it is a tenet in relativity theory that no actual process can transmit energy with a speed greater than that of light; so the associated wave “cannot correspond to a propagation of energy.” Hence de Broglie calls it “fictional” above.]

<sup>17</sup>[“Ondes et Quanta,” *Comptes rendus* 177 (1923), 507, in *Recherches d’un demi-siècle* (Paris: Albin Michel, 1976). We shall not attempt to follow de Broglie’s proof.]

It is *almost necessary* to suppose that the trajectory of the electron is stable *only* if the fictive wave passing at P' finds the [internal vibration of the] electron in phase with it. The wave must be in resonance [with the electron's internal vibration] over the length of the trajectory [actually followed by any orbiting electron].<sup>18</sup>

De Broglie then demonstrated that an equation equivalent to Bohr's equation (8) in Chapter 7 above followed from this "condition of stability." The general idea is that the requirement of staying in resonance with the electron's internal vibration around the orbit restricts the fictive matter waves to a particular set of wavelengths and also to particular distances from the nucleus, which turn out to be the same as the radii of Bohr's orbits. By virtue of the de Broglie relation,  $\lambda = h/p$ , these allowable wavelengths then determine the electron's momentum and hence the kinetic energy,  $KE = p^2/2m$ , of the system, leading to the discrete energy values (the potential energy being inversely proportional to the distance) that Bohr had been forced to postulate.

For since the electron is circling around the orbit, the ray of the fictive waves and the fictive waves themselves are also circling upon themselves around that orbit. Hence, since, by de Broglie's condition of stability, the internal periodic phenomenon of the electron must remain in phase with its guiding waves; therefore, those waves, as they continually superimpose each of their circuits on its previous ones, *must remain in phase with themselves*. This condition will be met, however, only if the circumference of the orbit is *equal to* the de Broglie wavelength, or twice, or three times, or *any integral multiple of the wavelength*.

But this is exactly what happens in the second, or third, or any Bohr orbit; in general, for the  $n^{\text{th}}$  Bohr orbit, the circumference  $2\pi a_n$  will equal  $n\lambda_n$ .<sup>19</sup> For instance, consider an electron in the first Bohr orbit of a hydrogen atom. The diameter  $2a_1$  of the  $n^{\text{th}}$  orbit in the hydrogen atom was shown by Bohr to be<sup>20</sup>

$$2a_n = n^2 \cdot \frac{h^2}{2\pi^2 me^2} \text{ cm.}$$

Using modern values for electron mass  $m = .910 \times 10^{-27}$  gm, electron charge  $e = 4.802 \times 10^{-10}$  esu, and Planck's constant  $h = 6.625 \times 10^{-27}$  erg-sec, we find the radius of the first orbit ( $n = 1$ ) to be  $a_1 = .530 \times 10^{-8}$  cm and the circumference to be  $2\pi a_1 = 3.33 \times 10^{-8}$  cm. On the other hand the electron's speed was given by<sup>21</sup>

$$mw^2 = \frac{e^2}{a},$$

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<sup>18</sup>["Ondes et Quanta," *Comptes rendus* 177 (1923), 507–508, in *Recherches d'un demi-siècle* (Paris: Éds, Albin Michel, 1976). De Broglie's symbols have been changed.]

<sup>19</sup>This general result is easy to show by adding subscripts to Eq. (i) of note 10 and Eq. 8 in the main text of Chapter VII. Between equations  $mw_n^2 = e^2/a_n$  and  $2a_n = n^2 h^2 / 2\pi^2 m e^2$ , eliminate  $e$  to obtain  $4\pi^2 a_n^2 = n^2 h^2 / m^2 w_n^2$ . Taking square roots then yields  $2\pi a_n = nh/mw_n$ ; but since  $h/mw_n = \lambda_n$ , we see that the orbital circumference  $2\pi a_n$  is always an integral multiple  $n$  of the electron's associated wavelength for that orbit.

Thus it was for a time accepted that in-phase overlapping of the wavelengths is what determines the eligible orbits of a particle. However, this neat result proved to be valid only for hydrogen, and to some extent helium. Success with the heavier elements required other methods, such as Schrödinger's in Chapter 10.

<sup>20</sup>See Bohr's equation (8) in Chapter 7 above.

<sup>21</sup>See Bohr's equation (4) and the related footnote in Chapter 7 above.

which, using the values previously obtained, yields a value for the electron's orbital speed in the orbit of radius  $a_1$ ,  $w_1 = 2.186 \times 10^8$  cm/sec.

According to de Broglie's relation between particle momentum and associated wavelength, then, the electron in the first hydrogen orbit will be associated with a wave of wavelength

$$\lambda_1 = \frac{h}{mw_1} = \frac{6.625 \times 10^{-27}}{.910 \times 10^{-27} \cdot 2.186 \times 10^8} = 3.330 \times 10^{-8} \text{ cm},$$

which is exactly the same length as the circumference of the first Bohr orbit!

On this hypothesis there can be no orbit of the electron between Bohr orbits *because* its phase wave cannot combine coherently with itself there. Those intermediate spaces are analogous to the dark bands in an interference pattern, where the phase waves interfere destructively. The sketch below is a symbolic representation of the wave dispositions for the first three orbits of hydrogen, drawn first on straight paths and then bent around into orbital circumferences. Note that the depicted shapes of the waves do not accurately represent either the actual motion of the fictive waves or their associated rays.



Figure 2: *de Broglie wavelengths for the first three Bohr orbits of hydrogen. In general the wavelength for the orbit of radius  $a_n$  is  $\lambda_n = 2\pi a_n/n$ . (The diagram is not drawn to scale.)*

### C. PACKETS OF MATTER WAVES: APPLICATION TO THE FREE PARTICLE

In a late work of his, reporting on his point of departure for developing the idea of matter waves, de Broglie stresses the merely approximate character of geometrical, or ray, optics<sup>22</sup> and, hence, of the old, Newtonian mechanics:

As early as 1923 I had formulated the fundamental idea that traditional Mechanics (in both its relativistic and classically Newtonian form) was only an approximation with the same range of validity as geometrical Optics. From that moment I was led to realize the necessity of constructing a new Mechanics, an undulatory Mechanics [...].

In every case where Geometrical Optics is sufficient to describe the propagation of the  $\Psi$  wave [as the matter wave came to be designated] [...] the

<sup>22</sup>See note 5 in Section A above.

trajectories, determined by the Classical Dynamics of a point mass [...] will be simply the rays of propagation of the  $\Psi$  wave [...].

And thus we arrive at one of the main ideas of the new Mechanics. Whereas the older Mechanics attributed a rigorous character to [the equations of these trajectories] and considered them valid everywhere, the new Mechanics gives the leading role to the wave. It considers the equations of the older Mechanics as approximations valid only when the approximation of Geometrical Optics is sufficient to describe the propagation of the wave.

Classical Dynamics thus appears to be only an approximation. It is applicable only when the index [of refraction]  $n$  relative to the  $\Psi$  wave varies only slightly in comparison with a wave-length or, what is essentially the same thing, when the potential  $V^{23}$  varies slowly over the distance of a wave-length. However, if the wave-length of the  $\Psi$  wave were infinitesimally small, the older Dynamics would be rigorously valid.<sup>24</sup>

Thus far we have not seen how the motion of material particles as determined by geometrical optics, that is, as being the trajectories, or rays, determined by the matter waves, is only approximate. For, as explained in Section B, the Bohr orbits of the electron in the hydrogen atom appeared to be exact, not approximate. In Section B, however, it was only claimed that the electron is localized in certain orbits; nothing was said about its motion around an orbit. The examples discussed in the 1923 articles did not manifest that approximate character. Now in order to make clear that the motion of a particle is not *exactly* the motion determined by geometrical optics, we shall imagine the motion of a free electron, such as one shot at a screen, as in the cathode-ray tube. We ask whether there is a wave phenomenon that moves toward the screen in roughly the same way as does the classical electron.

To answer this question we follow de Broglie's procedure in his dissertation,<sup>25</sup> written in 1924. There, in order to establish "a close connection between the propagation of the wave and the dynamics of the associated corpuscle,"<sup>26</sup> he made use of a familiar general wave phenomenon, known as a *group* of waves, or a *wave packet*, which was not studied in Junior Laboratory. A wave packet might be thought of as a wave phenomenon that concentrates its energy in a "burst." Many wave phenomena can exhibit "burst-like" features. For example, a vibrating string produces a steady tone, but two strings slightly out of tune also produce "beats," a regular rise and fall in volume. Similarly, a rock dropped in a pond causes a distinct *band* of ripples to spread out, rather than a constant undulation all across the pond.

Take a closer look at the disturbance caused by dropping a rock in a pond. Within the band, the ripples are moving just as a train of sine-waves would, except that each ripple *starts up* or *emerges* at the trailing edge of the band and *fades out* at its leading edge. The ripples are moving through the band, at a greater speed than the band itself,

<sup>23</sup>[In the case of the orbiting electron, this would be the electrical potential of the electric field due to the positively charged hydrogen nucleus. That is what causes the trajectory of the electron to curve analogously to the way in which an index of refraction  $n \propto 1/r$  would cause a light ray to curve in a circle. We shall see below how it is "essentially the same thing."]

<sup>24</sup>[L. de Broglie, *Non-linear Wave Mechanics: A Causal Interpretation* (Amsterdam: Elsevier, 1960), 7, 19–20.]

<sup>25</sup>The following account is based on his summary presentation in L. de Broglie, "On the Parallelism between the Dynamics of a Material Particle and Geometrical Optics," *op. cit.*, 10–11.

<sup>26</sup>*Ibid.*, 12.

but are noticeably present only inside the band. Consider a patch of water some distance from the point where the rock is dropped; that patch remains undisturbed until the band reaches it, which takes longer than the ripples would if they moved continuously from the rock. In fact, in water such a band moves at a speed that is only about half that at which the ripples in it are moving. But the band is nothing but a band of ripples. The ripples build up a distinct band, but disappear outside it. This makes sense only if the ripples are actually a sum of component waves which add up constructively to form the band, but add up destructively to cancel themselves out outside the band. The band of ripples is a moving reinforcement, or interference pattern.

Suppose, then, that a particle is accompanied not by one phase wave but by a collection of them. It is possible that the sum of the phase waves might produce a wave packet, a single localized region in which that sum had an amplitude other than zero, while cancelling itself out everywhere else. Like the band of ripples, the wave packet would move more slowly than the individual waves within it. The particle could then be thought of as riding along in the wave packet, as in Figure 3.



Figure 3

The speed of a component phase wave is called the *phase velocity*. The speed of the packet is called the *group velocity*. Now, the phase velocity is determined by the two de Broglie relations for the values for the total energy  $E$  and momentum  $p$  of the particle, since they determine  $\nu$  and  $\lambda$ , the product of which is the phase velocity  $u$ . The group velocity  $g$  of the wave packet is in turn determined by the mathematics of the addition of wave functions; however, the particle's velocity  $w$  is already contained in the quantity  $p$ . The wave packet is a leading candidate for fulfilling the role of a matter-wave phenomenon that would move in such a way as to determine the approximate location of the particle at any time. Hence, if it is to succeed in fulfilling that role, de Broglie must show that  $g = w$ . Recall, too, that in Section A the speeds  $w$  and  $u$  were assumed inversely proportional:  $wu = c^2$ . As we shall see, the mathematics of wave packets must retain this inverse proportionality between the speeds  $w$  and  $u$ .

Here are some examples of wave packets in various media. In a simple wave phenomenon, a disturbance of some amplitude in a medium propagates at a constant speed. In the simplest case from Junior Laboratory, the medium is a rope and the disturbance is a displacement up and down of particles along it, propagating in the one dimension of the string's extension when we shake it up and down once. When a rock is dropped into water, the disturbance is again an up-and-down displacement

in the medium of water, but now the propagation is in two dimensions across the water's surface. A sound wave coming from the striking of a gong propagates in three dimensions through the medium of air; this is possible because the displacement of particles is forward-and-back in the direction of propagation, longitudinal rather than transverse.

In Maxwell's theory of light, a disturbance from the flash of a signal light is a pulse in electric and magnetic field strengths that is both transverse and three-dimensional. The material medium, the ether, postulated by Maxwell was, however, soon rejected as having contradictory properties; thus the "medium" of light remains nothing but a distribution of potential energy in empty space. An electromagnetic pulse of light may be understood by analogy to the sound wave due to the striking of a gong, but with the medium removed and the amplitudes replaced by oscillating field strengths, transversely directed and oriented perpendicularly to each other.

The groups of phase waves of wave mechanics take a further step away from concreteness. They have no material medium, and their amplitudes are simply assigned the letter  $\Psi$ . They are groups of  $\Psi$  waves in a non-physical medium, which can, however, be characterized by an index of refraction:  $n = n(x, y, z, \nu)$ , as we have seen in Section B. Hence, the medium can be expected to manifest itself by its effect on the velocity of a wave group.

Before attempting to demonstrate what de Broglie termed the "Theorem of Group Velocity," namely, that the group velocity equals the particle velocity:  $g = w$ , we shall become familiar with the mathematics of the composition of a group of phase waves in general and of the determination of the group velocity.

Any function of the form  $f(x - ut)$  represents a configuration that travels with velocity  $u$ . For consider  $f(z)$ , where  $z$  is measured from some point that moves with speed  $u$  in the direction of increasing  $x$ ; so that the graph of  $f(z)$  is certainly moving with speed  $u$ . But, as Figure 4 shows,  $z = x - ut$ . Therefore the graph of  $f(x - ut)$  also moves with speed  $u$ . It is not necessarily periodic.



*Figure 4. The solid curve  $f(z)$  moves with speed  $u$ . The dotted curve shows its position at some earlier moment. As the drawing shows,  $z = x - ut$ ; and thus  $f(z)$  is identical to  $f(x - ut)$ .*

The function

$$\Psi(x, t) = A \sin 2\pi k(x - ut)$$

not only travels with velocity  $u$  as above; it, in addition, shows periodicity at spatial intervals  $\lambda$  such that  $2\pi k\lambda = 2\pi$  which gives  $\lambda = 1/k$  (this is apparent when  $t = 0$ ), and at time intervals  $T$  such that  $2\pi kuT = 2\pi$  from which it follows that  $T = 1/ku$  (apparent for  $x = 0$ ).  $\lambda$  is the *wavelength*, and  $T$  is called the *period*. The quantity  $k$ , the inverse of the wavelength, is called the *wave number* (it is the *number* of wavelengths per unit distance). The quantity  $A$  is the *amplitude*, the maximum “height” of the wave disturbance.

When written as above, namely

$$\Psi(x, t) = A \sin 2\pi k(x - ut)$$

the traveling wave may be said to be expressed in *velocity form*, inasmuch as it shows the velocity  $u$  explicitly.

The frequency is the inverse of the period; that is, variously expressed:

$$\nu = 1/T = ku = u/\lambda.$$

With these substitutions, the traveling, periodic wave given above may also be written in the form

$$\Psi(x, t) = A \sin 2\pi(kx - \nu t) \quad (1)$$

which may be called the *frequency form*; it shows the frequency  $\nu$  explicitly. Although the wave velocity is not here overtly expressed, it will be clear from the preceding that  $u = \nu\lambda = \nu/k$ .

Each of de Broglie’s phase waves must obey, in any one dimension, Equation 1. To see how a wave packet is composed, let us add two waves that differ slightly in frequency and wavelength. If

$$\Psi_1 = A \sin 2\pi(kx - \nu t) \quad \text{and} \quad \Psi_2 = A \sin 2\pi((k + \Delta k)x - (\nu + \Delta\nu)t),$$

then their sum<sup>27</sup> is

$$\Psi_{1+2} = 2A \cos 2\pi \left( \frac{\Delta k}{2}x - \frac{\Delta\nu}{2}t \right) \cdot \sin 2\pi \left( \frac{k+(k+\Delta k)}{2}x - \frac{\nu+(\nu+\Delta\nu)}{2}t \right).$$

We have manipulated this equation algebraically to bring out its formal resemblance to Equation 1. The sine factor here corresponds to the sine factor in Equation 1, but here the coefficient of  $x$  is the average of  $k$  and  $k + \Delta k$ , while the coefficient of  $t$  is the average of  $\nu$  and  $\nu + \Delta\nu$ ; thus the sine factor represents a wave whose wave

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<sup>27</sup>A crucial trigonometric identity for much of what follows is:

$$\sin a + \sin b = 2 \sin \left( \frac{a+b}{2} \right) \cdot \cos \left( \frac{a-b}{2} \right).$$

It can be derived, with some labor, from the better-known identities

$$\sin(a + b) = \sin a \cos b + \cos a \sin b$$

(and the special case in which  $\sin 2a = 2 \sin a \cos a$ ) and  $\cos(a - b) = \cos a \cos b + \sin a \sin b$ .

number is the average of the two component wave numbers and whose frequency is the average of the two component frequencies.

The amplitude  $A$  in Equation 1 corresponds here to the whole factor

$$2A \cos 2\pi \left( \frac{\Delta k}{2}x - \frac{\Delta\nu}{2}t \right),$$

which thus plays the role of a *variable* amplitude, the *envelope*. The maximum value of the envelope is  $2A$ , which is twice the amplitude  $A$  of either component. This indicates that the sum of the two waves attains a maximum wherever two crests or two troughs of the component waves add up. Since the envelope also involves a cosine term, and since the cosine exhibits the same wavelike shape as the sine, the envelope can itself be viewed as a wave: its wave number will be half the difference of the component wave numbers, and its frequency will be half the difference of the component frequencies. The compound wave formed by adding two components thus seems to be acting like a wave in two ways at once (see Figure 5).

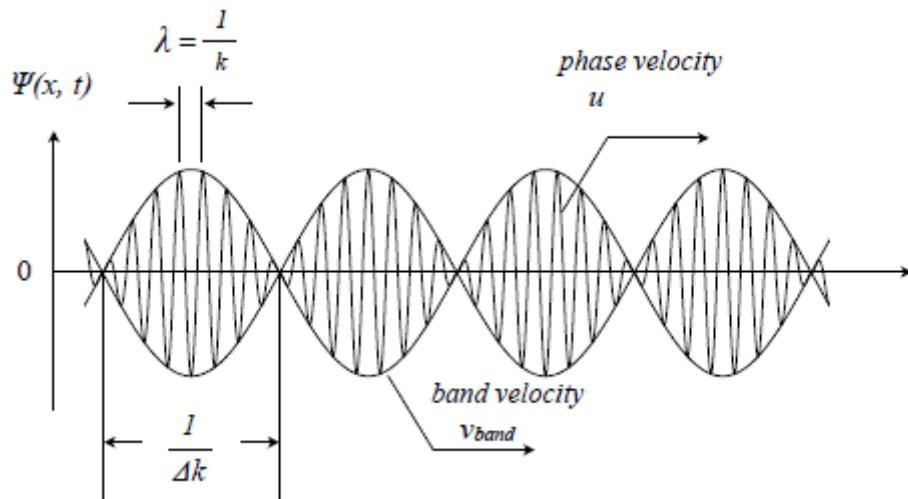


Figure 5

In the figure the dense inner line graphs the sine factor. Its wavelength is labeled as  $\lambda = 1/k$ . This is approximately true: since  $\Delta\lambda$  was chosen to be small, the wavelength of  $\Psi_2$  differs little from  $\lambda$ , the wavelength of  $\Psi_1$ , and the average of the two wavelengths differs from it even less. The speed of propagation of the inner-line wave is the phase velocity  $u$ . The more relaxed outline graphs the cosine factor, the envelope surrounding the higher-frequency wave. The graph also shows the meaning of the two factors in the expression for  $\Psi_{1+2}$ : the compound wave is a wave within a wave. Thus two component waves of slightly different frequencies and wavelengths will combine to form an interference pattern consisting of a succession of bands enveloping or containing a wave of shorter wavelength and higher frequency.

This is not quite where we want to be, since the envelope is an endless string of adjacent bands rather than a single isolated wave packet. Nevertheless, it permits us to form a simple equation deriving the velocity of any band in the envelope—which

could be viewed in isolation as a group formed of two component phase waves—from the properties of its two component phase waves. Since the speed of any wave in general is the product of its wavelength and frequency, and since we can read these values *for any band* from the coefficients in the cosine factor, the band velocity,  $u_{\text{band}}$ , may be expressed as

$$u_{\text{band}} = (\text{wavelength}) \times (\text{frequency}) = \frac{2}{\Delta k} \frac{\Delta\nu}{2} = \frac{\Delta\nu}{\Delta k} \quad (2)$$

Figure 6 shows how the two component waves build up the compound envelope and its bands. The two components are shown in a ratio of wavelengths of 9 : 8. At (a), crests of the longer and the shorter wave coincide to produce a maximum in their sum. Then at (b), after 4 full cycles of the longer and  $4\frac{1}{2}$  of the shorter, a crest of the longer component coincides with a trough of the shorter one, producing a node in the compound wave. At (c) both components display crests again, producing a maximum in their sum once more. Each repetition of the same interval brings the two components back out of phase  $180^\circ$  at a node, or back in phase at a common crest.



Figure 6

The pattern in Figure 6 must continue indefinitely. But what happens if we add a third component wave with a wavelength and frequency between those of the first two components? If we add a fourth? A fifth? Infinitely many? Figure 7 may suffice to answer these questions in a general way. It shows a sum of six component waves. The envelope will clearly have its maximum amplitude at every point where all the components reach a crest together, and these points will also be the centers of the bands. But each additional component wave increases the distance between the centers of bands. To see why, look once more at Figure 6.

There, a third component with a wavelength halfway between the two shown would cycle  $8\frac{1}{2}$  times between (a) and (c). If the third component were in phase with the first two at (a), then it would be out of phase with them at (c) and would subtract its amplitude from their sum. With proper choice of amplitudes, every second maximum could be nearly canceled; the distance between adjacent common maxima of all three components would then be double the distance for the first two alone. So by adding ever



Figure 7. Six component waves of the indicated wave numbers, two of which are shown on top, are added to produce more widely separated bands of greater amplitude.

more intermediate component waves—canceling out every third, fourth, fifth maximum, and so on—we can eventually move the centers of adjacent bands as far apart as we please.

Does each band stretch to fill the longer interval? Figure 7 suggests that it does not, but that instead the envelope cycles up and down near the baseline between bands that themselves remain narrow. As more and more intermediate component waves are added and the common crests become fewer and farther between, there are also more and more opportunities for every component at every spot in between to have an amplitude nearly equal and opposite to that of some other component; so that the amplitude of the envelope will fall off rapidly on both sides of each maximum, and tend everywhere else toward zero.

This suggests, and it can in fact be proved, that if we added a countable infinity of suitably selected<sup>28</sup> intermediate component waves while focusing our attention on a single band, the other bands would be removed to an infinite distance, leaving the single wave packet of Figure 3. This claim is analogous to that of Daniel Bernoulli that “all sonorous bodies contain potentially an infinity of sounds, and an infinity of corresponding ways of making their regular vibrations” (*Mechanics*, 201).<sup>29</sup>

To keep the amplitude of the packet finite, while adding infinitely many increments to it, we could, for example, let the amplitudes of the outermost components each be 1, that of the central one 1/2, those of the two halfway between the central and outermost

<sup>28</sup>The infinity of values of  $k$  between 8 and 9 must be everywhere dense on the interval [8,9]; that is, given any one of them, it must be impossible to find an interval containing it that does not also contain another—and, in fact, an infinity—of the selected points in its interior.

<sup>29</sup>In fact, given any “reasonable” finite curve represented by a function  $f(x)$  on an interval  $(0,L)$ , and such that  $f(0) = 0 = f(L)$ , we may determine the constants  $A_n$  such that the curve is represented by an infinite sum of sinusoidal curves:

$$f(x) = \sum_{n=1}^{\infty} A_n \sin(n\pi x/L).$$

We could imagine  $f(x)$  as representing a snapshot of the top half of a wave packet at any time. Similarly, if  $g(x, t)$  is a “reasonable” function, which here represents the forward motion of the top half of a wave packet, then it is possible to determine the constants  $B_n$  such that  $g$  may be represented as a sum of an

ones  $1/8$ , etc.—the amplitude of the packet would then be

$$2 + 2^0 \cdot (1/2)^1 + 2^1 \cdot (1/2)^3 + 2^2 \cdot (1/2)^5 \dots = 3.$$

In this way we could construct an envelope that is a single wave packet rather than an infinite series of bands. The same reasoning that led to Equation 2 for the bands in an envelope now applies to an envelope of only one band. Hence, we have for the velocity of the packet, the group velocity:

$$g = \frac{\Delta\nu}{\Delta k}. \quad (3)$$

The exact way in which the group would move depends on its index of refraction. Even though this medium in which the  $\Psi$  waves move is unknown, it can be characterized in one way by its effect on the speed of the waves. For just as in empty space (index of refraction constant:  $n = 1$ ) all electromagnetic waves, whatever their frequency, move at the same speed  $c$ , so, if the index of refraction were the same for  $\Psi$  waves of different frequencies, then every component phase wave in a group would have the same speed  $u$ . Under this condition, the phase velocity would also have to be equal to this constant  $u$ . What would the group velocity then be? Since

$$k = \frac{1}{\lambda} = \frac{\nu}{u},$$

therefore, where  $u$  is a constant,

$$g = \frac{\Delta\nu}{\Delta k} = \frac{\Delta\nu}{\Delta(\nu/u)} = \frac{\Delta\nu}{\Delta\nu/u} = u \frac{\Delta\nu}{\Delta\nu} = u,$$

and the wave packet would move with the same speed as the compound phase waves within it. But we want the packet to keep pace with the particle at speed  $w$ , which must be inversely proportional to  $u$ .

Already in Section B, in order to derive the Bohr orbits from matter waves, we saw that de Broglie had supposed that the index of refraction for them depended on both location and the frequency of the waves:  $n = n(x, y, z, \nu)$ , that they moved in a dispersive medium. Now we shall prove that the two de Broglie relations  $E = h\nu$  and  $p = h/\lambda$  imply that the  $\Psi$  waves are subject to dispersion. For,

$$u = \nu\lambda = \frac{E}{h} \frac{h}{p} = \frac{E}{p} = \frac{h\nu}{p}.$$

And

$$p = mw = \sqrt{m^2w^2} = \sqrt{2m \cdot \frac{mw^2}{2}} = \sqrt{2m(E - V)} = \sqrt{2m(h\nu - V)},$$

where the total energy of the particle minus its potential energy ( $E - V$ ) has been substituted for its kinetic energy. Substitution of the above expression for  $p$  into the

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infinite number of standing waves (compare *Mechanics*, 204):

$$g(x, t) = \sum_{n=1}^{\infty} B_n \sin(n\pi x/L) \cos(2\pi\nu t).$$

equation for  $u$  gives

$$u = \frac{h\nu}{\sqrt{2m(h\nu - V)}}.^{30} \quad (4)$$

Now, since  $V = V(x, y, z)$ , therefore, by Equation 4, the speeds,  $u$ , of the matter waves depend on their location and on their frequency,  $u = u(x, y, z, \nu)$ . Since the index of refraction is inversely proportional to the speed of the waves (see note 13 above), this implies that  $n = n(x, y, z, \nu)$  and that the matter waves do move in a dispersive medium, as de Broglie had supposed. Just as the index of refraction of a glass prism disperses light waves of different frequencies, so the dependence of the wave-speed  $u$  on the potential  $V$  and on the frequency of the waves is responsible for the dispersion of the  $\Psi$  waves.

In this case the group velocity,  $g$ , will *not* turn out to be equal to the velocity,  $u$ , of the component waves as happened above when we had supposed an index of refraction that was independent of the frequency. Instead the phase waves will ripple through the wave packet, leaving it behind. Recall that according to Equation 3 the wave packet will move with speed,  $g = \Delta\nu/\Delta k$ . Now, since  $k = 1/\lambda = \nu/u$ , therefore,  $\nu = ku$ , so that  $\nu$  is a function of  $k$ . Therefore,  $\nu$  may be differentiated with respect to  $k$ , and as  $\Delta k$  tends toward zero,  $\Delta\nu/\Delta k$  will approach the derivative of  $\nu$  with respect to  $k$ .<sup>31</sup> This yields

$$g = \frac{d\nu}{dk}, \quad (5)$$

which, de Broglie specifies, is to be evaluated at a value of  $k$  such that  $\nu = E/h$  (he conceives of this as the central frequency of the component waves).

This group velocity,  $g$ , is related to the particle velocity,  $w$ , through the de Broglie relation  $\lambda = h/p$  or  $k = p/h$ . Here  $k$  is a function of  $p$ , the momentum of the particle, and, clearly,  $dk/dp = 1/h$ . Taking Equation (5) and multiplying equals by equals gives

$$g \frac{1}{h} = \frac{d\nu}{dk} \frac{1}{h} = \frac{d\nu}{dk} \frac{dk}{dp}.$$

Then by the Chain Rule,

$$g \frac{1}{h} = \frac{d\nu}{dp}.$$

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<sup>30</sup> $V$  here is potential energy. If  $E$  is substituted for  $h\nu$  in Eq. 4, the resulting equation,

$$u = \frac{E}{\sqrt{2m(E - V)}}$$

is identical to Schrödinger's Equation 8, page 125. There he develops a differential equation for the  $\Psi$  waves like that for the vibrating string. Then by assuming that his Equation 8 is a solution to this differential equation, he is able to determine a time-independent differential equation for the part, designated " $\psi$ ," of the  $\Psi$ -waves that represents a standing wave.

<sup>31</sup>Although the domain of definition of the function  $\nu(k)$  is not a continuous interval, the fact that it is a countably infinite, everywhere dense subset of an interval allows its derivative to be defined in the same way as was done in Junior Mathematics.

When there are only *two* components differing by  $\Delta\nu$  and  $\Delta k$  the expression  $g = \Delta\nu/\Delta k$  is exact. When there is an infinity of component waves, the expression for group velocity is  $g = d\nu/dk$ , as the next equation states. This expression, too, is exact.

Like any derivative  $d\nu/dk$  must be evaluated at individual values of the independent variable. The resulting value for  $g$  will depend on whatever value is specified for the wave number  $k$ . Then, inasmuch as the wave packet comprises a *range* for  $\lambda$  and therefore for  $k$ , the packet may exhibit a corresponding *range* of velocities. This is the result not of approximation but of heterogeneity: we cannot get a more sharply defined velocity for the packet as a whole by any limiting procedure.

Multiplying both sides by the constant  $h$ ,

$$g = h \frac{d\nu}{dp} = \frac{d(h\nu)}{dp} = \frac{dE}{dp}.$$

This equation expresses the group velocity of the wave packet in terms of  $E$  and  $p$ , the total energy and the momentum, respectively, of the particle.

At this point we can prove de Broglie's Theorem of Group Velocity:<sup>32</sup> *If a group of  $\Psi$  waves is associated with the motion of a particle, and if the central frequency of the group corresponds to the total energy of the particle, then the group-velocity will be equal to the particle's velocity.* For we have just seen that  $g = dE/dp$ . But the total energy equals the kinetic energy plus the potential energy. Further,  $p = mw$ , so that  $p^2 = m^2w^2$  and thus the kinetic energy  $K$  can be written as  $p^2/2m$ ; substituting gives

$$\frac{dE}{dp} = \frac{d}{dp} \left( \frac{p^2}{2m} + V \right).$$

Furthermore, the potential energy  $V$  is a function of the spatial coordinates only, so it acts like a constant when one differentiates with respect to  $p$ ; and  $\frac{1}{2}m$  is simply a constant. Thus,

$$\frac{d}{dp} \left( \frac{p^2}{2m} + V \right) = \frac{1}{2m} \left( \frac{d}{dp}(p^2) + 0 \right) = \frac{1}{2m} 2p.$$

And in turn

$$\frac{1}{2m} 2p = \frac{mw}{m} = w;$$

And, therefore,

$$g = \frac{dE}{dp} = w.$$

When  $E$  equals the total energy of a particle, and the central frequency of the group corresponding to it equals  $E/h$ , then the group velocity equals the velocity of the particle. Q.E.D.

Thus, in a dispersive medium the wave packet travels with the same speed as the particle and transports the particle's energy—simply as a result of the laws of wave propagation. But this rose has a thorn. The very fact of dispersion that allows the wave packet to form also forces it to disperse; the leading edge of the packet will always be moving at a greater speed than its trailing edge.<sup>33</sup> The wave packet can supply everything that was classically attributed to the Newtonian particle except permanence of location.

## D. THE INTERPRETATION OF MATTER WAVES

So far matter waves have been presented as guiding material particles. Whereas at first de Broglie had viewed the matter wave properties of wavelength and frequency as *due to* the material particle's momentum and energy, respectively, in his exposition in English of the ideas he developed for his dissertation, he proposed that matter waves are *responsible for* the dynamical properties of material particles:

<sup>32</sup>L. de Broglie, *Non-linear Wave Mechanics: A Causal Interpretation* (Amsterdam: Elsevier, 1960), 24.

<sup>33</sup>It can be shown that (as one might expect) the leading edge will move with approximately the greatest velocity in the range mentioned in note 31 above, and the trailing edge with approximately the least. We cannot go into the details.

I shall adopt a point of view slightly different from those which I have developed up to now, *for I shall take the laws of wave propagation as fundamental, and seek to deduce from them, as consequences which are valid in certain cases only, the laws of the dynamics of a particle.*<sup>34</sup>

From this point of view, the particle would not only have wave properties; every property of the particle would be given to it by its accompanying wave.

DeBroglie was hardly the only physicist to wonder about the physical interpretation that should be given to the mathematical formalism of wave mechanics. As we will see in subsequent chapters, different thinkers have produced different ways to think about the apparent paradoxes that arise from trying to find common ground between the formal mathematics that applies to particles and the formal mathematics that applies to waves. And there are many more attempts than the ones we will consider.

The question of how best to understand matter waves is still an open one today.

## EXAMPLES AND EXERCISES WITH MATTER WAVES

1. If every particle is accompanied by a phase wave, why are wave effects not always evident? Consider Rutherford's experiment: a beam of alpha particles passes through gold foil, which is a lattice of regularly spaced atoms, with gaps between nuclei on the order of  $10^{-8}$  cm.

Since the alpha-particle is a charged helium atom, its mass will be four times that of the hydrogen atom. At the very end of Chapter III we found the mass of the hydrogen atom to be  $1.674 \times 10^{-24}$  gm; thus the alpha particle has mass  $m = 6.696 \times 10^{-24}$  gm. And in Chapter IV Rutherford cites the velocity of the alpha particle as  $v = 2.09 \times 10^9$  cm/sec. Then the wavelength associated with these alpha particles must be, by de Broglie's relation,

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.625 \times 10^{-27}}{6.696 \times 10^{-24} \cdot 2.09 \times 10^9} = 4.73 \times 10^{-13} \text{ cm.}$$

Thus the phase wave associated with the alpha particle has a wavelength some 100,000 times smaller than the  $10^{-8}$  cm "slit" through which it must pass between the gold atoms. This would be comparable to a beam of yellow light, wavelength  $5900 \times 10^{-8}$  cm, passing through a slit 5.9 cm wide—for the 100,000:1 ratio is the same in both cases. As we would not expect detectable diffraction in the optical case, neither would discernible diffraction effects be expected in the scattering of alpha-particles by gold foil.<sup>35</sup>

2. What is the wavelength associated with a 200g baseball traveling at 4000cm/sec (about 89.5 mph), in comparison with a 100-cm-wide doorway? In this case,  $\sin \theta$  is on the order of  $10^{-34}$ , and the first bands of the interference pattern are separated from the center by about  $10^{-33}$  (one millionth to more than the fifth power!) degree. The matter waves of perceptible bodies produce no perceptible effects. If one angstrom ( $10^{-8}$  cm)

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<sup>34</sup>[L. de Broglie, "On the Parallelism between the Dynamics of a Material Particle and Geometrical Optics," *op. cit.*, 11-12.]

<sup>35</sup>For diffraction of light of wavelength  $\lambda$  by a single slit of width  $d$ , the maximum separation of interference bands will be given by the formula  $\sin \theta = \lambda/d$  (see Appendix I below). With  $\lambda/d$  approximately equal to 1/100,000, the angular separation  $\theta$  will only be about .0005°.

is the smallest slit-width available, then even something as small as an alpha particle would have to be moving impossibly slowly to interact detectably with the opening. On the other hand, the very small mass of the electron makes it a promising candidate to have a discernible wavelength.

3. Calculate the wavelength of the phase wave of the electrons in Thomson's cathode ray experiment, for which Thomson in Chapter II tabulated a speed of  $2.8 \times 10^9$  cm/sec.

Using the values already cited, we have

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.625 \times 10^{-27}}{.910 \times 10^{-27} \cdot 2.8 \times 10^9} = 2.6 \times 10^{-9} \text{ cm.}$$

Calculate the angular separation of the first bright bands produced by passing the electron beam through a crystal lattice of atoms spaced at intervals of 5 angstroms ( $5 \times 10^{-8}$  cm).

We shall have

$$\sin \theta = \frac{\lambda}{d} = \frac{2.6 \times 10^{-9}}{5 \times 10^{-8}} = .052$$

which gives an angular separation of nearly 3 degrees. Diffraction effects of this size will certainly be detectable—if one knows one is looking for them!

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# FOUR LECTURES ON WAVE MECHANICS

ERWIN SCHRÖDINGER

## FIRST LECTURE<sup>1</sup>

### **1. Derivation of the fundamental idea of wave mechanics from Hamilton's analogy between ordinary mechanics and geometrical optics.**



*FIGURE 1*

When a *mass-point*  $m$  moves in a conservative field of force, described by the potential energy  $V(x, y, z)$ , then, if you let it start from a given point  $A$  with a given velocity, i.e. with a given energy  $E$ , you will be able to get it into another arbitrarily chosen point  $B$  by suitably "aiming," i.e. by letting it start in a quite definitely chosen *direction*. There is in general *one* definite dynamical orbit which leads from  $A$  to  $B$  with a *given energy*. This orbit possesses the property that

$$\delta \int_A^B 2T dt = 0, \quad (1)$$

and is defined by this property (Hamilton's principle in the form given to it by Maupertuis). Here  $T$  means the kinetic energy of the mass-point, and the equation means: consider the manifold of *all* orbits leading from  $A$  to  $B$  and subject to the law of conservation of energy ( $T + V = E$ ); among them the actual dynamical orbit is distinguished by the fact that, *for it* and for all infinitely adjacent orbits of the manifold, the  $\int_A^B$  has the *same* value[...]. Calling  $w = ds/dt$  the velocity of the mass-point, we have

$$2T = mw^2 = m \left( \frac{ds}{dt} \right)^2 = 2(E - V) = \frac{ds}{dt} \sqrt{2m(E - V)}$$

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<sup>1</sup>[London: Blackie & Sons, Ltd. (1928) and New York: Chelsea (1982). Our excerpt includes only the first lecture.]

by means of which equation (1) can be transformed into

$$\delta \int_A^B \sqrt{2m(E - V)} ds = 0.^2 \quad (2)$$

This form has the advantage that the variational principle is applied to a purely geometrical integral, which does not contain the time-variable, and further, that the condition of constant energy is automatically taken care of.

*Hamilton* found it useful to compare equation (2) with *Fermat's* principle, which tells us that in an optically non-homogeneous medium the actual light rays, i.e. the tracks along which energy is propagated, are determined by the "law of minimum time" (as it is usually called).

Let fig. 1 now refer to an optical medium of arbitrary non-homogeneity, e.g. the earth's atmosphere; then, if you have a searchlight at  $A$ , furnishing a well-defined beam, it will in general be possible to illuminate an arbitrarily chosen point  $B$  by suitably aiming at it with the searchlight. There is one definite light-path leading from  $A$  to  $B$ , which obeys, and is uniquely defined by, the law

$$\delta \int_A^B \frac{ds}{u} = 0. \quad (3)$$

Here  $ds$ , as before, means the element of the path, and  $u$  is the velocity of light, a function of the co-ordinates  $x, y, z$ .

The two laws contained in equations (2) and (3) respectively become *identical*, if we postulate that

$$u = \frac{C}{\sqrt{2m(E - V)}} \quad (4)$$

where  $C$  must be independent of  $x, y, z$  but may depend on  $E$ . Thus we have made a mental picture of an optical medium, in which the manifold of possible light-rays coincides with the manifold of dynamical orbits of a mass-point  $m$  moving with given energy  $E$  in a field of force  $V(x, y, z)$ . The fact that  $u$ , the velocity of light, depends not only on the coordinates but also on  $E$ , the total energy of the mass-point, is of the utmost importance.

This fact allows us to push the analogy a step farther by picturing the dependence on  $E$  as dispersion, i.e. as a dependence on frequency. For this purpose we must attribute to our light-rays a definite frequency  $\nu$ , depending on  $E$ . We will (arbitrarily) put

$$E = h\nu \quad (5)$$

( $h$  being Planck's constant), without dwelling too much on this assumption, which is very suggestive to modern physicists. Then this non-homogeneous and dispersive medium provides in its rays a picture of all the dynamical orbits of our particle. Now we can proceed a stage farther, putting the question: can we make a small "point-like" light signal move exactly like our mass-point? (Hitherto we have only secured the geometrical identity of orbits, quite neglecting the question of time-rate.) At first sight this seems impossible, since the velocity of the mass point,

$$w = \frac{1}{m} \sqrt{2m(E - V)}, \quad (6)$$

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<sup>2</sup>[This is equivalent to  $\partial \int_A^B mw ds = 0$ , since  $2m(E - V) = 2mT = m^2 w^2$ .

is (along the path, i.e. with constant  $E$ ) *inversely* proportional to the light-velocity  $u$  (see equation (4);  $C$  depends on  $E$  only). But we must remember that  $u$  is of course the ordinary *phase*-velocity, whereas a small light-signal moves with the so-called *group-velocity*, say  $g$ , which is given by

$$\frac{1}{g} = \frac{d}{d\nu} \left( \frac{\nu}{u} \right),^3$$

or, in our case, following equation (5), by

$$\frac{1}{g} = \frac{d}{dE} \left( \frac{E}{u} \right). \quad (7)$$

We will try to make  $g = w$ . The only means we have at our disposal for this purpose is a suitable choice of  $C$ , the arbitrary function of  $E$  that appeared in equation (4). From (4), (6), and (7), the postulate  $g = w$  becomes

$$\frac{d}{dE} \left( \frac{E\sqrt{2m(E-V)}}{C} \right) = \frac{m}{\sqrt{2m(E-V)}} \equiv \frac{d}{dE} \left( \sqrt{2m(E-V)} \right);^4$$

hence

$$\left( \frac{E}{C} - 1 \right) \sqrt{2m(E-V)}$$

is constant with respect to  $E$ . Since  $V$  contains the co-ordinates and  $C$  must be a function of  $E$  only, this relation can obviously be secured in a general way only by making the first factor vanish. Hence

$$\frac{E}{C} - 1 = 0 \quad \text{or} \quad C = E,$$

which gives equation (4) the special form

$$u = \frac{E}{\sqrt{2m(E-V)}}. \quad (8)$$

This assumption about phase-velocity is the only one which will secure absolute coincidence between the dynamical laws of motion of the mass-point and the optical laws of motion of light-signals in our imagined light-propagation. It is worthwhile mentioning that, according to (8),

$$u = \frac{\text{energy}}{\text{momentum}}. \quad (8')$$

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Now the fundamental idea of wave-mechanics is the following. The phenomenon, of which we believed we had given an adequate description in the old mechanics by

<sup>3</sup>[See section C of the de Broglie chapter, particularly equation 5, p. 119.]

<sup>4</sup>[Schrödinger is really setting  $1/g = 1/w$ . The term on the left is  $1/g$ , while the middle term is  $1/w$  (from eq. 6). But the middle term is also identically equal ( $\equiv$ ) to the term on the right; thus the term on the left equals the term on the right. Moreover both terms are derivatives with respect to  $E$ . Since, then, the two quantities in parentheses have *equal derivatives* with respect to  $E$ , they differ by *at most a constant* (that is, by something that does not vary with  $E$ ). The expression in the next line denotes that difference; therefore it "is constant with respect to  $E$ ."]

describing the motion of a mass-point, i.e. by giving its co-ordinates  $x, y, z$ , as functions of the time variable  $t$ , is to be described correctly according to the new ideas by describing a definite wave-motion, which takes place among waves of the type considered, i.e. of the definite frequency and velocity (and hence of the definite wave-length) which we ascribed to what we called "light" in the preceding. The mathematical description of a wave-motion will be furnished not by a limited number of functions of the one variable  $t$ , but by a continuous manifold, so to speak, of such functions, viz. by a function (or possibly several functions) of  $x, y, z$ , and  $t$ . These functions will be subject to a *partial* differential equation, viz. to some sort of *wave equation*.

\* \* \*

## 2. Ordinary mechanics only an approximation, which no longer holds for very small systems.

In replacing the ordinary mechanical description by a wave-mechanical description our object is to obtain a theory which comprises both ordinary mechanical phenomena, in which quantum conditions play no appreciable part, and, on the other hand, typical quantum phenomena. The hope of reaching this object resides in the following analogy. Hamilton's wave-picture, worked out in the way discussed above, contains *something* that corresponds to ordinary mechanics, viz. the *rays* correspond to the mechanical *paths*, and *signals* move like *mass-points*. But the description of a wave-motion in terms of *rays* is merely an approximation (called "geometrical optics" in the case of light-waves). It only holds if the structure of the wave phenomenon that we happen to be dealing with is coarse compared with the wave-length, and as long as we are only interested in its "coarse structure." The detailed fine structure of a wave phenomenon can never be revealed by a treatment in terms of rays ("geometrical optics"), and there always exist wave-phenomena which are altogether so minute that the ray-method is of no use and furnishes no information whatever. Hence in replacing ordinary mechanics by wave mechanics we may hope on the one hand to retain ordinary mechanics as an approximation which is valid for the coarse "macro-mechanical" phenomena, and on the other hand to get an explanation of those minute "micro-mechanical" phenomena (motion of the electrons in the atom), about which ordinary mechanics was quite unable to give any information[...].

The step which leads from ordinary mechanics to wave mechanics is an advance similar in kind to Huygens' theory of light, which replaced Newton's theory. We might form the symbolic proportion:

$$\begin{aligned} \text{Ordinary mechanics : Wave mechanics} &= \\ \text{Geometrical optics : Undulatory optics.} \end{aligned}$$

Typical quantum phenomena are analogous to typical wave phenomena like diffraction and interference.

For the conception of this analogy it is of considerable importance that the failure of ordinary mechanics does occur in dealing with very *tiny* systems. We can immediately control [i.e., ascertain] the order of magnitude at which a complete failure is to be

expected, and we shall find that it is exactly the right one. The wave-length, say  $\lambda$ , of our waves is (see equations (5) and (8))

$$\lambda = \frac{u}{\nu} = \frac{h}{\sqrt{2m(E - V)}} = \frac{h}{mw}, \quad (9)$$

i.e. Planck's constant divided by the momentum of the mass-point.<sup>5</sup> Now take, for the sake of simplicity, a circular orbit of the hydrogen-model, of radius  $a$ , but not necessarily a "quantized" one. Then we have by ordinary mechanics (without applying quantum rules):

$$mwa = n \frac{h}{2\pi},$$

where  $n$  is any real positive number (which for Bohr's quantized circles would be 1, 2, 3 ...; the occurrence of  $h$  in the latter equation is for the moment only a convenient way of expressing the order of magnitude). Combining the last two equations, we get

$$\frac{\lambda}{a} = \frac{2\pi}{n}.$$

Now in order that we may be justified in the application of ordinary mechanics it is necessary that the dimensions of the path calculated in this way should turn out to be large compared with the wave-length. This is seen to be the case as long as the "quantum number"  $n$  is large compared with unity. As  $n$  becomes smaller and smaller, the ratio of  $\lambda$  to  $a$  becomes less and less favourable. A complete failure of ordinary mechanics is to be expected precisely in the region where we actually meet with it, viz. where  $n$  is of the order of unity, as it would be for orbits of the normal size of an atom ( $10^{-8}$  cm).

### 3. Bohr's stationary energy-levels derived as the frequencies of proper vibrations of the waves.

Let us now consider the wave-mechanical treatment of a case which is inaccessible to ordinary mechanics; say, to fix our ideas, the wave-mechanical treatment of what in ordinary mechanics is called the motion of the electron in the hydrogen atom.

In what way are we to attack this problem?

Well, in very much the same way as we would attack the problem of finding the possible movements (vibrations) of an elastic body. Only, in the latter case the problem is complicated by the existence of two types of waves, longitudinal and transverse. To avoid this complication, let us consider an elastic fluid contained in a given enclosure. For the pressure,  $p$ , say, we should have a wave equation

$$\nabla^2 p - \frac{1}{u^2} \ddot{p} = 0, \quad (10)$$

$u$  being the *constant* velocity of propagation of longitudinal waves, the only waves possible in the case of a fluid. We should have to try to find the most general solution of this partial differential equation that satisfies certain boundary conditions at the surface of the vessel. The standard way of solving is to try

$$p(x, y, z, t) = \psi(x, y, z)e^{2\pi i \nu t},$$

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<sup>5</sup>[See Equation (8), page 103.]

which gives for  $\psi$  the equation

$$\nabla^2\psi + \frac{4\pi^2\nu^2}{u^2}\psi = 0 \quad (10')$$

$\psi$  being subject to the same boundary conditions as  $p$ . We then meet with the well-known fact that a regular solution  $\psi$  satisfying the equation and the boundary conditions cannot be obtained for *all* values of the coefficient of  $\psi$ , i.e. for *all* frequencies  $\nu$ , but only for an infinite set of discrete frequencies  $\nu_1, \nu_2, \nu_3, \dots, \nu_k, \dots$ , which are called the characteristic or proper frequencies (*Eigenfrequenzen*) of the problem or of the body. Call  $\psi_k$  the solution (ordinarily unique apart from a multiplying constant) that belongs to  $\nu_k$ , then—since the equation and the boundary conditions are homogeneous—

$$p = \sum_k c_k \psi_k e^{2\pi i(\nu_k t + \theta_k)} \quad (11)$$

will, with arbitrary constants  $c_k, \theta_k$ , be a more general solution and indeed be *the* general solution, if the set of quantities  $(\psi_k, \nu_k)$  is complete [...].

In the case of the waves which are to replace in our thought the motion of the electron, there must also be some quantity  $p$ , subject to a wave equation like equation (10), though we cannot yet tell the physical meaning of  $p$ . Let us put this question aside for the moment. In equation (10) we shall have to put

$$u = \frac{E}{\sqrt{2m(E - V)}}.^6 \quad (8)$$

This is not a constant; it depends (1) on  $E$ , that is, essentially on the frequency  $\nu$  ( $= E/h$ ); (2) on the coordinates  $x, y, z$ , which are contained in the potential energy  $V$ . These are the two complications as compared with the simple case of a vibrating fluid body considered above. Neither of them is serious. By the first, the dependence on  $E$ , we are restricted in that we can apply the wave equation only to a function  $p$  whose dependence on the time is given by

$$p \sim e^{\frac{2\pi i Et}{h}}$$

whence

$$\ddot{p} = -\frac{4\pi^2 E^2}{h^2} p. \quad (12)$$

We need not mind that, since it is precisely the same assumption (*Ansatz*) as would be made in any case in the standard method of solution. Substituting from (12) and (8) in (10) and replacing the letter  $p$  by  $\psi$  (to remind us that now, just as before, we are investigating a function of the coordinates only), we obtain

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0. \quad (13)$$

We now see that the *second* complication (the dependence of  $u$  on  $V$ , i.e. on the co-ordinates) merely results in a somewhat more interesting form of equation (13) as compared with (10'), the quantity multiplying  $\psi$  being no longer a *constant*, but depending on

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<sup>6</sup>[Compare Section C of the de Broglie chapter, especially equation 4.]

the coordinates. This was really to be expected, since an equation that is to embody the mechanical problem cannot very well help containing the potential energy of the problem. A simplification in the problem of the "mechanical" waves (as compared with the fluid problem) consists in the absence of boundary conditions.

I thought the latter simplification fatal when I first attacked these questions. Being insufficiently versed in mathematics, I could not imagine how proper vibration frequencies could appear *without* boundary conditions. Later on I recognized that the more complicated form of the coefficients (i.e. the appearance of  $V(x, y, z)$ ) takes charge, so to speak, of what is ordinarily brought about by boundary conditions, namely, the selection of definite values of  $E$ .

I cannot enter into this rather lengthy mathematical discussion here, nor into the detailed process of finding the solutions, though the method is practically the same as in ordinary vibration problems, namely: introducing an appropriate set of coordinates (e.g. spherical or elliptical, according to the form of the function  $V$ ) and putting  $\psi$  equal to a *product* of functions, each of which contains one coordinate only. I will state the result straightforwardly for the case of the hydrogen atom. Here we have to put

$$V = -\frac{e^2}{r} + \text{const.}, \quad (14)$$

$r$  being the distance from the nucleus. Then it is found that not for all, but only for the following values of  $E$ , is it possible to find regular, one-valued, and finite solutions:

$$\left. \begin{array}{l} (\text{A}) E_n = \text{const.} - \frac{2\pi^2 me^4}{h^2 n^2}; n = 1, 2, 3, 4, \dots \\ (\text{B}) E > \text{const.} \end{array} \right\} \quad (14')$$

The constant is the same as in (14) and is (in non-relativistic wave mechanics) meaningless, except that we cannot very well give it the value which is usually adopted for the sake of simplicity, *viz.* zero. For then all the values (A) would become negative. And a negative frequency, if it means anything at all, means the same as the positive frequency of the same absolute value. Then it would be mysterious why all positive frequencies should be allowed, but only a discrete set of negative ones. But the question of this constant is of no importance here.

You see that our differential equation automatically selects as the allowed  $E$ -values (A) the energy-levels of the elliptic orbits quantized according to Bohr's theory; (B) all energy-levels belonging to hyperbolic orbits. This is very remarkable. It shows that, whatever the waves may mean physically, the theory furnishes a method of quantization which is absolutely free from arbitrary postulates that this or that quantity must be an integer.

\* \* \*

## REMARKS

In 1928, Erwin Schrödinger was invited to address the Royal Institution in London, where he presented a series of lectures introducing his notion of "wave mechanics." As befitting such an introduction, his emphasis is on the broad outlines of the theory rather than detailed accounts of application. That said, by the end of the first lecture, which is all that is presented here, he has already stated what he takes to be one of

the key signs of the novelty and success of his approach. Schrödinger announces this novelty in the title of a series papers published two years earlier, "Quantization as an eigenvalue [or 'proper value'] problem."<sup>7</sup>

Quantization, of course, is a name for the fact we have been dealing with since learning about Bohr's model of the atom, namely, the restriction of electrons to discrete orbits with definite energies, what Bohr called "stationary states." De Broglie's notion of some kind of wave associated with the particle suggests that the motion of a particle may be explained in terms of the refraction of this wave. The forces acting on a particle would thus be due to differences in something analogous to the refractive index of transparent materials, and the discreteness of its allowed orbits would result from the fact that the wave must be in phase with itself in its course about the nucleus; it must be a standing wave. Schrödinger carries this analogy even farther, with his mathematical formulation of a differential equation completely describing the motion of the electron, a wave equation.

The equation, he points out in section 3, cannot be "solved" for just any values of its parameters, but, in the case of the term for the wave's frequency, only for "an infinite set of discrete frequencies [...] called the characteristic or proper frequencies (*Eigenfrequenzen*) of the problem." (The energies associated with these frequencies would then be the "proper values" or "eigenvalues" of the problem.) This set of frequencies can be likened to the harmonic series for a vibrating string, though, as we will see, there are other more spatially complicated forms of periodicity in the atom.

Those complications aside, most of what Schrödinger is saying is clear, even if it still requires a good deal of interpretation. Some of his argument, however, relies on mathematical relations and techniques that may be unfamiliar. In section 1, Schrödinger makes use of the calculus of variations and some reasoning from de Broglie to derive an expression for the phase-velocity of the electron. In section 3, he uses a variety of techniques for solving his differential equation including separation of variables and a complex exponential. Accounts of these relations and techniques follow.

### Calculus of Variations (Sec. 1): Least Action and Least Time

Leibniz in the *Essay on Dynamics* had defined "moving action" (*l'action motrice*) as the joint product of the "formal effect" in a motion—mass times a distance moved, or  $ms$ —and the velocity of the movement,  $v$  or  $s/t$ . (Note that action is only defined for a whole motion, covering a finite distance in a finite time.) Thus the quantity of action  $Q$  associated with any motion at constant speed can be expressed as  $msv$  or, equivalently, as

$$Q = msv = ms \cdot \frac{s}{t} = m \frac{s}{t} \cdot \frac{s}{t} \cdot t = mv^2 \cdot t.$$

Since kinetic energy,  $T$ , is  $\frac{1}{2}mv^2$ , we can also express the action associated with such a motion as

$$Q = 2T \cdot t.$$

If the speed is not constant, we must *integrate* the above expression over time, and thus the action  $Q$  will be

$$Q = \int_A^B 2T dt,$$

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<sup>7</sup>"Quantisierung als Eigenwertproblem," *Ann. Phys.* **79**, 361; **79**, 489; **80**, 437; **81**, 109 (1926).

where  $A$  and  $B$  refer respectively to the times at the beginning and the end of the motion.

*The Principle of Least Action*<sup>8</sup> (which Schrödinger cites as “Hamilton’s principle”) states as a fundamental dynamical law that the particulars of any motion are always arranged so as to *minimize* the total action associated with that motion. This is a very powerful principle. Together with the Principle of Conservation of Total Mechanical Energy it can be shown to produce, *as a consequence*, Newton’s Laws of Motion and hence the rest of mechanics. So in beginning his treatment with these principles, Schrödinger is going back to an alternative conceptualization for the very foundations of mechanics.

To see what it means for action to be minimized, consider a freely moving body which traverses a path between  $A$  and  $B$ . Now consider the *difference*  $\Delta Q$  between the action calculated over that actual path and over some other path (with different velocities and kinetic energies  $T'$ ) between the same two endpoints:

$$\Delta Q = \int_A^B 2T' dt - \int_A^B 2T dt = \Delta \int_A^B 2T dt.^9$$

Next, let the hypothetical path be only *infinitesimally* removed from the actual path. Then the difference in action will likewise become infinitesimal. It is represented by the special notation

$$\delta Q = \partial \int_A^B 2T dt.$$

For the symbol  $\delta$  read “the *variation of*.”

The variational principle states that for the *actual* path, and only for that path, the variation  $\delta Q$  will equal zero. Symbolically, this condition is stated

$$\delta Q \int_A^B 2T dt = 0.$$

It appears as equation (1) in Schrödinger’s lecture.

As we indicated above, this is analogous to using calculus to find a maximum or minimum point for a function of one variable  $y = f(x)$ , for here a strict analogue to the variational principle also holds. That is, for any maximum or minimum point in such a function, one could say that

$$\delta y = 0.$$

For, recall that at any maximum or minimum point the first derivative of the function,  $dy/dx$ , must equal zero. But a very small change  $\Delta y$  in a function caused by a very small change  $\Delta x$  is closely approximated by  $\Delta y = (dy/dx)\Delta x$ . As a result, at a maximum or minimum point the *variation of the function is, to a first approximation, equal to zero*. Thus one might expect that, analogously, the variation of the action integral was zero for the actual, least-action, path. Mathematicians managed to prove that this was indeed so.

The *Principle of Least Time* applies to light, and states that the path actually taken by a light beam in passing from  $A$  to  $B$  is always a path of minimum overall time,

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<sup>8</sup>It may have been discovered by Leibniz himself, but the direct evidence for that is lost. It was first published by Pierre-Louis Maupertuis in 1744.

<sup>9</sup>In this equation  $A$  and  $B$  are shorthand for the times at which the body is at the  $A$  and  $B$  of the figure. They are not specified as the same for the two paths; only the points themselves are.

compared to neighboring paths joining the same endpoints. It too can be restated in the “variational” form:

$$\delta \int_A^B dt = 0.$$

Note that if the light velocity is  $u = s/t$ , then  $t = s/u$  and  $dt = ds/u$ ; so that the principle may also be expressed:

$$\delta \int_A^B \frac{ds}{u} = 0.$$

This appears as equation (3) in Schrödinger’s lecture.

A related reformulation turns the time-integral of equation (1) into an integral over space, equation (2): note that  $msv = (mv)s$ , so that action can also be thought of as *momentum times distance traveled*. If  $v$  is not constant, but is given as a function of the distance traveled, we can integrate, getting

$$Q = \int_A^B mv ds,$$

where  $A$  and  $B$  correspond to the starting-point and endpoint of the motion, such that for that path the integral over distance  $s$  will always be equal to the time-integral over  $T$ ,

$$Q = \int_A^B 2T dt,$$

from above. Thus the variations of both of these integrals will equal zero for the same, least-action path.

Schrödinger uses this spatial identity of the paths and some reasoning borrowed from de Broglie about group and phase velocity to derive equation (8), which will prove essential for later reasoning. In fact, here, there is a strict likeness to something familiar. In the final section of his “Remarks on the preceding papers by Mr. Bernoulli” (*Mechanics*, 207-230), Euler confesses he does not know how to solve the wave equation for a string that varies in thickness along its length, i.e., when the velocity term is itself a function of the spatial term: “the determination of the movement of these strings appears to be beyond our powers” (230). This is precisely what we will have in Schrödinger’s wave equation (10), where the velocity  $u$  defined in equation (8) contains the potential  $V$ , which varies with position, in particular, with distance from the center of the atom.

### Solving Differential Equations (Sec. 3): Separation of Variables and Complex Exponentials

*A. Notation.* As was just noted above, in one sense, Schrödinger’s first approach to the wave equation, in equation (10), could not be more traditional. It, too, relates the spatial derivative to the temporal by a simple multiplicative factor, as we can see with a simple rearrangement:

$$\nabla^2 p = \frac{1}{u^2} \ddot{p}. \quad (10')$$

Two pieces of notation may be unfamiliar. The first is the double-dot notation  $(\ddot{p})$ , which stands for the second derivative of the function with respect to time. The second,

$\nabla$ , is simply a shorthand for the sum of the individual spatial derivatives. In three-dimensional space, then,  $\nabla^2 p$  just means

$$\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} + \frac{\partial^2 p}{\partial z^2}.$$

In the one-dimensional case of the vibrating string and its transverse wave, we could think of this second spatial derivative geometrically as the curvature: the more intense the curvature, the more intensely was that portion of the string subject to the restoring force. In the two-dimensional case of a stretched drumhead, we can imagine it being struck in the center and the disturbance thus produced spreading radially in all directions in the plane. Here, too, the wave is transverse: the drumhead moves up and down, but the wave moves from the center to the periphery. Since the wave moves across the surface of the drumhead, the relevant "curvature" in this case must be measured with respect to two dimensions, say  $x$  and  $y$ . The portions of the wave (call it  $\psi$ ) moving directly along the  $y$ -direction alone (say, away from and toward the drummer) would have a non-zero value for  $\frac{\partial^2 \psi}{\partial y^2}$  and a zero value for  $\frac{\partial^2 \psi}{\partial x^2}$ , and conversely for the portions of the wave moving along the  $x$ -direction alone (left to right); but the portion of the wave moving along a line from the center pointing forward *and* to the right would have non-zero degrees of curvature expressed in the second partials for both  $x$  and  $y$ . Finally, in three dimensions, it is possibly easier to think of a longitudinal wave, such as a pressure wave, where the wave function's value at any point in space represents the pressure of the medium at that point. Here, clearly, the wave equation will have to measure something analogous to the string's or the drumhead's curvature in all *three* spatial dimensions at once in order to correctly account for the propagation of that wave in time.

So much for notation. As noted above, Schrödinger employs the technique of separation of variables to solve his equation and also uses a complex exponential. We will describe both before considering how they are applied in this case.

*B. Separation of Variables.* The idea is that in order to solve a partial differential equation, one begins by trying out a function that is the product of two other functions of only some of the variables, for instance, of space and time. The usefulness of this can be seen from the product rule  $(fg)' = fg' + f'g$ . If  $f$  and  $g$  are functions of space and time respectively, then their derivatives with respect to the other coordinates are zero and that latter term drops out—e.g.,  $\frac{\partial}{\partial x}(f(x)g(t)) = f \cdot 0 + f'(x)g(t) = f'(x)g(t)$ —leaving equations that are easier to solve.

As for what, beyond a desire for an easier solution, might induce us to think the function we are looking for could be expressed as a product, we can note that this is just the form we see in the standing-wave solutions to the one-dimensional wave equation for the vibrating string. For a string free to move up and down along the  $y$ -axis and stretched along the  $x$ -axis from 0 to  $2\pi$ , the second harmonic could have the form  $y = \sin(x)\cos(\pi t)$ . The following pictures show how this function appears at times  $t = 0, 1, 2$ . The sinusoidal shape stays fixed in place, even as its amplitude diminishes to



0 and then passes over into the negative. But this is just what the separated form of

the wave-function says: there is a shape, a function of the spatial coordinate, that does not vary with time, and a changing amplitude-factor that is the same throughout the whole spatial extent of the wave-function.

In the case of Schrödinger's wave equation (10), he considers a "trial" solution that is the product of distinct spatial and temporal parts. We've already noted how this might facilitate finding a solution. A further simplification comes from the way the function of time is expressed, as a *complex exponential*.

*C. Complex Exponentials.* You will likely have encountered Euler's number,  $e$ , the base of the natural logarithm. And you may have encountered the imaginary unit  $i = +\sqrt{-1}$ , used in the definition of the *complex numbers*, which have the form  $a + bi$ , where  $a$  and  $b$  are real numbers. Euler proved that, if it has any meaning at all, the expression  $e^{i\theta}$  should be interpreted as equal to the complex number  $\cos \theta + i \sin \theta$ . If we imagine the complex numbers as represented in a plane, then the complex exponentials lie on the unit circle about the origin, and  $\theta$  represents the arc length proceeding counter-clockwise around the circumference, starting from the point  $1 + 0i$ .

Given the simplicity of the rules for differentiating and integrating the exponential, and the ease with which it could be recast as a simple real-valued sinusoidal function (i.e., by ignoring the imaginary part), the complex exponential earned itself a place in the physicist's mathematical toolbox. For our purposes, it is almost sufficient simply to know the rule

$$de^{ix} = d(\cos x + i \sin x) = -\sin x \, dx + i \cos x \, dx = ie^{ix} \, dx.$$

Given this, it's easy to see that the factor  $-4\pi^2\nu^2$  in (10') comes from differentiating the product  $\psi(x, y, z)e^{2\pi i \nu t}$  twice with respect to time, as does the similar factor in (12), after the substitution of  $E/h$  for the frequency  $\nu$ . Late in the next chapter, we will consider more about how the complex form of the solution affects interpretation.

*D. The Form of the Solutions.* In equation (11), Schrödinger points out what would be the general solution if this were simply the problem of finding the pressure waves in "an elastic fluid in a given enclosure." There are a lot of terms, but if one imagines sinusoidal functions for each of the  $\psi_k$ , each with its own amplitude  $c_k$ , and ignores the time-function and its frequencies and phase angles, it looks a lot like Bernoulli's formulation for the shape of the vibrating string. Bernoulli's component waves, of course, have wavelengths that are submultiples of the length of the string, and in this way, his "solution" to the problem already includes the so-called "boundary conditions," as does Schrödinger's equation (11) in a general way (in its selection of frequencies  $\nu_k$ ).

But by the time he gets to equation (14'), Schrödinger is referring to a far more definite set of solutions. Along the way, he notes two "complications" and one "simplification" of the wave equation for the electron in comparison with the fluid problem. One we noted above, the dependency of the "velocity" term  $u$  on the spatial coordinates, and the likeness between this and the problem Euler imagined, of the string of varying thickness. But it's the simplification that poses what could have been a "fatal" problem. In the case of Bernoulli's solution we just mentioned (as well as in that of Euler's reformulation), the boundary conditions did some of the work of selecting from among the infinite scope of possible solutions. Here, the electron could be *anywhere in space*, like one of de Broglie's "pilot waves."

In this first lecture to the Royal Institution introducing the very idea of wave mechanics to a scientifically literate, but not necessarily expert, audience, Schrödinger is

understandably less than completely informative concerning “the detailed process of finding the solutions,” which would entail a “rather lengthy mathematical discussion.” Nonetheless, given the significant work we have done both this year and last to understand wave phenomena and mechanics, we should pause to fill in a little bit of the story here.

In somewhat naive terms, beginning from de Broglie, we might have imagined the wave threading around the nucleus of the atom in one orbital plane, its crests and troughs aligning with one another. The functions that are unique solutions to Schrödinger’s wave equation at a given energy level, however, are rather more geometrically complicated. Schrödinger is a bit more forthcoming about their form in the second lecture:

The detailed behavior of the “elliptic” functions within the said region [i.e., those belonging to bound electrons, near the nucleus] cannot very well be described in a unique way, for the following reason. To *one* value of  $E_n$  there belongs in general not only one, but precisely  $n^2$  independent solutions of the wave equation. From the mathematical point of view this is an exception due to the particular form of the potential energy  $V$ , especially to its spherical symmetry[...]. Since the equation is linear and homogeneous, any linear aggregate with quite arbitrary coefficients [cf. equation (11)] will also be a solution belonging to the *same* proper value[...]. To give an example: from a set of solutions whose node-surfaces [i.e., surfaces with the same magnitude] are (1) concentric spheres, (2) co-axial cones, (3) planes passing through the cone-axis, you can form other solutions, in which the concentric spheres and co-axial cones are replaced by two sets of confocal paraboloids. This is only one of the simplest cases. In general, taking arbitrary coefficients, the system of node-surfaces will be *much* more complicated.

Two notes here: 1) the “magnitude” mentioned in the interpolation is the modulus squared of the complex number that is the value of the wave-function: if the number is  $a + bi$ , this is the non-negative real number  $a^2 + b^2$ ; 2) the wave-function is in general spread out in space, such that the node-surfaces formed by choosing a particular magnitude of the function give only some of the information about the geometry of the function, as a weather map might indicate gross features of the atmospheric pressure in a large region by tracing several lines of constant pressure (isobars). Perhaps you will have seen representations of the higher-order “orbitals” in a book of chemistry. It is these shapes and details about the atomic behavior of electrons that Schrödinger’s equations allowed physicists to understand, even as the difficult work of interpreting the physical meaning of the wave equation for a material particle was just beginning.



# CRITIQUE OF THE PHYSICAL CONCEPTS OF THE PARTICLE PICTURE

WERNER HEISENBERG

## THE PHYSICAL PRINCIPLES OF THE QUANTUM THEORY<sup>1</sup>

WERNER HEISENBERG

### CHAPTER II

#### CRITIQUE OF THE PHYSICAL CONCEPTS OF THE PARTICLE PICTURE

##### §I. The Indeterminacy Relations

The concepts of position, velocity, and energy have been derived from simple experiments of everyday experience, in which the mechanical behavior of macroscopic bodies is described by these words. These concepts were then carried over to electrons, since in some fundamental experiments electrons show a mechanical behavior similar to objects of everyday experience. But since we know that this similarity exists only in a limited region, the range of applicability of the concepts of the particle picture must be restricted in a corresponding way. According to Bohr,<sup>2</sup> one arrives at this restriction in the simplest way by recalling that all intuitible facts (i.e., facts describable in space and time) of atomic physics must *also* be describable in a wave picture.

The following considerations apply equally to each of the three space co-ordinates of the electron and are therefore carried out for only one. The fact that the position of an electron is known with a certain exactness  $\Delta x$  [at the time  $t$ ] can obviously be described in the wave picture by a wave function whose amplitude is significantly different from zero only in a small range of approximate magnitude  $\Delta x$ . A wave function constructed in this way can always be thought of as composed of a number of partial waves which interfere with each other in such a way as to reinforce one another within the small spatial range  $\Delta x$  but cancel one another everywhere outside that range. Such a configuration is called a *wave packet*. A general mathematical proposition states that it is always possible, through appropriate composition of the individual partial waves, to build up a wave packet of any desired shape. In the course of time such a wave packet will in general change its size and shape and, apart from special cases, will ultimately be dispersed over the whole of space. The velocity of the electron likewise corresponds to the velocity of the wave packet; however, no exact velocity can be defined for the

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<sup>1</sup>[*Die Physikalischen Prinzipien der Quantentheorie*, Leipzig (1930); also *The Physical Principles of the Quantum Theory*, trans. C. Eckart and F. C. Hoyt, Chicago (1930). The present selections were translated 1995 by C. Burke and E. Brann, slightly revised in 2007 by H. Higuera and in 2014 by R. Druecker.]

<sup>2</sup>N. Bohr, *Nature*, **121**, 580, 1928. [Note taken from English edition, giving citation to English version of Bohr's article.]

wave packet because, as was said, besides its forward motion, it also spreads and disperses itself. This dispersion thus occasions an indeterminacy in the definition of the momentum (mass times velocity) of the amount, say,  $\Delta p$ . Now, from the simplest laws of optics, together with the equations

$$[\lambda = \frac{h}{p} \quad \text{and} \quad v_g = \frac{h}{\mu\lambda_0}]^3$$

it can be derived that

$$\Delta x \Delta p_x \geq h. \quad (1)$$

For, think of the wave packet as being composed out of the superposition of plane [sinusoidal] waves, whose wave-lengths are to lie in the neighborhood of  $\lambda_0$ . Then, on the whole,  $n = \Delta x / \lambda_0$  crests or troughs fall in the region inside the packet. Outside the packet the plane waves are to cancel each other by interference; this is possible if, and only if, the totality of component plane waves contains some for which at least  $n + 1$  waves fall in the critical range. This gives

$$\frac{\Delta x}{\lambda_0 - \Delta\lambda} \geq n + 1,^4$$

where  $\Delta\lambda$  indicates approximately the range of wave-lengths which is necessary for the representation of the packet. Consequently

$$\frac{\Delta x \Delta\lambda}{\lambda_0^2} \geq 1.^5 \quad (2)$$

On the other hand, the group velocity of the waves is

$$v_g = \frac{h}{\mu\lambda_0}.^6 \quad (3)$$

<sup>3</sup>[Heisenberg derives these equations in an appendix and references them here rather than writing them out. For further details see footnote 6 below.]

<sup>4</sup>[The waves of longer and shorter wavelength must reinforce each other at the center of the packet and interfere at each end. Hence they must be out of coincidence by one-half wavelength at each end, which is only possible if the shorter waves are contained at least one more time than are the longer waves in the same distance  $\Delta x$ . If there are  $n = \Delta x / \lambda_0$  of the longer waves of length  $\lambda_0$  in the packet, then there must be at least  $n + 1$  of the shorter waves of length  $\lambda_0 - \Delta\lambda$  within the same region  $\Delta x$ .]

<sup>5</sup>[From the inequality at the end of the previous note,

$$\frac{\Delta x}{\lambda_0 - \Delta\lambda} \geq n + 1 = \frac{\Delta x}{\lambda_0} + 1,$$

collecting algebraic terms to the left and adding gives,

$$\frac{\Delta x \Delta\lambda}{\lambda_0(\lambda_0 - \Delta\lambda)} \geq 1,$$

which can be approximated to inequality (2) if  $\Delta\lambda$  is sufficiently small compared to  $\lambda_0$ .]

<sup>6</sup>[As just mentioned, Heisenberg derives equation (3) in an appendix. Here  $\mu$  is the mass of an electron. Now if in de Broglie's  $\lambda = h/p (= h/\mu v)$  one stipulates that the de Broglie wavelength of the *electron* is "the"  $\lambda_0$  of the *packet* and that the velocity of the electron equals the group velocity, one gets  $\lambda_0 = h/\mu v_{g_e}$ , from which eq. (3) follows immediately. But Heisenberg actually derives eq. (3) *directly from the Schrödinger wave equation* and, without relying on "particle" concepts. As he writes, "The wave theory does not consider electrons, [but] merely universal constants of the wave equation."]

The dispersion of the packet corresponding to the range  $\Delta\lambda$  is therefore characterized by [a range of velocities]

$$\Delta v_g \approx \frac{h}{\mu\lambda_0^2} \Delta\lambda.^7$$

By definition  $\Delta p_x = \mu\Delta v_g$ , and therefore by equation (2),

$$\Delta x \Delta p_x \geq h.^8$$

\* \* \*

The indeterminacy relations [...] specify the limits within which the concepts of the particle theory can be applied. Any use of the words "position" or "velocity" with an exactness exceeding that indicated by equation (1) is just as empty of content as the use of words whose sense has not been defined.<sup>9</sup>

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## §2. Confirmation of the Intedeterminacy Relations using Various Measuring Devices

The indeterminacy relations relate to the degree of exactness in our present (simultaneous) knowledge of the various quantum-theoretical magnitudes. Since these relations do not restrict the exactness, for example, of a position measurement alone or a velocity measurement alone, their effect expresses itself only in the fact that each experiment that makes possible a measurement of, say, position, necessarily disturbs the knowledge of the velocity to a certain degree. Let us suppose, for example, that the velocity of a [free] electron is exactly known, while the position is completely unknown. Then every subsequent observation of the position must alter the momentum of the electron, and this alteration must be indeterminate by an amount such that after the experiment is carried out our knowledge of the electron's motion is limited by the indeterminacy

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<sup>7</sup>[If one does *not* impose assumptions from the particle picture, then in the packet *both* the longer *and* the shorter waves have an equal claim to be considered "the" wavelength for purposes of equation (3). That equation is already written for the longer wavelength  $\lambda_0$ . Were it instead to be written for the shorter wavelength,  $\lambda_0 - \Delta\lambda$ , there would be determined a different group velocity,

$$v'_g = \frac{h}{\mu(\lambda_0 - \Delta\lambda)}$$

and the difference between  $v'_g$  and  $v_g$  is the "range of velocities"  $\Delta v_g$ . Thus

$$\Delta v_g = \frac{h}{\mu(\lambda_0 - \Delta\lambda)} - \frac{h}{\mu\lambda_0} = \frac{h\Delta\lambda}{\mu\lambda_0(\lambda_0 - \Delta\lambda)} \approx \frac{h\Delta\lambda}{\mu\lambda_0^2}.$$

<sup>8</sup>[Substituting from the equation for  $\Delta v_g$ ,  $\mu\Delta v_g = \mu \frac{h}{\mu\lambda_0^2} \Delta\lambda = h \frac{\Delta\lambda}{\lambda_0^2}$ . Therefore,  $\Delta x \Delta p_x = h \frac{\Delta x \Delta\lambda}{\lambda_0^2}$ ; that is, by equation (2),  $\Delta x \Delta p_x$  equals  $h$  times something  $\geq 1$ .]

<sup>9</sup>In this connection one should particularly remember that the human language quite generally permits the construction of sentences from which no consequences follow and which are therefore completely empty of content, although these sentences produce a kind of intuitible representation. For example, the assertion that besides our world there exists another world, with which any connection is impossible *in principle*, does not lead to any inference; nevertheless, accompanying this statement a kind of picture arises in the imagination. Obviously such a statement can neither be proved nor disproved—one should be especially careful in the use of the expression "in actuality" since it very often leads to assertions of the type just discussed.

relations. This will be confirmed in what follows, using some experiments as examples. But first let it be remarked that the indeterminacy relations evidently do not refer to the past. For if the velocity of the electron is known to begin with, and subsequently the position is exactly measured, then the electron's positions for the time *before* the measurement of position may also be exactly calculated. For this previous time, the quantity  $\Delta p \Delta x$  will be smaller than the usual limiting value. This knowledge of the past, however, is of a purely speculative character, since—because of the change in momentum caused by the position measurement—it can in no way enter as an initial condition in any calculation concerning the future of the electron, and never makes an appearance in any physical experiment at all. It is thus a pure matter of taste whether or not one is to ascribe to such a calculation concerning the past of the electron any physical reality.



Figure 5.<sup>10</sup>

a) *Determination of the position of a free particle.*—As a first example of the disturbance of the knowledge of a particle's momentum by an apparatus for measuring position, we choose the position measurement by means of a microscope.<sup>11</sup> Let the electron be moving at such a distance under the objective of the microscope that the cone of rays scattered from it has an angular opening  $\varepsilon$ . Let the wave-length and frequency of the light illuminating the electron be  $\lambda$  and  $\nu$ ; then the exactness in the position measurement of the  $x$ -direction (see Fig. 5) according to the [limit on resolving power of any optical instrument] is:<sup>12</sup>

$$\Delta x \approx \frac{\lambda}{\sin \varepsilon}. \quad (16)$$

But for a position measurement to be possible, at least one photon must be scattered from the electron and pass through the microscope to reach the eye of the observer. From this one photon, the electron receives a Compton recoil<sup>13</sup> of order of magnitude

<sup>11</sup>N. Bohr, *loc. cit.*

<sup>12</sup>[The resolving power of a lens is limited by the aperture of the lens, since any small opening will diffract any light it transmits. If the central maxima of the diffraction patterns of two objects then overlap to any great extent, those objects will be indistinguishable through the lens. The separation,  $\Delta x$ , at which two "point" objects can no longer be distinguished sets a limit to our ability to determine the position of an object with a microscope—a limit which depends on the angular aperture of the objective lens and the wavelength of the illuminating light. A derivation of equation (16) is given in the Note at the end of this chapter.]

<sup>13</sup>[Recall that the interaction of light with electrons can be understood as an *elastic collision* between electrons and photons if the photons of energy  $e = h\nu$  are also assigned momentum of amount  $p = h/\lambda$ .

In the sketch, a photon after rebounding from a particle will have momentum  $h/\lambda$ . If it enters the microscope it must fall within the angle  $\varepsilon$  and therefore will carry away momentum  $px$  in the  $x$ -direction, which can be as little as zero or as much as  $(h/\lambda) \sin \varepsilon$ . But since the direction of any particular photon cannot be distinguished by the microscope, the momentum of the particle is unknown within a range

$h/\lambda$ . The recoil cannot be known exactly, since within the bundle of rays (of angular opening  $\varepsilon$ ) the direction of the photon [entering the microscope] is unknown.<sup>14</sup> Thus there will be an uncertainty of the recoil in the  $x$ -direction of amount

$$\Delta p_x \sim \frac{h}{\lambda} \sin \varepsilon \quad (17)$$

and it follows for the knowledge of the electron's motion after the experiment that

$$\Delta x \Delta p_x \sim h. \quad (18)$$

Objections may at first be raised against this derivation: The reason for the indeterminacy of the recoil is, after all, that it is unknown which path within the bundle of rays the photon takes. One might thus try to determine this path by making the whole microscope movable and measuring the recoil that it receives from the photon. But this will not help to circumvent the indeterminacy relations; for there then immediately arises the question of the position of the microscope, and the position and momentum of the whole microscope will also be subject to equation (18). To be sure, the measurement of the position of the microscope could be neglected altogether if the electron and a fixed scale could be simultaneously observed through the movable microscope. But then one observation would require the simultaneous passage of at least two photons through the microscope to the observer—one from the scale and one from the electron—and a measurement of the recoil of the microscope would no longer yield information about the photon coming from the electron, and so on.

The whole discussion of this experiment characteristically makes use of the wave picture and the particle picture simultaneously. Here we make use of that duality essentially in the theory of radiation; for on the one hand we speak of bundles of rays and the laws of optics, and on the other hand, of photons and the recoils caused by them.

Another simple determination of position can be performed in the following way: Again let the velocity of the electron be completely known. Consider a set of possible paths which an electron might take in approaching a screen that contains a slit of width  $d$  (Fig. 6). If the electron passes through this slit, then evidently its position in the direction parallel to the screen is fixed with exactness  $\Delta x = d$ . If the oncoming electron is represented by a plane de Broglie wave, however, one sees immediately that diffraction will occur. The emerging wave will have a finite angular opening  $\alpha$  which, by the

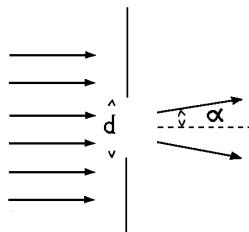
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equal to  $(h/\lambda) \sin \varepsilon$ .]



<sup>14</sup>[There is a lens across the aperture. If the microscope is focused properly, then according to ray-optics wherever the "ray" of light passes through the lens, it will be refracted onto the same point on the detecting screen.]

<sup>15</sup>[The figure is that of the 1930 Chicago edition and corrects an error in the Leipzig edition.]

Figure 6.<sup>15</sup>

simplest laws of optics,<sup>16</sup> will be given by

$$\sin \alpha \sim \frac{\lambda}{d}, \quad (19)$$

where  $\lambda$  is the wave-length of the de Broglie waves. Thus the momentum of the electron parallel to the screen, after the electron's passing through the slit, is uncertain by an amount

$$\Delta p_x = \frac{h}{\lambda} \sin \alpha \quad (20)$$

since  $h/\lambda$  is the momentum of the electron in the direction of the beam. Then, since  $\Delta x = d$ , it follows that

$$\Delta x \Delta p_x \sim h.$$

In this derivation, although no use is made of the wave-particle duality in the theory of radiation, it is indeed used in the theory of matter.

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## CHAPTER IV

### THE STATISTICAL INTERPRETATION OF QUANTUM THEORY<sup>17</sup>

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#### §3. Bohr's Concept of Complementarity

The world of concepts derived from everyday experience was for the first time left behind in Einstein's relativity theory. It became apparent that the ordinary concepts could only be applied to processes in which the velocity of the propagation of light could be regarded as practically infinite. The experiential material which has been refined through modern experimental physics thus necessitated the revision of received concepts and the development of new ones; but our thinking could adjust itself only slowly to that extended range of experience and the world of its concepts; and therefore relativity theory itself seemed at first abstract and alien. As is clear from what has been said, the experiences from the world of atoms compel us to an even more extensive renunciation of hitherto customary concepts. Indeed, our ordinary description of nature and especially the thought of a strict lawfulness in the processes of nature rest on the

<sup>16</sup>["The simplest laws of optics:" Heisenberg refers to the expression for single-slit diffraction,  $\sin \theta_1 = \lambda/d$ , where  $\theta_1$  is the half-width of the central maximum (see the Note at the end of this chapter).]

<sup>17</sup>[*Nature*, 121, 580, 1928. Again, citing the English version.]

assumption that it is possible to observe phenomena without appreciably influencing them. To co-ordinate a determinate cause to a determinate effect has a meaning only when we can observe effect and cause without simultaneously disturbing the process by our intervention. The law of causality in its classical form can thus, by its nature, be defined only for isolated systems. But in atomic physics there is in general connected with each observation a finite disturbance that is to a certain degree uncontrollable, as was from the very beginning only to be expected in the physics of what are in principle the smallest units. Since, on the other hand, every space-time description of a physical process is conditioned by the observation of the process, it follows that the space-time description of processes on the one hand, and the classical law of causality on the other, represent complementary and mutually exclusive features of the physical event. What corresponds to this situation in the formalism of the theory is the fact that while a mathematical model of quantum theory exists, this model cannot be interpreted as a simple connection of things in space and time. Through this complementarity of the space-time description on the one hand, and of the causal connection on the other, there arises moreover a peculiar ambiguity in the concept "observation" in that it is left arbitrary which objects are to be counted as belonging to the observed system and which are to be regarded as means of observation. In the formalism of the theory this arbitrariness has the consequence that often quite heterogeneous methods can be used for the interpretation of a physical experiment [...]. But even if one accepts the arbitrariness mentioned, the concept "observation" belongs strictly speaking to the world of ideas drawn from our everyday experience. It can be carried over to atomic phenomena only when due regard is paid to the limitation placed on all space-time pictures by the indeterminacy relations. For every observation is by definition bound to space and time; therefore, this concept has meaning only within the boundaries specified by those relations. It has already been mentioned that there are special cases in which the requirements of the classical law of causality can be brought into agreement with a spatio-temporal description to a certain approximation. In general, however, the situation can be characterized by something like the following diagram:

### CLASSICAL THEORY

Space-time description [and] Causality

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It is only after attempting to adjust the formation of one's concepts to this fundamental complementarity of space-time description and causality, that one is in a position to judge whether the methods of quantum theory are free of inconsistency [...]. The adaptation of our thought and our language to the experiences of atomic physics is indeed associated with great difficulties, just as it had been for relativity theory. In rel-

ativity theory the earlier philosophical discussions of the problems of space and time proved to be very serviceable to this adaptation. In a similar way one can profit in atomic theory from the discussions, fundamental to all epistemology, concerning the difficulties connected with the separation of the world into subject and object. Quite a few abstractions which are characteristic of modern theoretical physics will be found to have been already discussed in the philosophy of past centuries. While these abstractions could in the past be rejected as thought-play by the natural scientist intent only on realities, the more refined experimental art of modern physics now forces us to discuss them thoroughly.

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## M. BORN: THE PROBABILITY INTERPRETATION

Physicists generally came to accept the mathematical formalism of the  $\Psi$  waves as initiated by de Broglie and developed by Schrödinger. However, there was a lively debate over the *interpretation* of them. Einstein, for example, as we shall see later on, thought that, in some sense, the  $\Psi$  function did not give the complete account of entities like electrons because it was based upon inadequate concepts of classical physics.

Aside from this suggestion there seem to be, roughly speaking, three possibilities. As was seen in Chapter 8, de Broglie thought of an electron as simultaneously *both* a particle *and* a wave. Secondly, one might hold that an electron is *only* a wave, and not a particle at all. De Broglie's second presentation of his idea of wave mechanics suggests the following reasoning: Huygens and Young saw that if wave optics is correct, there really are no light particles but only light waves that appear as straight-line particle paths due to the smallness of the wavelength in comparison with the size of the objects with which the waves interact. So too it should be the case that if wave mechanics is correct, there really are no material particles but only  $\Psi$  waves that appear as particles in certain situations. This is the approach taken by Schrödinger. He considered that a particle was simply a wave packet, and he associated the function  $\Psi$  in a certain way with the density of charge in space.

The third approach, the so-called "Copenhagen interpretation," according to which an electron is *either* a particle *or* a wave—in the sense that it exhibits now particle-like behavior, now wave-like behavior—but never both simultaneously, was the one developed by Bohr and Heisenberg.

The Copenhagen complementarity interpretation of the electron was joined with an interpretation of the wave function  $\Psi$  proposed by Max Born. According to this interpretation, the wave function at any point in space,  $\Psi(x, y, z, t)$ , is to be viewed as determining a *probability density*—that is, the probability, per unit volume, of *observing*<sup>18</sup> a particle very near that point.

In the following passage from his textbook,<sup>19</sup> Born begins the presentation of his interpretation by opposing that of Schrödinger:

In the preceding sections we have had a series of facts brought before us which seem to indicate unequivocally that not only light, but also electrons

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<sup>18</sup>"Observing" includes, for example, having a particle cause a glow on a screen at a point.

<sup>19</sup>*Atomic Physics* (New York: Hafner, 1962), 96-100.

and matter, behave in some cases like a wave process, in other cases like pure corpuscles. How are these contradictory aspects to be reconciled?

To begin with, Schrödinger attempted to interpret corpuscles, and particularly electrons, as *wave packets*. Although his formulae are entirely correct, his interpretation cannot be maintained, since on the one hand, as we have already explained above, the wave packets must in course of time become dissipated [see below], and on the other hand the description of the interaction of two electrons as a collision of two wave packets in ordinary three-dimensional space lands us in grave difficulties.<sup>20</sup>

The interpretation generally accepted at present goes back to the present writer. According to this view, the whole course of events is determined by the laws of probability; to a state in space there corresponds a definite probability, which is given by the de Broglie wave associated with the state. A mechanical process is therefore accompanied by a wave process, the guiding wave, described by Schrödinger's equation, the significance of which is that it gives the probability of a definite course of the mechanical process. If, for example, the amplitude of the guiding wave is zero at a certain point in space, this means that the probability of finding the electron at this point is vanishingly small.

The physical justification for this hypothesis is derived from the consideration of scattering processes from the two points of view, the corpuscular and the undulatory. The problem of the scattering of light by small particles of dust or by molecules, from the standpoint of the classical wave theory, was worked out long ago. If the idea of light quanta is to be applied, we see at once that the number of incident light quanta must be put proportional to the intensity of the light at the place concerned, as calculated by the wave theory. This suggests that we should attempt to calculate the scattering of electrons by atoms, by means of wave mechanics. We think of an incident beam of electrons as having a de Broglie wave associated with it. When it passes over the atom this wave generates a secondary spherical wave; and analogy with optics suggests that a certain quadratic expression formed from the wave [function  $\Psi$ ] should be interpreted as the current strength, or as the number of scattered electrons.<sup>21</sup> On carrying out the calculation it has been found that for scattering by a nucleus we get exactly Rutherford's formula. Many other scattering processes were afterwards subjected to calculation in this way, and the results found in good

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<sup>20</sup>[Born's second reason against the possibility of maintaining Schrödinger's interpretation is the following: The extension of Schrödinger's theory to an interaction between two particles involved six spatial coordinates, three for each particle. Thus, on the most natural generalization of Schrödinger's theory, the  $\Psi$  waves became waves in a non-physical, six-dimensional space, a consequence which does not accord with the interpretation of the  $\Psi$  waves as representing physical waves. And attempts to treat a two-particle situation in a different way so as to preserve the physical character of the  $\Psi$  wave had not born fruit.]

<sup>21</sup>[See Chapter 8, note 9, p. 105. We know that  $p \propto N \propto I \propto F^2$ . Analogously, for the matter wave function  $\Psi(x,y,z,t)$ , the probability of finding the particle in a certain region, Born proposed, would be the integral of the modulus squared of the wave-function over that region. Though the value of the wave-function is complex, its modulus squared is always real and non-negative. If the wave-function is "normalized," such that its magnitude over all space is set equal to 1, then the probability of finding its particle in a given region will always be  $\leq 1$ .]

agreement with observation. These are the grounds for the conviction of the correctness of the principle of associating wave [function] with number of particles (or probability). . . .

What, then, is a problem with physical meaning? This is for us the really important question, for clearly enough the corpuscular and wave ideas cannot be fitted together in a homogeneous theoretical formalism, without giving up some fundamental principles of the classical theory. The unifying concept is that of probability; this is here much more closely interwoven with physical principles than in the older physics.

The following passage<sup>22</sup> presents an analogy as an aid to understanding Born's hypothesis:

Born assumed that the De Broglie wave associated with a scattered beam of electrons would be a measure of the probability for that particular state of scattering. In general, therefore, the square of the amplitude of the De Broglie wave of an electron determines the probability of finding the electron in a given region of space.

We may illustrate this point by drawing an analogy between the De Broglie waves of a collection of particles and the water waves on the ocean. If we watch the ocean, we observe that the surface is in constant agitation. The disturbances range from small ripples to large waves. The greater the amplitude of a wave, that is, the higher above the surface of the ocean is the crest of the wave, the more intense is the disturbance of the water at that point. Where there is no disturbance at all, the water is perfectly smooth and the amplitude of the wave is zero. We now picture the space surrounding an electron or a swarm of electrons as being similar to the surface of the ocean. But the waves with which we are now concerned are not physical ones, but rather probability waves, or waves that are a measure of the probability for finding the electron, or groups of electrons, at particular points in space. The greater the intensity of a De Broglie wave at a point, the greater is the probability for finding the electron there; should the amplitude of the De Broglie wave vanish at any point, the probability for finding the electron there is zero.

Suppose we consider an electron in a region of space in which the De Broglie wave is spread out uniformly, so that the amplitude of the wave is everywhere the same. This means that there is an equal probability of finding the electron at any point in this region. What happens, then, if we perform an experiment in which we look for the electron and locate it at a given point in this region? For example, we can place a fluorescent screen in some position and if the electron happens to strike it, we observe a scintillation at the point where it hits the screen. Since we know that the electron is precisely at this point of scintillation on the screen, the probability of finding the electron there is one and the probability of finding the electron elsewhere at this time is zero. This means that we may think of the De Broglie wave describing the electron, which originally was spread out

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<sup>22</sup>H. Boorse and L. Motz, edd., *The World of the Atom*, Vol. II, 1079.

uniformly, as now concentrated in a tiny packet. Thus, by performing an experiment we have altered the nature of the wave describing the electron and therefore the future unfolding of the probability.

This interpretation appealed to Born for the additional reason that it brings particles into close analogy with light. As we saw, de Broglie and Einstein linked the Maxwellian wave with the photon by making the square of the amplitude of (the electric component of) that wave at any point give the probability that a photon will interact with an atom or electron there. Adopting an analogous interpretation for  $\Psi$  made particles and light that much more similar mathematically and, it was hoped, would help in understanding whatever real kinship they must have.

While Born's probability interpretation of  $\Psi$  became an essential part of the orthodox Copenhagen interpretation, Schrödinger, Einstein and, after 1952, de Broglie dissented. Schrödinger, for example, wrote in 1953<sup>23</sup>:

The wave v. corpuscle dilemma is supposed to be resolved by asserting that the wave field merely serves for the computation of the probability of finding a particle of given properties at a given position if one looks for it there. But once one deprives the waves of reality and assigns them only a kind of informative role, it becomes very difficult to understand the phenomena of interference and diffraction on the basis of the combined action of discrete single particles. It certainly seems easier to explain particle tracks in terms of waves than to explain the wave phenomenon in terms of corpuscles.

Thus, when Heisenberg speaks of a "probability function" in the discussion that follows, he is referring to  $\Psi$ .

## THE COPENHAGEN INTERPRETATION OF QUANTUM THEORY<sup>24</sup>

WERNER HEISENBERG

The Copenhagen interpretation of quantum theory begins with a paradox. Every physical experiment, it matters not whether it refers to a phenomenon of daily life or to atomic physics, must be described through the concepts of classical physics. These classical concepts form the language by which we indicate the arrangement of our experiments and determine the results; and we cannot replace them by any others. Nevertheless the application of these concepts is limited by the relations of indeterminacy. We must keep in mind this limited range of applicability of the classical concepts while using them, but we cannot and should not try to improve them.

For a better understanding of this paradox it is useful to see how the interpretation of an experiment in classical physics differs from that of an experiment in quantum theory. In Newton's celestial mechanics, for instance, we may start by measuring the position and the velocity of the planet whose motion we are going to study. The results of the observation are translated into mathematics by deriving numbers for the coordinates and the momenta of the planet from the observation. Then the equation of

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<sup>23</sup>[“What Is Matter?” *Scientific American* (September, 1953), 56.]

<sup>24</sup>[From Chapter III of *Physik und Philosophie*, Stuttgart (1959); also *Physics and Philosophy: The Revolution in Modern Science* (1962). The present selection was translated 1995 by C. Burke and E. Brann.]

motion is used to determine from these values of the co-ordinates and momenta at a given time the values of these co-ordinates or any other properties of the system at a later time, and in this way the astronomer can predict the properties of the system at a later time. He can, for instance, predict the exact time for an eclipse of the moon.

In quantum theory the procedure is somewhat different. We might, for instance, be interested in the motion of an electron in a cloud chamber and could determine by some kind of observation the initial position and velocity of the electron. But this determination will not be exact. It will at least contain the inexactnesses [*die Ungenauigkeiten*] which follow necessarily from the indeterminacy relations and will probably contain besides, still very much greater inexactnesses which are conditioned by the difficulties of the experiment. The first of these inexactnesses gives us the possibility of translating the result of the observation into the mathematical formalism of quantum theory. A probability function is written down which represents the experimental situation at the time of the measurement, including the possible inexactness of the measurement.

This probability function represents a mixture of two different elements, [on the one hand] a fact and [on the other hand] the degree of our knowledge of a fact. It represents a fact in so far as it assigns to the initial situation a probability of 1, that is, complete certainty. It is completely certain that the electron has moved with the observed velocity at the observed position. "Observed" does mean, to be sure, observed within the exactitude of the experiment. It represents the degree of our knowledge insofar as another observer might perhaps have known the position of the electron even more exactly. The experimental error or the inexactness of the experiment can, at least to a certain degree, be regarded as not a property of the electron but as a deficiency in our knowledge of the electron. This deficiency in knowledge, too, is expressed through the probability function.

In classical physics, too, careful observation must take observational errors into consideration. The result one then gets is a probability distribution for the initial values of the co-ordinates and velocities and therefore something similar to the probability function of quantum mechanics. But the special uncertainty which necessarily follows from the indeterminacy relations is missing in classical physics.

As soon as the probability function in quantum theory has been determined for the initial time from the observation, one can calculate the function at any later time from the laws of quantum theory and can thereby determine beforehand the probability that a measurement will yield a certain value for the magnitude to be measured. We can, for instance, predict the probability of finding the electron at a later time at a certain point in the cloud chamber. It should be emphasized, however, that the probability function does not in itself represent a course of events in time. It represents something like a tendency for events [*Vorgänge*], the possibility of events or our knowledge of them. The probability function can be connected with actuality [*Wirklichkeit*] only when one essential condition is fulfilled: when a new measurement or observation is made to determine a certain property of the system. Only then does the probability function allow us to calculate the probable result of the new measurement. The result of the measurement will in this case again be stated in terms of classical physics. . . .

It has already been said that the atom consists of a nucleus and of electrons moving around the nucleus. It has also been stated that the concept of an electronic orbit is somewhat doubtful. Against the latter formulation a first objection might be that it should be possible at least in principle to observe the electron in its orbit. . . . [However] one can easily see that it is evidently not possible to observe the orbit of the elec-

tron around the nucleus. [The development of the probability function in time] shows not a wave packet that moves around the nucleus, but one that moves away from the nucleus, since the first photon [to strike the electron]<sup>25</sup> will already have knocked the electron out of the atom. This is so because the momentum of the  $\gamma$ -ray quantum must be considerably larger than the original momentum of the electron if the wavelength of the  $\gamma$ -ray is much smaller than the size of the atom. Therefore, the first photon is already sufficient to knock the electron out of the atom, and one can never observe more than one point in the orbit of the electron. Hence one does not fall into a contradiction with experience if one asserts that there are, in fact, no electron-orbits in the ordinary sense.

The next observation . . . will thus show the electron on its path away from the atom. In the most general sense it is impossible to describe intuitively what happens between two consecutive observations. It is of course tempting to say that the electron must have been somewhere during the time between the two observations and that therefore it must have described some kind of orbit or path, even if it should be impossible to establish this path. This would be a reasonable argument in classical physics. But in quantum theory it would be case of a misuse of language which, as we will see later, cannot be justified. We may leave it open for the moment, whether this warning is an assertion about the way in which we should speak about atomic events or an assertion about the events themselves—whether it is a matter, as it were, of epistemology or of ontology. In any case, we have to use the most extreme caution about the formulation of any assertion which concerns the behavior of atomic particles.<sup>26</sup>

Actually we need not speak of particles at all. For many experiments it is more convenient to speak of *matter waves*; for instance, of standing oscillations of the electron-matter about the atomic nucleus. Such a description would, to be sure, directly contradict the other description if one did not pay attention to the limits set by the indeterminacy relations. Through these limitations the contradiction is avoided. The use of the concept of matter waves is convenient, for example, when dealing with the radiation emitted by the atom. By means of its frequency and intensity the radiation gives information about the oscillating charge distribution in the atom, and there the wave picture comes much nearer to the truth than the particle representation. Bohr therefore advocated the use of both pictures, which he called “complementary” to each other. The two pictures are of course mutually exclusive, because a certain thing cannot at the same time be a particle (that is, a substance confined to a very small volume) and a wave (that is, a field spread out over a large space); but the two pictures complete each other. By playing with both pictures, by passing over from the one picture to the other and back again, we finally get the right impressions of the strange kind of reality that

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<sup>25</sup>[Heisenberg refers to an earlier discussion of the possibility of observing the electron through a hypothetical microscope which uses high energy  $\gamma$ -rays, whose wave-length is smaller than the size of the atom.]

<sup>26</sup>[In *The Physical Principles of the Quantum Theory* [33–34], Heisenberg adds the following about atomic orbitals: “[For any energy level] there is . . . always a small but finite probability of finding the [“bound”] electron at a great distance from the center of the atom. [At that distance] the potential energy [is almost zero]. The kinetic energy is always positive; so that the total energy is therefore certainly greater than the energy of the stationary state under consideration [which must be negative, and quite sizably so for lower energy-levels]. This paradox finds its resolution when the energy imparted to the electron by the photon used in making the position measurement is taken into account. This energy is considerably greater than the ionization energy of the electron, and thus suffices to prevent any violation of the law of conservation of energy.”]

lurks behind our atomic experiments.

Bohr uses the concept of "complementarity" at several places in the interpretation of quantum theory. The knowledge of the position of a particle is complementary to the knowledge of its velocity or momentum. If we know the one magnitude with great exactness, we cannot determine the other with high exactness without losing again the first knowledge. But we ought to know both in order to describe the behavior of the system. [Similarly,] the space-time description of the atomic events is complementary to their causal, or deterministic, description. The probability function satisfies an equation of motion [namely, the Schrödinger equation], similar to that for the co-ordinates in Newtonian mechanics. The function's change in the course of time is completely determined by the quantum mechanical equation, but it provides no description in space and time. Through an observation, on the other hand, a space-time description is enforced. Nevertheless, by changing our knowledge of the system, it interrupts the [temporal] course of the probability function, which had been determined by calculation. . . .

An obstacle to the understanding of this interpretation always arises, however, when we ask the familiar question: But what "actually" happens in an atomic event? First of all, it has been said before that the measurement and the results of an observation must always be described in terms of classical physics. But what one derives from the observation is a probability function, that is, a mathematical expression that combines assertions about "possibilities" or "tendencies" with assertions about our knowledge of facts. So we cannot completely objectify the result of an observation. We cannot describe what "happens" [*passiert*] between this observation and the next. It looks at first as if we had thus introduced a subjective element into the theory, as if we meant to say that what happens depends on how we observe it—or at least on the fact that we observe it. Before we discuss this objection, it is necessary to explain very exactly why one would get into the very greatest difficulties if one wanted to try to describe what happens [*geschieht*] between two consecutive observations.

For this purpose it is convenient to discuss the following thought experiment. Let us assume that a small source of monochromatic light radiates toward a black screen with two small holes in it. The diameter of the holes need not be much greater than the wave length of the light, but the distance between them must be considerably greater. At some distance behind the screen a photographic plate is to register the incoming light. If we describe this experiment in terms of the wave picture, we will say that the primary wave penetrates through the two holes; there will thus be two secondary spherical waves which depart from the two holes and which interfere with one another; and that their interference will produce on the photographic plate a pattern of stronger and weaker intensities, the so-called interference bands.

The blackening of the photographic plate is a quantum chemical process, produced by single light photons. Therefore, it must also be possible to describe the experiment in terms of photons as well. Now if it were permissible to speak about what happens to the single photon between its emission from the light source and its absorption in the photographic plate, one could argue as follows: The single photon can go either through the first or the second hole. If it goes through the first hole and is scattered there, its probability for being later absorbed at a certain point on the photographic plate is independent of whether the second hole is closed or open. The probability distribution on the plate must be the same as if only the first hole were open. If we repeat the experiment many times and collect all cases in which the photon has gone through

the first hole, the blackening of the plate should correspond to this probability distribution. If now we consider only those photons that have gone through the second hole, the blackening distribution should correspond to that probability distribution which is derived from the assumption that only the second hole was open. The total blackening, therefore, should thus be exactly the sum of the blackenings in the two cases—in other words, there should be no interference bands. But we know this is not correct, and the experiment will undoubtedly show the interference bands.<sup>27</sup> From this we recognize that the assertion that the photon must have gone either through the one or through the other hole is problematic and leads to contradictions. This example shows clearly that the concept of the probability function does not allow a spatio-temporal description of what happens between two observations. Any attempt to find such a description would lead to contradictions; this means that the concept "happening" [*Geschehen*] must be restricted to observation.

Now, this is surely a very peculiar result, since it seems to indicate that observation plays a decisive role in the event and that actuality differs, depending upon whether we observe it or not. To make this point clearer we have to analyze the process of observation yet more closely.

To begin with, it is important here to recall that in natural science we are not interested in the universe as a whole, which includes ourselves, but that we direct our attention to certain parts of the universe and make those the object of our study. In atomic physics this part is ordinarily a very small object, namely an atomic particle or a group of such particles, though sometimes it is much larger; the size does not here matter. But it *is* important that a large part of the universe, which includes ourselves, does not belong to the "object."

The theoretical interpretation of an experiment starts with...two steps.... In the first step we have to describe the arrangement of the experiment, if necessary combined with a first observation described in terms of classical physics, and we have to translate this description into a probability function. This probability function then satisfies the laws of quantum theory, and its change in the course of time, which takes place continuously, can be calculated from the initial conditions. In this consists the

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<sup>27</sup>[In (a-c) below it is assumed that each individual photon goes *either* through hole 1 or through hole 2; at (b) is a graph representing the individual *single-slit* diffraction patterns due to holes 1 and 2 separately. Then if many photons are directed toward the slits the expected result would be (c), the sum of the two patterns (Heisenberg calls this "the sum of the blackenings"). But when the experiment is actually performed, the result exhibits the *double slit* diffraction pattern (f) that we ordinarily associate with waves passing through a pair of slits, as depicted in (d-f).]



second step. The probability function combines objective and subjective elements. It contains assertions about probabilities, or better, tendencies (*potentia* in Aristotelian philosophy), and these assertions are completely objective; they do not depend on any observer. It contains, besides, assertions about our knowledge of the system, which of course have to be subjective insofar as they can indeed be different for different observers. In especially favorable cases the subjective element in the probability function can be quite neglected in comparison with the objective one. The physicists then speak of a "pure case." [reiner Fall].

When we now come to the next observation, the result of which was to be predicted from the theory, it is very important to be clear about the fact that the object has to interact [*in Wechselwirkung stehen*] with the other part of the world, namely, the experimental device, the measuring rod, etc., before or at least at the moment of observation. This means that the equation of motion for the probability function must now take into account the influence which the interaction with the measuring device exerts on the system. This influence introduces a new element of indeterminacy, since the measuring device is necessarily described in the concepts of classical physics. But such a description contains all the uncertainties concerning the microscopic structure of the device which we already know from thermodynamics. Since, besides, the device must be connected with the rest of the world, it actually contains the uncertainties of the microscopic structure of the whole world. These uncertainties may be called objective insofar as they are simply a consequence of the fact that we describe the experiment in the terms of classical physics; their details do not depend upon the observer. They may be called subjective insofar as they indicate our incomplete knowledge of the world.

After this interaction has taken place, the probability function contains the objective element of a "tendency" or "possibility" and the subjective element of incomplete knowledge, even if it had at first been a matter of a "pure case." It is just for this reason that the result of the observation cannot generally be predicted with certainty. What can be predicted is the probability of a certain result of the observation, and this assertion about the probability can be checked by repeating the experiment many times. The probability function, unlike the mathematical formalism of Newtonian mechanics, does not describe a determinate event but, at least with respect to the process of observation, a totality of possible events.

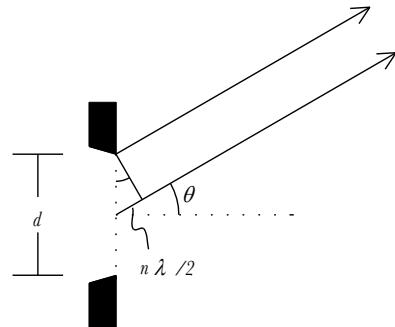
The observation itself changes the probability function discontinuously. It selects from all possible events the one that has actually taken place. Since through the observation our knowledge of the system has changed discontinuously, its mathematical representation has also changed discontinuously, and we therefore speak of a "quantum leap." If someone wanted to derive a criticism of quantum theory from the ancient saying "*Natura non facit saltus*" [nature makes no leaps] we can reply that our *knowledge* can surely change suddenly and that just this fact, the discontinuous change in our knowledge, justifies the use of the term "quantum leap."

Therefore, the transition from the possible to the actual takes place during the act of observation. If we want to describe what happens in an atomic event, we have to begin with the fact that the word "happens" can apply only to the observation, not to the situation between two observations. In doing so, it designates the physical, not the psychical act of observation, and we may say that the transition from the possible to the actual takes place as soon as the interaction of the object with the measuring device, and thereby with the rest of the world, has come into play. The transition is not connected with the registering of the observational result in the mind of the observer. The

discontinuous change in the probability function does, to be sure, take place through the act of registering; for it is that discontinuous change of our knowledge at the moment of registering which is imaged in the discontinuous change of the probability function.

## SINGLE-SLIT DIFFRACTION AND LIMIT OF OPTICAL RESOLUTION

1. *Single-slit diffraction.* Let there be a narrow slit of width  $d$ , illuminated uniformly along the axis perpendicular to the plane of the slit. As in Huygens' treatment, consider the plane of the slit to be populated by infinitely many centers of wavelets, expanding in all forward directions. Thus the light beam will spread out as it leaves the slit.

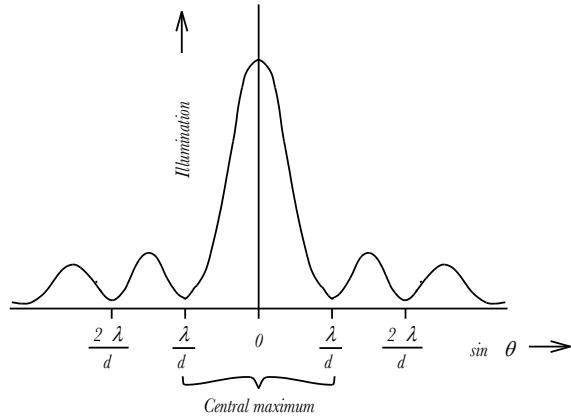


There will be some angle, say  $\theta$ , at which the wavelets that were emitted from *one edge* of the slit and from the *center* of the slit, respectively, will cover distances that differ by an integral number of half-wavelengths and arrive together at some distant point—where they will mutually cancel, being exactly out of phase with one another. The innumerable remaining wavelets may be similarly paired for mutual cancellation; so that the overall result will be a dark spot at angle  $\theta$  from the perpendicular axis.

In the right triangle thus formed with hypotenuse  $d/2$  and one leg an integral multiple of  $\lambda/2$ , the marked angle will be equal to  $\theta$  and will have sine given by

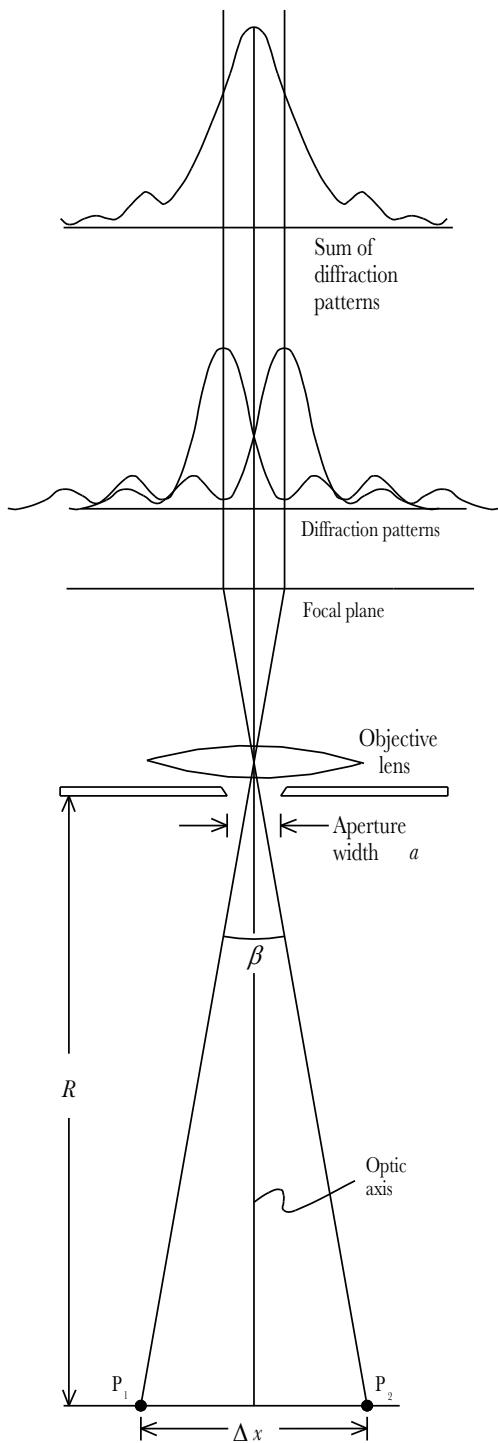
$$\sin \theta = \frac{n\lambda/2}{d/2} = \frac{n\lambda}{d} .$$

Since  $n$  is any integer, there will be alternating bands of illumination and darkness for all angles up to  $90^\circ$  either side of the perpendicular axis. But in practice the greatest illumination is found within the “central maximum,” that region bounded by the two minima for which  $n = 1$  (called “first-order” minima).



Suppose these minima appear at angles  $\theta_1$  on either side of the axis. Then  $\theta_1$  will be the *angular half-width* of the central maximum, and will be given by

$$\sin \theta_1 = \frac{\lambda}{d} .$$



2. *Optical resolution.*<sup>1</sup> Consider points  $P_1$  and  $P_2$  on the surface of some object. Let their angular separation be  $\beta$ , and let it be supposed that both points emit or reflect light of wavelength  $\lambda$ . For the sake of simplicity, we will let the aperture through which light is admitted to the instrument be a slit of width  $a$  (a circular aperture can be analogously treated, but numerous complications arise for that case). Light from each point forms its own independent diffraction pattern with a central maximum flanked by pairs of minima. As shown in the previous section 1, each central maximum will have an angular half-width equal to  $\theta_1$  such that

$$\sin \theta_1 = \lambda/a .$$

Now the central maxima of the two patterns lie in the focal plane of the instrument lens and (since rays passing through the center of a lens are not bent) must be separated from one another by the angle  $\beta$ . But as aperture  $a$  is made smaller, the angular half-width of each central maximum increases, until eventually  $\theta_1 = \beta$ —that is, the central maximum of each pattern coincides with a first-order minimum of the other pattern. The central bright maxima will then be immediately adjacent to one another. Inspection of the sum of the two intensity graphs

<sup>1</sup> After Curtis Wilson, c. 1980.

under these conditions shows that instead of forming two distinct bands, the central maxima will merge into a *single band*.

Someone viewing such an image through the instrument would be quite unable to distinguish either of these maxima from the other; and thus the points  $P_1$  and  $P_2$  would become *indistinguishable*. No increase of magnifying power, so long as the same aperture width is retained, can remedy this limitation. However, if the aperture width  $a$  is increased even the slightest amount, so that the separation between the two patterns increases by any degree at all, there will be found a dip between the two maxima when the sum of the intensity graphs is plotted as before. Thus, that the central maximum of each pattern shall coincide with the first-order minimum of the other is a *limiting condition* for the resolution of the images of two points; it is called *Rayleigh's criterion*.

Heisenberg's equation (16), p. 202 above, derives directly from Rayleigh's criterion. For suppose  $\theta_1 = \beta$  as described above; that is, let

$$\sin \beta = \lambda/a . \quad (1)$$

Let the object distance be  $R$ , and suppose also that angle  $\beta$  is very small. Then  $\Delta x$  is the chord of a circle with center at the vertex of  $\beta$ , and so it very nearly equals the arc which it subtends. This small arc equals  $R \times \beta$  (radians); while in its turn a very small angle  $\beta$  (in radians) nearly equals  $\sin \beta$ . This gives  $\Delta x \approx R \times \sin \beta$ , so that

$$\sin \beta \approx \Delta x/R . \quad (2)$$

From equations (1) and (2) it follows that

$$\frac{\Delta x}{R} \approx \frac{\lambda}{a} . \quad (3)$$

Similarly, the aperture of width  $a$  located at distance  $R$  from a point will subtend an angle  $\varepsilon$  such that, if  $\varepsilon$  is very small,

$$\sin \varepsilon \approx a/R ,$$

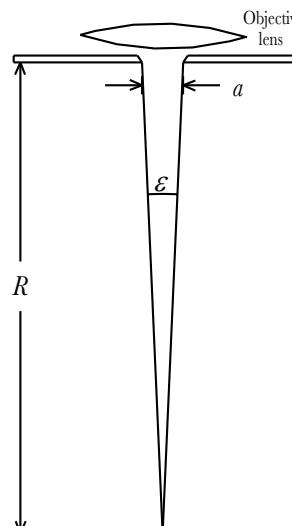
from which

$$a \approx R \sin \varepsilon . \quad (4)$$

Substitution of equation (4) into equation (3) above yields

$$\frac{\Delta x}{R} \approx \frac{\lambda}{R \sin \varepsilon}$$

which becomes Heisenberg's equation (16), when  $R$  is canceled from both sides.  
Q.E.D.



# THE POLARIZATION OF LIGHT

## OPTICS PRACTICUM 1

### INTRODUCTION

In Planck, Einstein, and Bohr, we've seen that light, previously thought to be wave-like, exhibits behavior characteristic of discrete, particle-like quanta. In de Broglie, we've seen that at least one body previously thought to be particle-like, the electron, exhibits wave-like behaviors, both when confined to the atom and when moving freely. In this portion of the semester, we will return to the study of photons, but now with the further complications introduced by Schrödinger's and Heisenberg's extension of the "matter wave" theory and attempts to set mechanics on a new footing. Paul Dirac's *Principles of Quantum Mechanics* continues this work, and while part of what makes the book so important is its new theory of the electron, we will read only the Introduction, where Dirac elaborates some of the key features of his account not with reference to electrons, but in terms of the behavior of photons.<sup>1</sup>

One element of that behavior that will be important for Dirac's account—as well as for much of the substantial experimental work we have left to do this term—is polarization. In 1690, Christian Huygens discovered the key phenomenon while investigating the Iceland spar (or clear calcite) crystal. Light passing through the crystal was refracted into two differently directed rays, one obeying the usual laws of refraction, the other apparently not. Further, when Huygens placed one crystal atop another in the same orientation, he found that the two rays were not split a second time. In this orientation, the extraordinary ray was again irregularly refracted, and the ordinary ray regularly refracted, but when one of these crystals was then rotated in the plane of their contact by 90 degrees, the inverse occurred. Huygens hypothesized that the two rays were composed of two distinct species of light, filtered, as it were, by the crystal: "One would say that [the regular ray] in passing through the upper piece [of crystal] has lost something which is necessary to move the matter which serves for the irregular refraction; and that likewise [the irregular ray] has lost that which was necessary to move the matter which serves for regular refraction."<sup>2</sup> (Examination of the refraction in the crystal is proposed in section (J) below.)

Little to no progress in understanding was made in the 18th century, but a few related phenomena were uncovered in the 19th, two of them important and relevant to us. First, around 1810, Étienne-Louis Malus published the results of his research into polarization, showing that light reflected from an otherwise transparent surface and entering a suitably oriented Iceland spar crystal was *not* split into two rays, and further, that when direct light was made to enter the crystal and split, and then the two rays exiting the crystal were projected onto water, only one was reflected. In investigating

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<sup>1</sup>Though, as Dirac notes, "The association of particles with waves discussed above is not restricted to the case of light, but is, according to modern theory, of universal applicability" (Introduction, sec. 3).

<sup>2</sup>Christian Huygens, *Traité de la lumière* (Paris, 1690), 90.

the effect of other orientations of the crystal on the quantity of light transmitted, Malus formulated a law that quantitatively expresses this relation, which we will employ extensively and discuss presently. Indeed, Malus's identification of what appeared to him as an orientation of light itself is what led him to dub the phenomenon "polarization." Second, Faraday discovered that the axis of polarization of light could be sensibly rotated by a sufficiently powerful magnetic field, especially when the light was made to pass through a dense medium such as water.<sup>3</sup> A theory that could plausibly account for polarization (among many other phenomena) arrived with Maxwell. Light, he asserted, is electromagnetic radiation, an electric and a magnetic wave—perpendicular to and in phase with each other—propagating through the luminiferous ether. On that account, the phenomena of polarization are easy to understand. The electric and magnetic components of the wave can, so long as they remain mutually perpendicular, point in any direction in the plane perpendicular to the wave's direction of propagation, as the radius of a circle can connect the center with any point on its circumference. Polarization, then, would be made possible by the two-dimensional freedom of direction of oscillation characteristic of a transverse wave, in this case, that of light's electric and magnetic components. On this view, what Huygens saw in the Iceland spar could be explained by hypothesizing that the crystal divides unpolarized light into differently directed portions.<sup>4</sup>

Soon, when we turn to Dirac, we will have to grapple with the quantum character of light once again, but for now, we will familiarize ourselves further with the phenomena of polarization in terms in which it is adequately accounted for—and perhaps most naturally expressed—namely, those of classical electromagnetic theory. A bit of terminology: as the light wave progresses, if the axis of oscillation of the electric field remains fixed, the light is said to be *linearly polarized*; if instead it rotates, the light is said to be *elliptically polarized*; in the special case of elliptical polarization where the electric vector rotates *and* maintains the same amplitude throughout its rotation, the light is *circularly polarized*. We will explore mostly linear polarization, though knowledge of the other forms is necessary for understanding some of the more complicated optical equipment we will later use. A diagrammatic representation of the various types of polarization is presented below.

A simple piece of equipment we will use frequently is the linear polarizer. Instead of splitting beams of light into two perpendicularly polarized components, linear polarizers allow light polarized along one axis to pass, and absorb all light polarized perpendicular to that axis. At intermediate angles, only some of the light passes. As stated above, Malus specifies this relation. If  $I_0$  is the intensity of the light that would pass if the axes of the polarizer and the entering light were aligned, and  $\theta$  is the angle between them, then the intensity  $I$  of the light that passes is

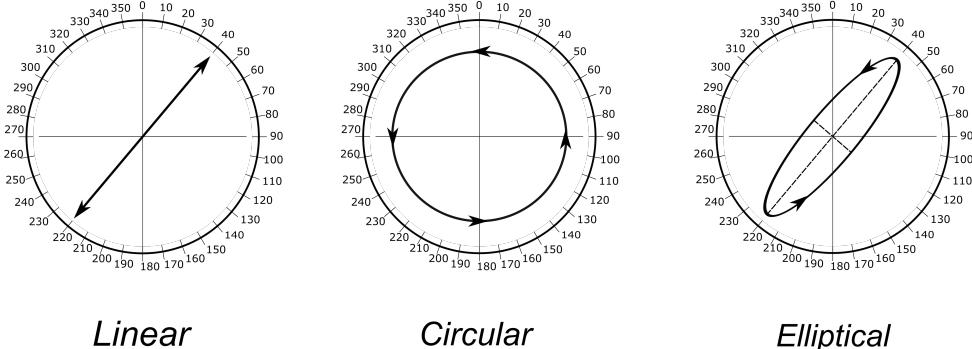
$$I = I_0 \cos^2 \theta. \tag{5}$$

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<sup>3</sup>See Faraday, *Experimental Researches in Electricity*, Nineteenth Series, *Phil. Trans. R. Soc. Lond.* **122** (1846), 1–20, and Maxwell, "A Dynamical Theory of the Electric Field," article 8.

<sup>4</sup>Maxwell discusses the electromagnetic theory of polarization and relates the polarizing effect of birefringent materials to the differing dielectric constant in different directions in the crystals in *A Treatise on Electricity and Magnetism* (Oxford, 1873), articles 791–797. He discusses Faraday's demonstration and the effect of magnetism on polarization in articles 806–831.

<sup>5</sup>Dirac formulates the law differently, as involving the sine, but only because he reckons the angle starting from  $90^\circ$  away. We will follow Malus's convention, as has become the norm.



**Types of polarization.** Here are shown the types of polarization of light discussed above. The light is conceived to be traveling perpendicular to the plane of the page, and the arrows represent the directions of polarization. In this frame of reference, linearly polarized light that is oriented along the axis from  $0^\circ$  to  $180^\circ$  is said to be vertically polarized.

Many of the phenomena of polarization will prove crucial to our future study, so in this practicum we will verify Malus's Law experimentally, and begin to familiarize ourselves with some of the other equipment we'll be using in upcoming practica.

That equipment includes a laser light source, a photodiode detector (with attached signal amplifier, power supply, and voltmeter), a depolarizer, a diffraction grating, several linear polarizers, and two kinds of devices we have not yet discussed: half-wave plates, and quarter-wave plates. The linear polarizers, half-wave plates, and quarter-wave plates all look nearly identical. The half-wave plates are marked " $\lambda/2$ ," and the quarter-wave plates are marked " $\lambda/4$ " near their centers. Descriptions of the effects of half- and quarter-wave plates are given in the relevant sections below and, for the curious, a longer account is offered in the final section of this chapter. Finally, the polarizers are set in disks with fine angle markings and all the elements are arranged together in a straight line on an optical bench, which will allow us to investigate the phenomena of polarization with exactitude, by measuring intensities of light at different angle settings of multiple polarizers. A schematic representation of the full setup is shown below and the positions are marked for later reference.



## PRACTICUM

- Begin by removing any optical elements that are attached to the bench standing between the laser and the detector. In order to remind ourselves of the wave-like properties of light, we can shine the laser light through a diffraction grating onto a piece of paper or an index card to reveal the characteristic interference pattern of dots that indicates maxima and minima of the light wave.
- Next, we will examine the photodiode detector, used to measure the intensity of light passing through our various arrangements of polarizers. The sensitive ele-

ment in the detector exploits the photoelectric effect. Here, unlike in the Einstein practicum, we are interested in only the magnitude of the overall current and not the kinetic energy of ejected electrons, since that current is proportional to the light intensity. That said, the circuit we are using is designed (with the attached resistor) such that the electric potential generated by the device is proportional to current, and that voltage is more readily measured (with the help of the signal amplifier) than the current. All this by way of saying that the readings of light intensity will be in terms of DC voltage on the attached voltmeter. The power supply should be at 25V. Shine the laser directly on the detector and read the voltage off the voltmeter. Obstruct the beam with your hand and watch the effect on the readings. Even moving your hand or body in the vicinity of the optics table can change the reading (slightly), so be aware of this in taking precise measurements.

- (C) The mechanics of the production of light are beyond us, especially in the case of light-emitting diodes or lasers. For us, a laser is simply a convenient light source, in two ways: it has a narrow beam that can be easily directed, and it is monochromatic, so that a color filter can screen out other sources of light, allowing us to make measurements with confidence. Because of the way it is produced, however, it happens that laser light is also typically linearly polarized, which we can confirm with a linear polarizer and the photodiode detector. Shine the laser light through a linear polarizer placed directly in front of the detector (at P3 in the diagram above). Determine the direction of polarization of the laser light by adjusting the angle of the linear polarizer to get the maximum signal from the detector. The zero degree mark for the linear polarizer signifies vertical polarization plus or minus a few degrees. Slowly rotate the polarizer to get the maximum and minimum readings and thereby determine the direction and degree of polarization of the laser light. The minima and maxima should be  $90^\circ$  apart.
- (D) As a consequence of the incomplete polarization of the laser light, just demonstrated, we will begin all our subsequent experiments on polarization by passing the light through a depolarizer. Set a linear polarizer in front of the detector at P3 and the smaller depolarizer in front of the laser (at the position marked "depol."). Confirm that the light is mostly depolarized by rotating the linear polarizer near P3 to different angles and noting the maximum and minimum voltage readings from the detector and their positions. Again, leave the depolarizer in place for all the measurements described below.
- (E) Interpose a second linear polarizer at P1 and align them as follows: Set the one closest to the detector at P3 to  $0^\circ$  and adjust the one at P1 to produce the maximum intensity reading, which should be near its  $0^\circ$ , but may be as far as  $15^\circ$  away. Take care to note this deviation; this is the new "zero" for that polarizer and all your future readings must take it into account. Verify that when the polarizer at P1 is turned  $90^\circ$  from its aligned position no light passes (*i.e.*, the voltmeter reads near zero). A typical reading near zero here is 0.01V.
- (F) Now take measurements to verify Malus's law. With the depolarizer in place, and linear polarizers at P1 and P3 and aligned for a maximum signal, take a baseline reading ( $I_0$ ) and then adjust the angle ( $\theta$ ) between the two polarizers (it shouldn't matter which you turn or which way you turn it) by  $10^\circ$  at a time until  $\theta$  has passed

through 90 degrees. Note the readings  $I$  from the detector at each angle and compare them with the formula:

$$I = I_0 \cos^2 \theta.$$

- (G) Now, we will interpose a third linear polarizer at P2 between the first two (at P1 and P3). Before placing it there, align the polarizers at P1 and P3 for a maximum signal, with P3 set at  $0^\circ$  as a benchmark. Now place a third linear polarizer at P2 and adjust it until you get a maximum signal, your new  $I_0$  for this experiment (likely slightly lower than without a polarizer at P2). Now turn the polarizer at P3 to  $90^\circ$ . This should result in a near-complete extinction of the signal from the detector (around 0.01V). Next, set LP2 to  $45^\circ$  from its starting position and note the reading from the detector. Depending on your understanding of how the polarizers work, you might or might not be surprised. Try to account for your readings theoretically and quantitatively. On the basis of this account, make and test predictions about the results for other settings of the three polarizers. Is Malus's Law still in effect? What do linear polarizers *do* to the light?
- (H) As noted above, we will make frequent use not only of linear polarizers but of so-called *half-wave plates* as well. For practical purposes, it may be sufficient to simply describe their effect: they *change* the direction of polarization of linearly polarized light by twice the difference in angle between their primary axis and that of the direction of polarization of the incoming light. We can demonstrate these effects by replacing the linear polarizer at P2 in the setup for (G) with a half-wave plate. Begin by aligning the linear polarizers at P1 and P3 in the usual way (for maximum signal with P3 at  $0^\circ$ ) and then put the half-wave plate between them at P2, and adjust it for a maximum reading on the detector (again, this should be near  $0^\circ$  and should be marked down as your new  $I_0$  for any subsequent calculations). Turn P3 until the signal is at its minimum, which should be very nearly  $90^\circ$ . Now turn the half-wave plate in the direction of increasing angle until the signal is at its maximum (which should be near  $45^\circ$ ). Note the reading on the detector. How does this differ from the analogous setup with three linear polarizers? Confirm the effect of the half-wave plate by setting it at, say,  $15^\circ$  and  $30^\circ$  away from the vertical and finding the corresponding angle settings for P3 that give the maximum signal.
- (I) A similar piece of equipment with a useful effect is the quarter-wave plate. Again, we begin with a description of the effect for which the device was created: vertically polarized light incident upon a quarter-wave plate aligned at  $45^\circ$  will emerge *circularly* polarized. If you have time, try to produce and confirm this effect. Remove the half-wave plate from the setup for (H) and align the polarizers at P1 and P3 as usual. Place a quarter-wave plate at P2 and adjust it (near  $0^\circ$ ) to produce the maximum signal. You can adjust P3 to confirm that the light emerging from the quarter-wave plate is still vertically polarized. Turn P3 until the signal is at its minimum, near  $90^\circ$ . Now turn the quarter-wave plate until the signal is at its maximum, which should be near  $45^\circ$ . If the light emerging from the quarter-wave plate is circularly polarized, this should show up as an equality of intensities for all positions of the linear polarizer at P3. If it is unevenly distributed, you can try noting the maximum and minimum readings, adjusting the quarter-wave plate's orientation by a few degrees, then measuring again to see whether your readings are closer to being consistent with circular polarization. If you still have time left, you

can try to verify that the light passing through the quarter-wave plate in this way is circularly polarized and not just unpolarized, by interposing a second quarter-wave plate between P2 and P3 turned to  $90^\circ$ ; the second quarter-wave plate should emit linearly polarized light, which you will be able to confirm with the linear polarizer at P3.

## ADDITIONAL ACTIVITIES

- (J) The laboratory has samples of Iceland spar suitable for demonstrating the polarization of light without the intervention of lasers and other specially designed optical equipment. Draw a dot on a piece of paper, and place a sample of crystal on it. Rotate the crystal and note that while one image of the dot stays still (the ordinary ray), the other does not (the extraordinary ray). Place a second crystal atop the first so that all their faces are parallel. Note that in this orientation the image is not split a second time. Rotate the second crystal and note the appearance of two more dots, and their disappearance when the rotation reaches a right angle.

## WAVEPLATES

Optical elements that affect the state of polarization of light as our half- and quarter-wave plates do are useful. They are made from materials like the calcite crystal in which polarization was first discovered. Materials like that are called *birefringent* in that they refract incoming light in two different ways, depending on how its polarization aligns with their internal structure. A waveplate is a sample of this material suitably prepared so as to produce a definite effect such as the ones mentioned above.

Birefringent materials, because of their crystalline structure—that is, because of the regular arrangement of atoms within them—have different electrical properties and thus different refractive indices for components of light lying along their axes (again, *cf.* Maxwell, *Treatise on Electricity and Magnetism*, vol. 2, §§794–797). This has the effect that light polarized along one of these axes moves slower (at least in terms of phase) than it does along the other. A half-wave plate is constructed so that light of a definite wavelength will have the component polarized along its “slow” axis retarded by one half a period. Perpendicularly related components of the light that emerges thus remain in phase with each other, such that the light is polarized linearly, just in a different direction. By contrast, the quarter-wave plate—which, as the name indicates, retards one component by a quarter-period—does not leave the components in phase with one another, with the result that linearly polarized light passing through it will not (if it is not aligned at  $0^\circ$  or  $90^\circ$ ) emerge linearly polarized, but will instead take on some kind of *elliptical* polarization.

## CHAPTER 12

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# THE PRINCIPLES OF QUANTUM MECHANICS

PAUL DIRAC<sup>1</sup>

## FROM THE PREFACE TO THE FIRST EDITION

The methods of progress in theoretical physics have undergone a vast change during the present century. The classical tradition has been to consider the world to be an association of observable objects (particles, fluids, field, etc.) moving about according to definite laws of force, so that one could form a mental picture in space and time of the whole scheme. This led to a physics whose aim was to make assumptions about the mechanism and forces connecting these observable objects, to account for their behaviour in the simplest possible way. It has become increasingly evident in recent times, however, that nature works on a different plan. Her fundamental laws do not govern the world as it appears in our mental picture in any very direct way, but instead they control a substratum of which we cannot form a mental picture without introducing irrelevancies. The formulation of these laws requires the use of the mathematics of transformations. The important things in the world appear as the invariants (or more generally the nearly invariants, or quantities with simple transformation properties) of these transformations. The things we are immediately aware of are the relations of these nearly invariants to a certain frame of reference, usually one chosen so as to introduce special simplifying features which are unimportant from the point of view of general theory.

The growth of the use of transformation theory, as applied first to relativity and later to the quantum theory, is the essence of the new method in theoretical physics. Further progress lies in the direction of making our equations invariant under wider and still wider transformations. This state of affairs is very satisfactory from a philosophical point of view, as implying an increasing recognition of the part played by the observer in himself introducing the regularities that appear in his observations, and a lack of arbitrariness in the ways of nature, but it makes things less easy for the learner of physics. The new theories, if one looks apart from their mathematical setting, are built up from physical concepts which cannot be explained in terms of things previously known to the student, which cannot even be explained adequately in words at all. Like the fundamental concepts (e.g. proximity, identity) which every one must learn on his arrival into the world, the newer concepts of physics can be mastered only by long familiarity with their properties and uses.

From the mathematical side the approach to the new theories presents no difficulties, as the mathematics required (at any rate that which is required for the development of physics up to the present) is not essentially different from what has been current for a considerable time. Mathematics is the tool specially suited for dealing

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<sup>1</sup>Fourth Edition, Oxford University Press, 1958.

with abstract concepts of any kind and there is no limit to its power in this field. For this reason a book on the new physics, if not purely descriptive of experimental work, must be essentially mathematical. All the same the mathematics is only a tool and one should learn to hold the physical ideas in one's mind without reference to the mathematical form. In this book I have tried to keep the physics to the forefront, examining the physical meaning underlying the formalism wherever possible. The amount of theoretical ground one has to cover before being able to solve problems of real practical value is rather large, but this circumstance is an inevitable consequence of the fundamental part played by transformation theory and is likely to become more pronounced in the theoretical physics of the future.

With regard to the mathematical form in which the theory can be presented, an author must decide at the outset between two methods. There is the symbolic method, which deals directly in an abstract way with the quantities of fundamental importance (the invariants, etc., of the transformations) and there is the method of coordinates or representations, which deals with sets of numbers corresponding to these quantities. The second of these has usually been used for the presentation of quantum mechanics (in fact it has been used practically exclusively with the exception of Weyl's book *Gruppentheorie und Quantenmechanik*). It is known under one or other of the two names 'Wave Mechanics' and 'Matrix Mechanics' according to which physical things receive emphasis in the treatment, the states of a system or its dynamical variables. It has the advantage that the kind of mathematics required is more familiar to the average student, and it is the historical method.

The symbolic method, however, seems to go more deeply into the nature of things. It enables one to express the physical laws in a neat and concise way, and will probably be increasingly used in the future as it becomes better understood and its own special mathematics gets developed. For this reason I have chosen the symbolic method, introducing the representatives later merely as an aid to practical calculation. This has necessitated a complete break from the historical line of development, but this break is an advantage through enabling the approach to the new ideas to be made as direct as possible.

P. A. M. D., 29 May 1930

**St. John's College, Cambridge**

## THE PRINCIPLE OF SUPERPOSITION

### 1. The need for a quantum theory

Classical mechanics has been developed continuously from the time of Newton and applied to an ever-widening range of dynamical systems, including the electromagnetic field in interaction with matter. The underlying ideas and the laws governing their application form a simple and elegant scheme, which one would be inclined to think could not be seriously modified without having all its attractive features spoilt. Nevertheless it has been found possible to set up a new scheme, called quantum mechanics, which is more suitable for the description of phenomena on the atomic scale and which is in some respects more elegant and satisfying than the classical scheme. This possibility is due to the changes which the new scheme involves being of a very profound character and not clashing with the features of the classical theory that make it so attractive, as a result of which all these features can be incorporated in the new scheme.

The necessity for a departure from classical mechanics is clearly shown by experimental results. In the first place the forces known in classical electrodynamics are inadequate for the explanation of the remarkable stability of atoms and molecules, which is necessary in order that materials may have any definite physical and chemical properties at all. The introduction of new hypothetical forces will not save the situation, since there exist general principles of classical mechanics, holding for all kinds of forces, leading to results in direct disagreement with observation. For example, if an atomic system has its equilibrium disturbed in any way and is then left alone, it will be set in oscillation and the oscillations will get impressed on the surrounding electromagnetic field, so that their frequencies may be observed with a spectroscope. Now whatever the laws of force governing the equilibrium, one would expect to be able to include the various frequencies in a scheme comprising certain fundamental frequencies and their harmonics. This is not observed to be the case. Instead, there is observed a new and unexpected connexion between the frequencies, called Ritz's Combination Law of Spectroscopy, according to which all the frequencies can be expressed as differences between certain terms, the number of terms being much less than the number of frequencies. This law is quite unintelligible from the classical standpoint.

One might try to get over the difficulty without departing from classical mechanics by assuming each of the spectroscopically observed frequencies to be a fundamental frequency with its own degree of freedom, the laws of force being such that the harmonic vibrations do not occur. Such a theory will not do, however, even apart from the fact that it would give no explanation of the Combination Law, since it would immediately bring one into conflict with the experimental evidence on specific heats. Classical statistical mechanics enables one to establish a general connexion between the total number of degrees of freedom of an assembly of vibrating systems and its specific heat. If one assumes all the spectroscopic frequencies of an atom to correspond to different degrees of freedom, one would get a specific heat for any kind of matter very much greater than the observed value. In fact the observed specific heats at ordinary temperatures are given fairly well by a theory that takes into account merely the motion of each atom as a whole and assigns no internal motion to it at all.

This leads us to a new clash between classical mechanics and the results of experiment. There must certainly be some internal motion in an atom to account for its

spectrum, but the internal degrees of freedom, for some classically inexplicable reason, do not contribute to the specific heat. A similar clash is found in connexion with the energy of oscillation of the electromagnetic field in a vacuum. Classical mechanics requires the specific heat corresponding to this energy to be infinite, but it is observed to be quite finite. A general conclusion from experimental results is that oscillations of high frequency do not contribute their classical quota to the specific heat.

As another illustration of the failure of classical mechanics we may consider the behaviour of light. We have, on the one hand, the phenomena of interference and diffraction, which can be explained only on the basis of wave theory; on the other, phenomena such as photo-electric emission and scattering by free electrons, which show that light is composed of small particles. These particles, which are called photons, have each a definite energy and momentum, depending on the frequency of the light, and appear to have just as real an existence as electrons, or any other particles known in physics. A fraction of a photon is never observed.

Experiments have shown that this anomalous behaviour is not peculiar to light, but is quite general. All material particles have wave properties, which can be exhibited under suitable conditions. We have here a very striking and general example of the breakdown of classical mechanics – not merely an inaccuracy in its laws of motion, but an *inadequacy of its concepts to supply us with a description of atomic events*.

The necessity to depart from classical ideas when one wishes to account for the ultimate structure of matter may be seen, not only from experimentally established facts, but also from general philosophical grounds. In a classical explanation of the constitution of matter, one would assume it to be made up of a large number of small constituent parts and one would postulate laws for the behaviour of these parts, from which the laws of the matter in bulk could be deduced. This would not complete the explanation, however, since the question of the structure and stability of the constituent parts is left untouched. To go into this question, it becomes necessary to postulate that each constituent part is itself made up of smaller parts, in terms of which its behaviour is to be explained. There is clearly no end to this procedure, so that one can never arrive at the ultimate structure of matter on these lines. So long as *big* and *small* are merely relative concepts, it is no help to explain the big in terms of the small. It is therefore necessary to modify classical ideas in such a way as to give an absolute meaning to size.

At this stage it becomes important to remember that science is concerned only with observable things and that we can observe an object only by letting it interact with some outside influence. An act of observation is thus necessarily accompanied by some disturbance of the object observed. We may define an object to be big when the disturbance accompanying our observation of it may be neglected, and small when the disturbance cannot be neglected. This definition is in close agreement with the common meanings of big and small.

It is usually assumed that, by being careful, we may cut down the disturbance accompanying our observation to any desired extent. The concepts of big and small are then purely relative and refer to the gentleness of our means of observation as well as to the object being described. In order to give an absolute meaning to size, such as is required for any theory of the ultimate structure of matter, we have to assume that *there is a limit to the fineness of our powers of observation and the smallness of the accompanying disturbance – a limit which is inherent in the nature of things and can never be surpassed by improved technique or increased skill on the part of the observer*. If the object under obser-

vation is such that the unavoidable limiting disturbance is negligible, then the object is big in the absolute sense and we may apply classical mechanics to it. If, on the other hand, the limiting disturbance is not negligible, then the object is small in the absolute sense and we require a new theory for dealing with it.

A consequence of the preceding discussion is that we must revise our ideas of causality. Causality applies only to a system which is left undisturbed. If a system is small, we cannot observe it without producing a serious disturbance and hence we cannot expect to find any causal connexion between the results of our observations. Causality will still be assumed to apply to undisturbed systems and the equations which will be set up to describe an undisturbed system will be differential equations expressing a causal connexion between conditions at one time and conditions at a later time. These equations will be in close correspondence with the equations of classical mechanics, but they will be connected only indirectly with the results of observations. There is an unavoidable indeterminacy in the calculation of observational results, the theory enabling us to calculate in general only the probability of our obtaining a particular result when we make an observation.

## 2. The polarization of photons

The discussion in the preceding section about the limit to the gentleness with which observations can be made and the consequent indeterminacy in the results of those observations does not provide any quantitative basis for the building up of quantum mechanics. For this purpose a new set of accurate laws of nature is required. One of the most fundamental and most drastic of these is the *Principle of Superposition of States*. We shall lead up to a general formulation of this principle through a consideration of some special cases, taking first the example provided by the polarization of light.

It is known experimentally that when a plane-polarized<sup>2</sup> light is used for ejecting photo-electrons, there is a preferential direction for the electron emission. Thus the polarization properties of light are closely connected with its corpuscular properties and one must ascribe a polarization to the photons. One must consider, for instance, a beam of light plane-polarized in a certain direction as consisting of photons each of which is plane-polarized in that direction and a beam of circularly polarized light as consisting of photons each circularly polarized. Every photon is in a certain *state of polarization*, as we shall say. The problem we must now consider is how to fit in these ideas with the known facts about the resolution of light into polarized components and the recombination of these components.

Let us take a definite case. Suppose we have a beam of light passing through a crystal of tourmaline, which has the property of letting through only light plane-polarized perpendicular to its optic axis. Classical electrodynamics tells us what will happen for any given polarization of the incident beam. If this beam is polarized perpendicular to the optic axis, it will all go through the crystal; if parallel to the axis, none of it will go through; while if polarized at an angle  $\alpha$  to the axis, a fraction  $\sin^2 \alpha$  will go through it.<sup>3</sup> How are we to understand these results on a photon basis?

A beam that is plane-polarized in a certain direction is to be pictured as made up of photons each plane-polarized in that direction. This picture leads to no difficulty in the cases when our incident beam is polarized perpendicular or parallel to the optic

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<sup>2</sup>[What is now typically called "linearly polarized."]

<sup>3</sup>[This is Malus's Law, but measured relative to the absorptive axis.]

axis. We merely have to suppose that each photon polarized perpendicular to the axis passes unhindered and unchanged through the crystal, while each photon polarized parallel to the axis is stopped and absorbed. A difficulty arises, however, in the case of the obliquely polarized incident beam. Each of the incident photons is then obliquely polarized and it is not clear what will happen to such a photon when it reaches the tourmaline.

A question about what will happen to a particular photon under certain conditions is not really very precise. To make it precise one must imagine some experiment performed having a bearing on the question and inquire what will be the result of the experiment. Only questions about the results of experiments have a real significance and it is only such questions that theoretical physics has to consider.

In our present example the obvious experiment is to use an incident beam consisting of only a single photon and to observe what appears on the back side of the crystal. According to quantum mechanics the result of this experiment will be that sometimes one will find a whole photon, of energy equal to the energy of the incident photon, on the back side and other times one will find nothing. When one finds a whole photon, it will be polarized perpendicular to the optic axis. One will never find only a part of a photon on the back side. If one repeats the experiment a large number of times, one will find the photon on the back side in a fraction  $\sin^2\alpha$  of the total number of times. Thus we may say that the photon has a probability  $\sin^2\alpha$  of passing through the tourmaline and appearing on the back side polarized perpendicular to the axis and a probability  $\cos^2\alpha$  of being absorbed. These values for the probabilities lead to the correct classical results for an incident beam containing a large number of photons.

In this way we preserve the individuality of the photon in all cases. We are able to do this, however, only because we abandon the determinacy of the classical theory. The result of an experiment is not determined, as it would be according to classical ideas, by the conditions under the control of the experimenter. The most that can be predicted is a set of possible results, with a probability of occurrence for each.

The foregoing discussion about the result of an experiment with a single obliquely polarized photon incident on a crystal of tourmaline answers all that can legitimately be asked about what happens to an obliquely polarized photon when it reaches the tourmaline. Questions about what decides whether the photon is to go through or not and how it changes its direction of polarization when it does go through cannot be investigated by experiment and should be regarded as outside the domain of science. Nevertheless some further description is necessary in order to correlate the results of this experiment with the results of other experiments that might be performed with photons and to fit them all into a general scheme. Such further description should be regarded, not as an attempt to answer questions outside the domain of science, but as an aid to the formulation of rules for expressing concisely the results of large numbers of experiments.

The further description provided by quantum mechanics runs as follows. It is supposed that a photon polarized obliquely to the optic axis may be regarded as being partly in the state of polarization parallel to the axis and partly in the state of polarization perpendicular to the axis. The state of oblique polarization may be considered as the result of some kind of superposition process applied to the two states of parallel and perpendicular polarization. This implies a certain special kind of relationship between the various states of polarization, a relationship similar to that between polarized beams in classical optics, but which is now to be applied, not to beams, but to

the states of polarization of one particular photon. This relationship allows any state of polarization to be resolved into, or expressed as a superposition of, any two mutually perpendicular states of polarization.

When we make the photon meet a tourmaline crystal, we are subjecting it to an observation. We are observing whether it is polarized parallel or perpendicular to the optic axis. The effect of making this observation is to force the photon entirely into the state of parallel or into the state of perpendicular polarization. It has to make a sudden jump from being partly in each of these two states to being entirely in one or other of them. Which of the two states it will jump into cannot be predicted, but is governed only by probability laws. If it jumps into the parallel state it gets absorbed and if it jumps into the perpendicular state it passes through the crystal and appears on the other side preserving this state of polarization.

### 3. Interference of photons

In this section we shall deal with another example of superposition. We shall again take photons, but shall be concerned with their position in space and their momentum instead of their polarization. If we are given a beam of roughly monochromatic light, then we know something about the location and momentum of the associated photons. We know that each of them is located somewhere in the region of space through which the beam is passing and has a momentum in the direction of the beam of magnitude given in terms of the frequency of the beam by Einstein's photo-electric law – momentum equals frequency multiplied by a universal constant. When we have such information about the location and momentum of a photon we shall say that it is in a definite *translational state*.

We shall discuss the description which quantum mechanics provides of the interference of photons. Let us take a definite experiment demonstrating interference. Suppose we have a beam of light which is passed through some kind of interferometer, so that it gets split up into two components and the two components are subsequently made to interfere. We may, as in the preceding section, take an incident beam consisting of only a single photon and inquire what will happen to it as it goes through the apparatus. This will present to us the difficulty of the conflict between the wave and corpuscular theories of light in an acute form.

Corresponding to the description that we had in the case of the polarization, we must now describe the photon as going partly into each of the two components into which the incident beam is split. The photon is then, as we may say, in a translational state given by the superposition of the two translational states associated with the two components. We are thus led to a generalization of the term 'translational state' applied to a photon. For a photon to be in a definite translational state it need not be associated with one single beam of light, but may be associated with two or more beams of light which are the components into which one original beam has been split.<sup>4</sup> In the accurate mathematical theory each translational state is associated with one of the wave functions of ordinary wave optics, which wave function may describe either a single beam or two or more beams into which one original beam has been split. Translational states are thus superposable in a similar way to wave functions.

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<sup>4</sup>The circumstance that the superposition idea requires us to generalize our original meaning of translational states, but that no corresponding generalization was needed for the states of polarization of the preceding section, is an accidental one with no underlying theoretical significance.

Let us consider now what happens when we determine the energy in one of the components. The result of such a determination must be either the whole photon or nothing at all. Thus the photon must change suddenly from being partly in one beam and partly in the other to being entirely in one of the beams. This sudden change is due to the disturbance in the translational state of the photon which the observation necessarily makes. It is impossible to predict in which of the two beams the photon will be found. Only the probability of either result can be calculated from the previous distribution of the photon over the two beams.

One could carry out the energy measurement without destroying the component beam by, for example, reflecting the beam from a movable mirror and observing the recoil. Our description of the photon allows us to infer that, *after* such an energy measurement, it would not be possible to bring about any interference effects between the two components. So long as the photon is partly in one beam and partly in the other, interference can occur when the two beams are superposed, but this possibility disappears when the photon is forced entirely into one of the beams by an observation. The other beam then no longer enters into the description of the photon, so that it counts as being entirely in the one beam in the ordinary way for any experiment that may subsequently be performed on it.

On these lines quantum mechanics is able to effect a reconciliation of the wave and corpuscular properties of light. The essential point is the association of each of the translational states of a photon with one of the wave functions of ordinary wave optics. The nature of this association cannot be pictured on a basis of classical mechanics, but is something entirely new. It would be quite wrong to picture the photon and its associated wave as interacting in the way in which particles and waves can interact in classical mechanics. The association can be interpreted only statistically, the wave function giving us information about the probability of our finding the photon in any particular place when we make an observation of where it is.

Some time before the discovery of quantum mechanics people realized that the connexion between light waves and photons must be of a statistical character. What they did not clearly realize, however, was that the wave function gives information about the probability of *one* photon being in a particular place and not the probable number of photons in that place. The importance of the distinction can be made clear in the following way. Suppose we have a beam of light consisting of a large number of photons split up into two components of equal intensity. On the assumption that the intensity of a beam is connected with the probable number of photons in it, we should have half the total number of photons going into each component. If the two components are now made to interfere, we should require a photon in one component to be able to interfere with one in the other. Sometimes these two photons would have to annihilate one another and other times they would have to produce four photons. This would contradict the conservation of energy. The new theory, which connects the wave function with probabilities for one photon, gets over the difficulty by making each photon go partly into each of the two components. Each photon then interferes only with itself. Interference between two different photons never occurs.

The association of particles with waves discussed above is not restricted to the case of light, but is, according to modern theory, of universal applicability. All kind of particles are associated with waves in this way and conversely all wave motion is associated with particles. Thus all particles can be made to exhibit interference effects and all wave motion has its energy in the form of quanta. The reason why these general phenomena

are not more obvious is on account of a law of proportionality between the mass or energy of the particles and the frequency of the waves, the coefficient being such that for waves of familiar frequencies the associated quanta are extremely small, while for particles even as light as electrons the associated wave frequency is so high that it is not easy to demonstrate interference.

#### 4. Superposition and indeterminacy

The reader may possibly feel dissatisfied with the attempt in the two preceding sections to fit in the existence of photons with the classical theory of light. He may argue that a very strange idea has been introduced – the possibility of a photon being partly in each of two states of polarization, or partly in each of two separate beams – but even with the help of this strange idea no satisfying picture of the fundamental single-photon processes has been given. He may say further that this strange idea did not provide any information about experimental results for the experiments discussed, beyond what could have been obtained from an elementary consideration of photons being guided in some vague way by waves. What, then, is the use of the strange idea?

In answer to the first criticism it may be remarked that the main object of physical science is not the provision of pictures, but is the formulation of laws governing phenomena and the application of these laws to the discovery of new phenomena. If a picture exists, so much the better; but whether a picture exists or not is a matter of only secondary importance. In the case of atomic phenomena no picture can be expected to exist in the usual sense of the word 'picture,' by which is meant a model functioning essentially on classical lines. One may, however, extend the meaning of the word 'picture' to include any *way of looking at the fundamental laws which makes their self-consistency obvious*. With this extension, one may gradually acquire a picture of atomic phenomena by becoming familiar with the laws of the quantum theory.

With regard to the second criticism, it may be remarked that for many simple experiments with light, an elementary theory of waves and photons connected in a vague statistical way would be adequate to account for the results. In the case of such experiments quantum mechanics has no further information to give. In the great majority of experiments, however, the conditions are too complex for an elementary theory of this kind to be applicable and some more elaborate scheme, such as is provided by quantum mechanics, is then needed. The method of description that quantum mechanics gives in the more complex cases is applicable also to the simple cases and although it is then not really necessary for accounting for the experimental results, its study in these simple cases is perhaps a suitable introduction to its study in the general case.

There remains an overall criticism that one may make to the whole scheme, namely, that in departing from the determinacy of the classical theory a great complication is introduced into the description of Nature, which is a highly undesirable feature. This complication is undeniable, but it is offset by a great simplification provided by the general *principle of superposition of states*, which we shall now go on to consider. But first it is necessary to make precise the important concept of a 'state' of a general atomic system.

Let us take any atomic system, composed of particles or bodies with specified properties (mass, moment of inertia, etc.) interacting according to specified laws of force. There will be various possible motions of the particles or bodies consistent with the laws of force. Each such motion is called a *state* of the system. According to classical

ideas one could specify a state by giving numerical values to all the coordinates and velocities of the various component parts of the system at some instant of time, the whole motion being then completely determined. Now the argument of [the end of Section 1, where Dirac says, "there is a limit to the fineness of our powers of observation"] shows that we cannot observe a *small* system with that amount of detail which classical theory supposes. The limitation in the power of observation puts a limitation on the number of data that can be assigned to a state. Thus a state of an atomic system must be specified by fewer or more indefinite data than a complete set of numerical values for all the coordinates and velocities at some instant of time. In the case when the system is just a single photon, a state would be completely specified by a given translational state in the sense of §3 together with a given state of polarization in the sense of §2.

A state of a system may be defined as an undisturbed motion that is restricted by as many conditions or data as are theoretically possible without mutual interference or contradiction. In practice the conditions could be imposed by a suitable preparation of the system, consisting perhaps in passing it through various kinds of sorting apparatus, such as slits and polarimeters, the system being left undisturbed after the preparation. The word 'state' may be used to mean either the state at one particular time (after preparation), or the state throughout the whole of time after the preparation. To distinguish these two meanings, the latter will be called a 'state of motion' when there is liable to be ambiguity.

The general principle of superposition of quantum mechanics applies to the states, with either of the above meanings, of any one dynamical system. It requires us to assume that between these states there exist peculiar relationships such that whenever the system is definitely in one state we can consider it as being partly in each of two or more other states. The original state must be regarded as the result of a kind of *superposition* of the two or more new states, in a way that cannot be conceived on classical ideas. Any state may be considered as the result of a superposition of two or more other states, and indeed in an infinite number of ways. Conversely any two or more states may be superposed to give a new state. The procedure of expressing a state as the result of superposition of a number of other states is a mathematical procedure that is always permissible, independent of any reference to physical conditions, like the procedure of resolving a wave into Fourier components. Whether it is useful in any particular case, though, depends on the special physical conditions of the problem under consideration.

In the two preceding sections examples were given of the superposition principle applied to a system consisting of a single photon. §2 dealt with states differing only with regard to the polarization and §3 with states differing only with regard to the motion of the photon as a whole.

The nature of the relationships which the superposition principle requires to exist between the states of any system is of a kind that cannot be explained in terms of familiar physical concepts. One cannot in the classical sense picture a system being partly in each of two states and see the equivalence of this to the system being completely in some other state. There is an entirely new idea involved, to which one must get accustomed and in terms of which one must proceed to build up an exact mathematical theory, without having any detailed classical picture.

When a state is formed by the superposition of two other states, it will have properties that are in some vague way intermediate between those of the two original states and that approach more or less closely to those of either of them according to

the greater or less 'weight' attached to this state in the superposition process. The new state is completely defined by the two original states when their relative weights in the superposition process are known, together with a certain phase difference, the exact meaning of weights and phases being provided in the general case by the mathematical theory. In the case of the polarization of a photon their meaning is that provided by classical optics, so that, for example, when two perpendicularly plane polarized states are superposed with equal weights, the new state may be circularly polarized in either direction, or linearly polarized at an angle  $\frac{1}{4}\pi$ , or elliptically polarized, according to the phase difference.

The non-classical nature of the superposition process is brought out clearly if we consider the superposition of two states, *A* and *B*, such that there exists an observation which, when made on the system in state *A*, is certain to lead to one particular result, *a* say, and when made on the system in state *B* is certain to lead to some different result, *b* say. What will be the result of the observation when made on the system in the superposed state? The answer is that the result will be sometimes *a* and sometimes *b*, according to a probability law depending on the relative weights of *A* and *B* in the superposition process. It will never be different from both *a* and *b*. *The intermediate character of the state formed by superposition thus expresses itself through the probability of a particular result for an observation being intermediate between the corresponding probabilities for the original states*,<sup>5</sup> not through the result itself being intermediate between the corresponding results for the original states.

In this way we see that such a drastic departure from ordinary ideas as the assumption of superposition relationships between states is possible only on account of the recognition of the importance of the disturbance accompanying an observation and of the consequent indeterminacy in the result of the observation. When an observation is made on any atomic system that is in a given state, in general the result will not be determinate, i.e., if the experiment is repeated several times under identical conditions several different results may be obtained. It is a law of nature, though, that if the experiment is repeated a large number of times, each particular result will be obtained in a definite fraction of the total number of times, so that there is a definite *probability* of its being obtained. This probability is what the theory sets out to calculate. Only in special cases when the probability for some result is unity is the result of the experiment determinate.

The assumption of superposition relationships between the states leads to a mathematical theory in which the equations that define a state are linear in the unknowns. In consequence of this, people have tried to establish analogies with systems in classical mechanics, such as vibrating strings or membranes, which are governed by linear equations and for which, therefore, a superposition principle holds. Such analogies have led to the name 'Wave Mechanics' being sometimes given to quantum mechanics. It is important to remember, however, that *the superposition that occurs in quantum mechanics is of an essentially different nature from any occurring in the classical theory*, as is shown by the fact that the quantum superposition principle demands indeterminacy in the results of observations in order to be capable of a sensible physical interpretation. The analogies are thus liable to be misleading.

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<sup>5</sup>The probability of a particular result for the state formed by superposition is not always intermediate between those for the original states in the general case when those for the original states are not zero or unity, so there are restrictions on the 'intermediateness' of a state formed by superposition.



# OPTICS LAB: INTRODUCTION

## OPTICS PRACTICUM 2

### INTRODUCTION

In our readings from *The Principles of Quantum Mechanics*, Dirac proposes thought experiments to spell out some of the peculiar logic of quantum theory. We will perform versions of those experiments ourselves in the quantum optics laboratory in the basement of Mellon Hall. All will employ the same basic suite of equipment, which includes some devices like those used in the polarization practicum—lasers, photodiode detectors, and a variety of polarizers and waveplates—as well as some new elements: a high-speed coincidence detector and individual photon counters, a computer interface to display results of experiments, beam-splitters and mirrors to direct light, and perhaps most consequentially, a down-conversion crystal, an optical element so called because it converts some portion of a beam of light of a higher frequency to a pair of beams of light of lower frequencies (in our setup, from the 405 nm laser to a pair of beams at wavelengths near 810 nm).

What we will do in this practicum is not one of Dirac's thought experiments, but they all depend on something like it, namely, the ability to grapple with light as quanta. All the elements of our apparatus help us to do this, but perhaps none so much as the down-conversion crystal and the detectors. The crystal works for reasons it takes advanced quantum mechanics to explain, and so to explain its action is beyond our scope, but at least some of its practical effects are understandable, and in a way it resembles the Iceland spar in exhibiting birefringence. In our final practicum, we will depend on a distinctly non-classical effect of an arrangement of two such crystals. As stated above, the crystal splits a small portion of a beam of laser light into two dimmer beams—*much* dimmer—so dim, in fact, that our powerfully amplified photodetectors and fast coincidence counters can register individual photons (though they do not register every photon).

In this practicum, in order to familiarize ourselves with the equipment for later practica, we will use it to demonstrate the particle-like character of light, by sending light through a beam-splitter and closely measuring the light that emerges. The beam-splitter exploits the partial reflection that occurs at the interface between two media to send incident light into two different directions or to combine incident beams into a single beam (see Fig. 1). The phenomenon of partial reflection is familiar (e.g., in any window pane), but predicting how light composed of photons will behave in the beam-splitter takes a little bit of thought. A naive first thought, preserving both the phenomenon of partial reflection and the theory of light quanta, might be that each photon of light striking a partially reflecting surface is split into two photons, one reflected, one transmitted. But if you look at a partial reflection, think about the conservation of energy and the relation of energy and wavelength, and realize that the colors of the reflected image are the same as the original, and not some longer-wavelength colors, you can see that this can't be what is happening.



Figure 1: Light enters the beam-splitter from  $A$  or  $B$ , and exits to either  $C$  or  $D$ .

A second thought, perfectly adequate and effectively a version of the theory we will test, preserves the integrity of the photon in the face of the phenomenon of partial reflection, claiming only that *some photons are reflected, some are transmitted*. This is compatible with many different accounts of what determines which photons go which way. Despite being broadly indeterminate in this way, it is definite enough to have one important testable prediction: a single photon leaving the beam-splitter must emerge from one or another side, and not both. If the beam is dim enough and the counters sensitive enough and the coincidence detectors fast enough (and we have good reasons to believe they all are), we can test this prediction. In Figure 2, if the laser light enters the beam-splitter and detectors are placed at  $B$  and  $B'$ , we should (almost) never find a “coincidence”—i.e., a count occurring within the time window of our coincidence detector, on the order of several nanoseconds—between firings of the detectors at  $B$  and  $B'$ . (More on the detector at  $A$  in the description of the analysis of results below. More, too, on that “never.”)



Figure 2: Light from one beam leaving the down-conversion crystal ( $DC$ ) enters the beam-splitter, which either transmits it to detector  $B$  or reflects it to detector  $B'$ .

While our authors often frame their thought experiments in terms of the behavior of a single photon or a single electron, we must recall considerations like Heisenberg's and Dirac's about the inevitability of disturbing single particles with any interaction leading to measurement. We cannot usefully observe a single photon “in flight,” as it

were, to confirm that it behaves as our theory says it must. More than that, because of the extreme delicacy (and therefore lack of accuracy) of the measurements we are trying to take (registering *single* photons!), we cannot rely on the results of a single measurement. We will instead aggregate the results of thousands, tens of thousands, and even millions of measurements.

The sort of question to which such results can provide an answer, then, is statistical in nature: according to the theories we are trying to test, what results are possible? And in this particular case, how well *correlated* are the individual detections of photons from the two outputs of the beam-splitter? If light is composed of photons and our instruments are perfect, there should be near-perfect *anti-correlation* between the two detectors: if one fires in a given 4 ns window, the other should not, except in the extremely unlikely instance that two photons happen to be coming through the beam-splitter during that same window of time. Let's make the measure of correlation and anti-correlation more quantitative.

If  $P(BB')$  is the probability of both detectors firing within our detection window, and  $P(B)$  and  $P(B')$  are the probabilities of detector  $B$  or  $B'$  firing within that time, then a measure of the correlation of the two detectors firing at the same time (which we will call  $g$ ) is

$$g = \frac{P(BB')}{P(B) \cdot P(B')} .$$

Again, if light is composed of photons thus going either one way or the other through the beam-splitter,  $P(BB')$  should be zero, with the result that  $g$  is zero. If not, then the firing of detector  $B$  may be completely unrelated to the firing of detector  $B'$ . Both detectors would simply fire randomly at some average rate. Therefore, on this latter hypothesis, the probability that both  $B$  and  $B'$  will fire in a given time is simply the product of the probability that  $B$  will fire and the probability that  $B'$  will fire; that is,  $P(BB') = P(B) \cdot P(B')$ . If this is the case, the correlation  $g$ , which compares those two probabilities, will equal one. There is no classical theory of the behavior of light that predicts correlations less than one. Our competing theories thus make distinct predictions about the outcome of the experiment.

Our practicum will involve collecting data that will give us a measurement for  $g$ . If  $g < 1$ , you will have shown that the classical account is inadequate to explain the results, and this presence of anti-correlation is consistent with the theory that light is composed of photons. (A  $g$  equal to zero is ideal. Various factors, including the sensitivity of our instruments and the difficulty of excluding every photon except the ones from our light source, ensure that our measurement of  $g$  will never be zero. Anything less than one, however, is not explainable in terms of classical mechanics and is therefore taken as consistent with the quantum theory of light.)

## DATA COLLECTION

The extreme sensitivity of our instruments makes it important to control the light that is reaching them as stringently as possible, so we can be sure the conclusions we draw about the nature of light from our experiments are well-founded. In the present case, that means counting detections at our  $B$  and  $B'$  detectors *only when light is detected at A, also*. As a practical matter, you can take data without this additional restriction, too,

and compare results. Including coincidences with counts at A, our formula for  $g$  must change:

$$g = \frac{P(ABB')}{P(AB) \cdot P(AB')} .$$

To acquire numbers for our probabilities, we will take counts over a five second time period. The number of counts in each detector is proportional to the probability of light hitting that detector. We will normalize everything to the counts at detector A, expressing all our counts as fractions of the total counts at A. We will denote the number of counts at detector A as  $N(A)$ , etc., so that

$$P(ABB') = \frac{N(ABB')}{N(A)}$$

$$P(AB) = \frac{N(AB)}{N(A)}$$

$$P(AB') = \frac{N(AB')}{N(A)} .$$

Substituting these values in our equation for  $g$ , we get

$$g = \frac{N(A) \cdot N(ABB')}{N(AB) \cdot N(AB')} .$$

## ERROR

If you flip a coin 100 times, you would expect it to come up heads somewhere in the neighborhood of 50 times. It would, however, be surprising if it came up heads exactly 50 times every time you did a run of 100 coin flips. Accordingly, if in one trial a coin came up heads only 48 times, you would not immediately conclude that it was unbalanced. In other words, there is a distribution of possible outcomes; even if the coin is perfectly symmetrical and its probability of coming up heads is exactly 50%, there is a substantial probability of a given trial showing a different result.

This is the reasoning behind calculating an "error range" for measurements, a range of possible outcomes of measurements consistent with a certain probable outcome. The realm of statistics is vast. For our purposes, in this and most of the remaining experiments, it is sufficient to make use of some straightforward assumptions about how results will be distributed.

If we assume that each detector fires at a constant average rate and the probability of each firing is independent of the time since the last firing, then we can treat the data as giving us a Poisson distribution around a mean. The standard deviation for a Poisson distribution is calculated as the square root of the mean. Therefore, we can treat each number of counts as a mean, plus or minus a standard deviation that is calculated as the square root of that mean. Since we are dealing with several different numbers, we will normalize each standard deviation by dividing by its own mean. We end up with

$$\frac{\sqrt{N(A)}}{N(A)}, \frac{\sqrt{N(ABB')}}{N(ABB')}, \frac{\sqrt{N(AB)}}{N(AB)}, \frac{\sqrt{N(AB')}}{N(AB')} .$$

Another way to write these fractions is

$$\frac{1}{\sqrt{N(A)}}, \frac{1}{\sqrt{N(ABB')}}, \frac{1}{\sqrt{N(AB)}}, \frac{1}{\sqrt{N(AB')}}.$$

Of these four factors, only  $\frac{1}{\sqrt{N(ABB')}}$  will be significant, since the others will have denominators that are very large in comparison with it. Our error is determined by multiplying our  $g$  term by this normalized standard deviation term. So, we calculate the range of  $g$  values

$$g \pm \frac{g}{\sqrt{N(ABB')}}.$$

and if the largest value of  $g$  in this range is less than 1, we take that as being consistent with the theory that light is composed of photons.

## SAFETY

In order to preserve your eyesight, *safety goggles must be worn at all times while the laser is on*. In order to preserve the sensitive photodetectors, the overhead lights in the lab *must be turned off* when they are active. Strips of safe, low-power green LED lights have been arranged so that there is some illumination while performing experiments.



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# SINGLE PHOTON INTERFERENCE AND SUPERPOSITION

## OPTICS PRACTICUM 3

### INTRODUCTION

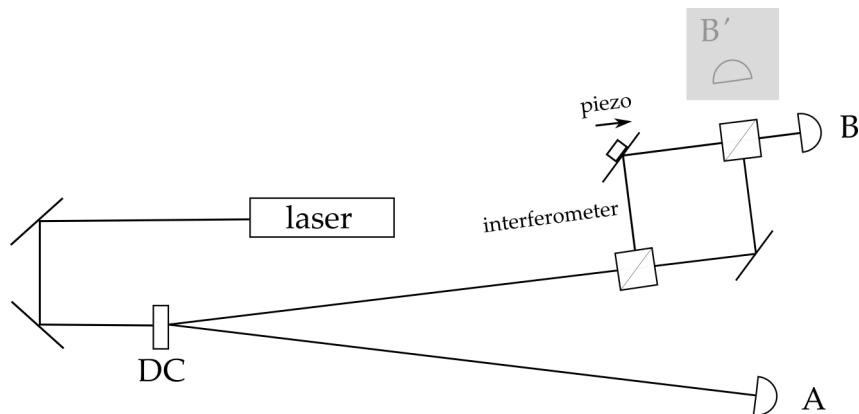
In section 3 of *The Principles of Quantum Mechanics*, in order to develop his notion of "superposition" further, Dirac proposes to describe what happens when a single photon enters an "interferometer." With the use of our equipment, we can carry out this experiment in fact.

Our interferometer makes use of an arrangement of two beam-splitters and two mirrors to separate and then recombine one beam of light. One of the mirrors is fixed, and the other is movable. The latter is very gradually moved so as to change the length of one of the paths by which the light makes its way through the apparatus. This changing of one path length is what will allow interference effects to appear, as light of a single frequency is recombined with itself with different degrees of shift in phase, just as different distances to the screen in double-slit diffraction create an interference pattern. Since the mirror is uniformly advanced by a constant interval and the result of measurement is graphed after each nudge, the interference will manifest itself as a familiar sinusoidal pattern in the output at the detector, oscillating between a maximum intensity and zero, as if two beams of light were being made to constructively and destructively interfere with each other. Dirac's account invites us to think about how the state of a single photon must be described if it, too, is subject to interference. How can a single photon interfere with itself? According to Dirac, "we must now describe the photon as going partly into each of the two components into which the incident beam is split."

### THE SINGLENESS OF PHOTONS

For our experiment to be a useful occasion for thinking through this account of superposition, we need to be reasonably sure that there is only one photon at a time in the interferometer. A brief calculation of how many photons are in the apparatus at a time follows.

If the maximum rate of detection of photons from the laser is 87,500 per second (which, even after painstaking adjustment of the precise positions of all the optical elements, would be on the high end for our equipment), and the detectors register one out of every 10 photons (a conservative estimate, given the efficiency ratings of the detectors, which may be as high as 50%), then the number of photons coming through per second could be as many as  $87,500/0.1$  or 875,000. Since the speed of light is  $3 \times 10^{10}$  centimeters per second, the "number" of photons that could be found in each centimeter at any one time is



*Experimental setup for detecting single-photon interference. An optional second detector can be set up at  $B'$  if desired after the main demonstration is complete.*

$$\frac{875,000 \text{ per sec}}{3 \times 10^{10} \text{ cm/sec}} = 2.9 \times 10^{-5}.$$

The length of the interferometer will vary slightly each time it is set up, but one of its arms is generally about 20 cm long. Therefore, the average number of photons in the interferometer at any one time is

$$2.9 \times 10^{-5} \text{ per cm} \times 20 \text{ cm} = 5.8 \times 10^{-4}.$$

Or, since this is a number much less than one, we can say that the *chance* of there being a photon from the laser in the interferometer at any given instant is 0.058% or about 1 in 1700. The chance that two are present, therefore, is almost 3 million to one. Consequently, we can be reasonably sure that the overwhelming majority ( $> 99.9\%$ ) of photons coming through the interferometer and being registered at the detectors have traveled through it unaccompanied. Any interference effects they suffer must somehow be due to themselves.

## COLLECTING DATA

Recall from the last practicum using this equipment that *the overhead lights must not be on* while the sensitive photodiode detectors are on. Recall also that *safety glasses must be worn* when the blue laser is on.

When the experiment is running, the mirror will move a small distance every tenth of a second and then the photon counters will count how many photons they detect. The computer interface will form a graph of these totals as it records them.

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# THE “QUANTUM ERASER”

## OPTICS PRACTICUM 4

### INTRODUCTION

In section 3 of “The Principles of Quantum Mechanics,” as we’ve already seen, Dirac uses the example of the interference of photons as an example of his principle of “superposition,” here applied not only to the states of polarization of photons (which may or may not pass through a linear polarizer), but also to their “translational states,” that is, to the multiple paths they are somehow inhabiting, according to the description Dirac says quantum mechanics provides, even of what is unobservable. Having demonstrated that even single photons may produce an interference pattern, we now turn to Dirac’s further development of this idea. He writes:

Let us consider now what happens when we determine the energy in one of the components [the spatially separated beams within the interferometer]. The result of such a determination must be either the whole photon or nothing at all. Thus the photon must change suddenly from being partly in one beam and partly in the other to being entirely in one of the beams. This sudden change is due to the disturbance in the translational state of the photon which the observation necessarily makes [...]. Our description of the photon allows us to infer that, after such an energy measurement, it would not be possible to bring about any interference effects between the two components. So long as the photon is partly in one beam and partly in the other, interference can occur when the two beams are superposed, but this possibility disappears when the photon is forced entirely into one of the beams by an observation.

We will do our best to realize this thought-experiment, though we cannot reproduce it exactly.<sup>1</sup> As in the previous practicum, here we will send one of our beams of down-converted light through an interferometer. Now, however, in each leg of the interferometer there will be a half-wave plate (see Figure 1). Recall from the polarization practicum that half-wave plates rotate the polarization of the light by twice the difference in angle between the polarization of the light and the angle of the half-wave plate. The photons that enter the interferometer are vertically polarized. Both half-wave plates should be set at zero degrees at the beginning of the practicum, so that at first they are not changing the angle of polarization.

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<sup>1</sup>One version of such an experiment that is closer to Dirac’s description is reported in Walborn, Terra Cunha, Pádua, and Monken, “Double-slit quantum eraser,” *Phys. Rev. A* **65** 033818 (2002).

## PRACTICUM

Verify that the setup, with the waveplates included and set to vertical, gives the characteristic sinusoidal interference pattern as in the single photon interference practicum. Now, turn one of the half-wave plates to 45 degrees. This will rotate the polarization of the photon in that leg of the interferometer by 90 degrees. Verify that the interference pattern disappears.

Dirac says that the detection of the energy of a photon in an interferometer, which would decisively indicate that the photon is in the path where its energy is measured, will make it impossible to "bring about any interference effects between the two components." It appears that changing the polarization of the photons that go through one of the legs of the interferometer has a similar effect. Dirac's thought-experiment invites us to think of changing the polarization of the photons in one of the paths of the interferometer by 90° as equivalent to making an "observation." We do not, in fact, have anything in our apparatus that would detect the polarization of the photon coming through the interferometer, though such apparatus is certainly available to us. But somehow the mere possibility of being able to detect which path the photon took through the interferometer seems to produce effects equivalent to those Dirac says would result from actually making an observation.

Now, as it has become common to say, we will "erase" the "which-path" information by putting a linear polarizer turned to 45° in front of the detector, and will thereby allow the interference effects to reappear, perhaps surprisingly. Some find it significant that individual photons do not encounter the linear polarizer in front of the detector until *after* they have already traversed the interferometer. Some think it important to note that, relative to the 45° linear polarizer, the 0° and 90° components of the incoming light are equally passable, and come to be polarized in the same direction. However matters may stand with these and similar sorts of considerations, it is worthwhile to trace each possible path of the photon through the interferometer and determine under which circumstances (i.e., which settings of the waveplates and polarizer) the two paths in the interferometer are in principle distinguishable. You can test your hypotheses by trying other arrangements of the various optical elements and seeing what results you get.

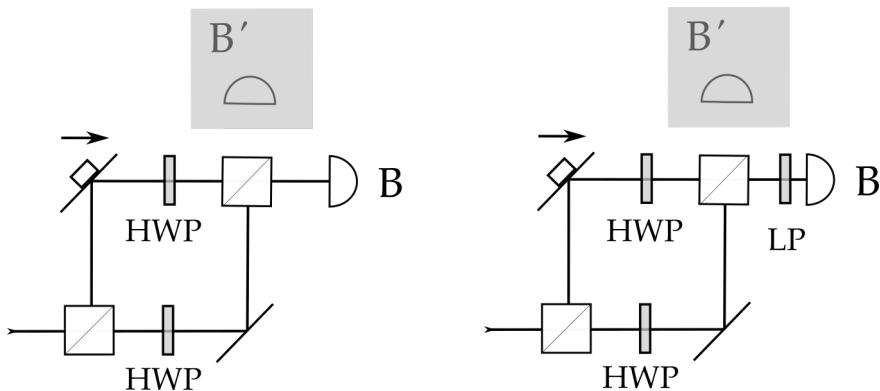


Figure 1 — Experimental setup for the "quantum eraser," showing the two stages of the demonstration. An optional second detector can be set up at  $B'$  if desired after the main demonstration is complete.

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# CAN QUANTUM-MECHANICAL DESCRIPTION OF REALITY BE CONSIDERED COMPLETE?

EINSTEIN, PODOLSKY, AND ROSEN<sup>1</sup>

## 1.

Any serious consideration of a physical theory must take into account the distinction between the objective reality, which is independent of any theory, and the physical concepts with which the theory operates. These concepts are intended to correspond with the objective reality, and by means of these concepts we picture this reality to ourselves.

In attempting to judge the success of a physical theory, we may ask ourselves two questions: (1) "Is the theory correct?" and (2) "Is the description given by the theory complete?" It is only in the case in which positive answers may be given to both of these questions, that the concepts of the theory may be said to be satisfactory. The correctness of the theory is judged by the degree of agreement between the conclusions of the theory and human experience. This experience, which alone enables us to make inferences about reality, in physics takes the form of experiment and measurement. It is the second question that we wish to consider here, as applied to quantum mechanics.

Whatever the meaning assigned to the term *complete*, the following requirement for a complete theory seems to be a necessary one: *every element of the physical reality must have a counterpart in the physical theory*. We shall call this the condition of completeness. The second question is thus easily answered, as soon as we are able to decide what are the elements of the physical reality.

The elements of the physical reality cannot be determined by a priori philosophical considerations, but must be found by an appeal to results of experiments and measurements. A comprehensive definition of reality is, however, unnecessary for our purpose. We shall be satisfied with the following criterion, which we regard as reasonable. *If, without in any way disturbing a system, we can predict with certainty (i.e., with probability equal to unity) the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity.* It seems to us that this criterion, while far from exhausting all possible ways of recognizing a physical reality, at least provides us with one such way, whenever the conditions set down in it occur. Regarded not as a necessary, but merely as a sufficient, condition of reality, this criterion is in agreement with classical as well as quantum-mechanical ideas of reality.

To illustrate the ideas involved let us consider the quantum-mechanical description of the behavior of a particle having a single degree of freedom. The fundamental concept of the theory is the concept of *state*, which is supposed to be completely characterized by the wave function  $\psi$ , which is a function of the variables chosen to describe

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<sup>1</sup>*Physical Review* 47 (1935), 777–80.

the particle's behavior.

\* \* \*

A definite value of the [spatial] coordinate, for a particle in [the sort of state described by quantum mechanics] is thus not predictable, but may be obtained only by a direct measurement. Such a measurement however disturbs the particle and thus alters its state. After the coordinate is determined, the particle will no longer be in the [same] state.... The usual conclusion from this in quantum mechanics is that *when the momentum of a particle is known, its coordinate has no physical reality*.

More generally, it is shown in quantum mechanics that, if [two physical quantities are in the indeterminacy relation to each other,] then the precise knowledge of one of them precludes such a knowledge of the other. Furthermore, any attempt to determine the latter experimentally will alter the state of the system in such a way as to destroy the knowledge of the first.

From this follows that either (1) *the quantum-mechanical description of reality given by the wave function is not complete* or (2) *when [two physical quantities are in the indeterminacy relation to each other,] the two quantities cannot have simultaneous reality*. For if both of them had simultaneous reality—and thus definite values—these values would enter into the complete description, according to the condition of completeness. If then the wave function provided such a complete description of reality, it would contain these values; these would then be predictable. This not being the case, we are left with the alternatives stated.

In quantum mechanics it is usually assumed that the wave function *does* contain a complete description of the physical reality of the system in the state to which it corresponds. At first sight this assumption is entirely reasonable, for the information obtainable from a wave function seems to correspond exactly to what can be measured without altering the state of the system. We shall show, however, that this assumption, together with the criterion of reality given above, leads to a contradiction.

## 2.

For this purpose let us suppose that we have two systems, I and II, which we permit to interact from the time  $t = 0$  to  $t = T$ , after which time we suppose that there is no longer any interaction between the two parts. We suppose further that the states of the two systems before  $t = 0$  are known.

[Because of the mathematics involved, we will not be able to follow the example constructed by Einstein, Podolsky, and Rosen. However Bohr has described<sup>2</sup> a thought-experiment which, he claims, captures the essential features of the EPR argument:]

The particular quantum-mechanical state of two free particles, for which they [i.e., EPR] give an explicit mathematical expression, may be reproduced, at least in principle,<sup>3</sup> by a simple experimental arrangement, com-

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<sup>2</sup>In his reply to the EPR paper, itself entitled "Can quantum-mechanical description of physical reality be considered complete?" *Physical Review* 48 (1935), 696—702.

<sup>3</sup>The obvious impossibility of actually carrying out, with the experimental technique at our disposal, such measuring procedures as are discussed here and in the following does clearly not affect the theoretical argument, since the procedures in question are essentially equivalent with atomic processes, like the Compton effect, where a corresponding application of the conservation theorem of momentum is well established.

prising a rigid diaphragm with two parallel slits, which are very narrow compared with their separation, and through each of which one particle with given initial momentum passes independently of the other. If the momentum of this diaphragm is measured accurately before as well as after the passing of the particles, we shall in fact know the sum of the components perpendicular to the slits of the momenta of the two escaping particles, as well as the difference of their initial positional coordinates in the same direction,<sup>4</sup> while of course the ... difference of the components of their momenta, and the sum of their positional coordinates, are entirely unknown. In this arrangement, it is therefore clear that a subsequent single measurement either of the position or of the momentum of one of the particles [namely, system I] will automatically determine the position or momentum, respectively, of the other particle [system II] with any desired accuracy; at least if the wave-length corresponding to the free motion of each particle is sufficiently short compared with the width of the slits.<sup>5</sup>

[EPR continue:]

We see therefore that, as a consequence of two different measurements performed upon the first system, [either the position or the momentum of the second system may be measured with any desired accuracy]. On the other hand, since at the time of measurement the two systems no longer interact, no real change can take place in the second system in consequence of anything that may be done to the first system. This is, of course, merely a statement of what is meant by the absence of an interaction between the two systems.

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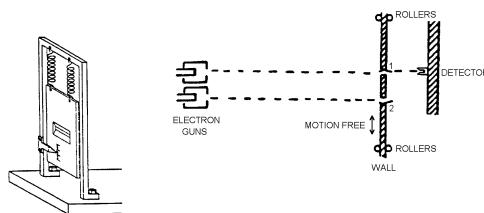
Thus, by measuring either [the position of I] or [the momentum of I,] we are in a position to predict with certainty, and without in any way disturbing the second system, either the value of the [position] or the value of the [momentum of the second system].

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<sup>4</sup>[Let  $p_1$  and  $p_2$  be the vertical components of the momentum of the particles after they have passed through the top and bottom slits, respectively. And let  $P$  be the vertical component of the momentum of the diaphragm after the two particles have passed through the slits. If we assume that before the particles pass through the slits the vertical components of the momentum of the two particles and of the diaphragm were all zero, then by the conservation of momentum,  $p_1 + p_2 = -P$ .]

Let  $x_1$  and  $x_2$  be the coordinates of the vertical position of the particles just after they have passed through the top and bottom slits, respectively. And let  $d$  be the distance between the two slits. Then just after the two particles pass through the slits,  $x_1 - x_2 = d$ .]

<sup>5</sup>[In his account of his discussions with Einstein, Bohr includes the figure below on the left to illustrate a similar experiment involving only one slit. Below on the right is a figure illustrating the double-slit experiment; the detector is a Geiger counter.]



In accordance with our criterion of reality, in the first case we must consider the [position of II] as being an element of reality, in the second case the [momentum of II] is an element of reality....

Previously we proved that either (1) the quantum-mechanical description of reality given by the wave function is not complete or (2) *when [two physical quantities are in the indeterminacy relation to each other,] the two quantities cannot have simultaneous reality.* Starting then with the assumption that [quantum mechanics] does give a complete description of the physical reality, we arrived at the conclusion that two physical quantities, [which are related by the indeterminacy relations], can have simultaneous reality. Thus the negation of (1) leads to the negation of the only other alternative (2). We are thus forced to conclude that the quantum-mechanical description of physical reality given by wave functions is not complete.

One could object to this conclusion on the grounds that our criterion of reality is not sufficiently restrictive. Indeed, one would not arrive at our conclusion if one insisted that two or more physical quantities can be regarded as simultaneous elements of reality *only when they can be simultaneously measured or predicted.* On this point of view, since either one or the other, but not both simultaneously, of the quantities [momentum] and [position of the second system] can be predicted, they are not simultaneously real. This makes the reality of [the momentum] and [position of the second system] depend upon the process of measurement carried out on the first system, which does not disturb the second system in any way. No reasonable definition of reality could be expected to permit this.

While we have thus shown that the wave function does not provide a complete description of the physical reality, we left open the question of whether or not such a description exists. We believe, however, that such a theory is possible.

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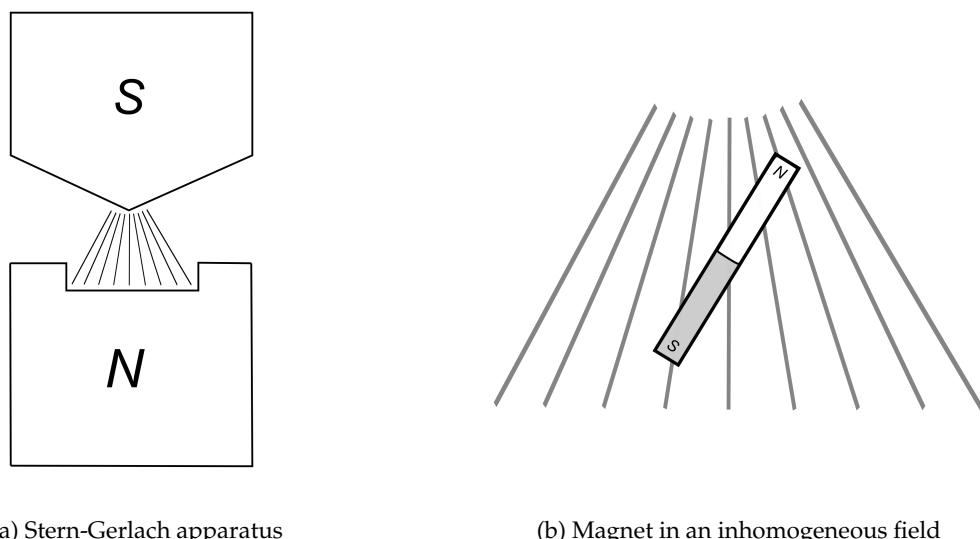
# BELL'S THEOREM

J. S. BELL

## INTRODUCTION

The paper we are about to read takes up the issues raised by Einstein, Podolsky, and Rosen in a new way. Physicist J. S. Bell gives a novel mathematical form to the suppositions of “hidden variables” and “locality” and then shows that this is in contradiction with the mathematical form of the predictions of quantum mechanics. In this chapter, we will read Bell’s original paper and then confirm by means of experiment that the particles we have been studying do not behave in the way Bell’s formulation shows they would have to if they were subject to a local hidden variables theory.

The particles we have been studying are photons, but Bell makes his argument in terms of the behavior of electrons, in a special state that we have not studied. The import is the same: quantum mechanics says that two characteristics to be measured stand in a relation of mutual indeterminacy; Bell considers a situation in which two particles produced by the same process are measured separately and the supposedly indeterminate quantity in each is to be inferred from the result of the measurement of that same quantity in the other. Though the import is the same, to understand Bell’s paper, we have to understand something about the particular state and the characteristics he is talking about. The feature of interest is electron “spin.”



(a) Stern-Gerlach apparatus

(b) Magnet in an inhomogeneous field

In 1922, Otto Stern and Walther Gerlach performed what turned out to be a very consequential experiment, though its full significance was not recognized until years later. The experiment was conceived in order to test then-current theories of the atom based on Bohr’s model. The evidence for or against the favored theory was to be found

in the magnetic response of individual atoms. In particular, the revolution of the electron about the nucleus ought to count, according to Maxwell's equations, as a loop of current, effectively making the atom a tiny magnet. The theory Stern and Gerlach were testing predicted that the angular momentum of the electron measured in a particular direction ought to be quantized, just as the Bohr orbits are. The experiment consisted in firing a collimated beam of silver atoms through a powerful and inhomogeneous magnetic field like the one pictured on the left in the figure above.

Now, if the orientation of the atomic "magnet" were such as is pictured on the right, it would be subject not only to a counterclockwise torque, but also—since the magnetic field is stronger near the top than near the bottom (since the field lines are more concentrated there)—to a net force pulling it upwards. If many atoms were projected through the field at random orientations, some would be pulled up and some pushed down, some more and some less. If the degree of magnetization in these directions is quantized, however—that is, if the only physically meaningful answers to the question "in which direction is this magnet oriented?" are "up" and "down"—one would expect the beam of atoms to be split, with no intermediate results. This is precisely what was found, as can be seen in the image below, taken from the original paper.

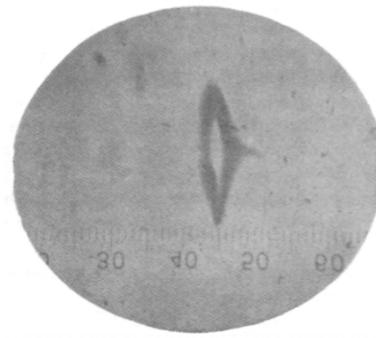


Fig. 3.

Later, it was recognized that this experimental result was consistent with what the second generation of quantum-mechanical theories (e.g., Schrödinger's) held, namely, that there ought to be something like an *intrinsic* angular momentum, or "spin," associated with the electron, one that does not result from its orbiting the nucleus, but from its inherent character. The mathematics behind this prediction are well beyond us, but the Stern-Gerlach experiment demonstrates it adequately. In our practice, we have been working with the polarization of the photon, and from the first, it has exhibited the same quantization: while a beam of light, composed of many photons, may show partial effects as described by Malus's Law, a single photon faced with a linear polarizer either passes through it or does not pass through it. Bell assumes his readers are familiar with the phenomenon of electron spin and with the apparatus for detecting it.

The quantization of intrinsic spin is of particular importance for his derivation, since he considers a pair of electrons the net spin of which is null (this is the special "singlet spin state" to which he refers) moving independently of one another in opposite directions, such that they can be subject to measurements at different locations. Now, quantization means that different axial directions (or "components") of an electron's spin stand to one another in the "indeterminacy relation"; that is, quantum me-

chanics says they cannot in principle be assigned simultaneous reality. If the direction of an electron's spin is measured in the z-direction, quantum mechanics says it is *indeterminate* in the x- and y-directions. This is the same indeterminacy relation found in Bohr's reformulation of EPR's argument, there, between the positions and momenta of two linked particles. Bell's mathematical reformulation of one version of EPR's view that quantum mechanical description of reality is importantly incomplete is notable for both its clarity and its testability. Remarks on the form of his argument follow the paper.

## ON THE EINSTEIN PODOLSKY ROSEN PARADOX

J. S. BELL

### I. Introduction

The paradox of Einstein, Podolsky and Rosen<sup>1</sup> was advanced as an argument that quantum mechanics could not be a complete theory but should be supplemented by additional variables. These additional variables were to restore to the theory causality and locality.<sup>2</sup> In this note that idea will be formulated mathematically and shown to be incompatible with the statistical predictions of quantum mechanics. It is the requirement of locality, or more precisely that the result of a measurement on one system be unaffected by operations on a distant system with which it has interacted in the past, that creates the essential difficulty. There have been attempts<sup>3</sup> to show that even without such a separability or locality requirement no "hidden variable" interpretation of quantum mechanics is possible. These attempts have been examined elsewhere<sup>4</sup> and found wanting. Moreover, a hidden variable interpretation of elementary quantum theory<sup>5</sup> has been explicitly constructed. That particular interpretation has indeed a grossly non-local structure. This is characteristic, according to the result to be probed here, of any such theory which reproduces exactly the quantum mechanical predictions.

### II. Formulation

With the example advocated by Bohm and Aharonov,<sup>6</sup> the EPR argument is the following. Consider a pair of spin one-half particles formed somehow in the singlet spin state and moving freely in opposite directions. Measurements can be made, say by Stern-Gerlach magnets, on selected components of the spins  $\sigma_1$  and  $\sigma_2$ . If measurement of the component  $\sigma_1 \cdot \mathbf{a}$ , where  $\mathbf{a}$  is some unit vector, yields the value +1 then, according

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<sup>1</sup>A. Einstein, N. Rosen and B. Podolsky, *Phys. Rev.* **47** 777 (1935).

<sup>2</sup>"But on one supposition we should, in my opinion, absolutely hold fast: the real factual situation of the system  $S_2$  is independent of what is done with the system  $S_1$ , which is spatially separated from the former." Albert Einstein in *Albert Einstein, Philosopher Scientist*, (Edited by P.A. Schilp), p. 85, Library of Living Philosophers, Evanston, Illinois (1949).

<sup>3</sup>J. Von Neumann, *Mathematische Grundlagen der Quanten-mechanik*, Verlag Julius-Springer, Berlin (1932), [English translation: Princeton University Press (1955)]; J.M. Jauch and C. Piron, *Helv. Phys. Acta* **36**, 827 (1963).

<sup>4</sup>J.S. Bell, to be published.

<sup>5</sup>D. Bohm, *Phys. Rev.*, **85**, 166 and 180 (1952).

<sup>6</sup>D. Bohm and Y. Aharonov, *Phys. Rev.* **108**, 1070 (1957).

to quantum mechanics, measurement of  $\sigma_2 \cdot \mathbf{a}$  must yield the value  $-1$  and vice versa.<sup>7</sup> Now we make the hypothesis [of Einstein, cited above], and it seems one at least worth considering, that if the two measurements are made at places remote from one another the orientation of one magnet does not influence the result obtained with the other. Since we can predict in advance the result of measuring any chosen component of  $\sigma_2$ , by previously measuring the same component of  $\sigma_1$ , it follows that the result of any such measurement must actually be predetermined. Since the initial quantum mechanical wave function does not determine the result of an individual measurement, this predetermination implies the possibility of a more complete specification of the state.

Let this more complete specification be effected by means of parameters  $\lambda$ . It is a matter of indifference in the following whether  $\lambda$  denotes a single variable or a set, or even a set of functions, and whether the variables are discrete or continuous. However, we write as if  $\lambda$  were a single continuous parameter. The result  $A$  of measuring  $\sigma_1 \cdot \mathbf{a}$  is then determined by  $\mathbf{a}$  and  $\lambda$ , and the result  $B$  of measuring  $\sigma_2 \cdot \mathbf{b}$  in the same instance is determined by  $\mathbf{b}$  and  $\lambda$ , and

$$A(\mathbf{a}, \lambda) = \pm 1; B(\mathbf{b}, \lambda) = \pm 1. \quad (1)$$

The vital assumption [of the quote from Einstein] is that the result  $B$  for particle 2 does not depend on the setting  $\mathbf{a}$  of the magnet for particle 1, nor  $A$  on  $\mathbf{b}$ .<sup>8</sup>

If  $\rho(\lambda)$  is the probability distribution of  $\lambda$  then the expectation value of the product of the two components  $\sigma_1 \cdot \mathbf{a}$  and  $\sigma_2 \cdot \mathbf{b}$  is

$$P(\mathbf{a}, \mathbf{b}) = \int d\lambda \rho(\lambda) A(\mathbf{a}, \lambda) B(\mathbf{b}, \lambda).^9 \quad (2)$$

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<sup>7</sup>[In some physical processes akin to those envisaged by EPR (e.g., the “singlet spin state”), one component of the direction of spin  $\sigma_2$  (the component in the direction  $\mathbf{a}$ ) could be inferred, without disturbing it, from the result of a measurement of that same component in the spin  $\sigma_1$  of its counterpart. Symbolically, this latter measurement is expressed as the “dot product” of the two vectors:  $\sigma_1 \cdot \mathbf{a}$ . Briefly, if two unit vectors span an angle  $\theta$ , their dot product yields  $\cos \theta$ , ranging from  $+1$  when the vectors point in the same direction, through  $0$  when they are perpendicular, to  $-1$  when they point in opposite directions. As we saw from the Stern-Gerlach experiment, though, electron spin is quantized, so there are only two possible outcomes of the measurements: the spin of the particle points in the direction measured ( $+1$ ) or it points in the opposite direction ( $-1$ ). The use of the dot product here, then, is somewhat loose, connoting a general comparison of directions.]

<sup>8</sup>[Bell is here highlighting what is significant about the functional notation in equation (1), namely, that the results of the measurements  $A$  and  $B$  are determined completely and solely by the variables listed in their definitions.]

<sup>9</sup>[According to the hypothesis Bell is investigating, the “more complete specification” of the particles’ state, the extra information that would tell the observer who knew it which way the particle would respond to a given measurement, is given by  $\lambda$ . Equation (2) considers all the possible  $\lambda$ ’s and weights them according to how likely each is. Mathematically, that means integrating over all the possible values of  $\lambda$  and weighting each by its likelihood, represented by the probability distribution  $\rho(\lambda)$ . It may be helpful to note that  $P$  was likely chosen to stand for “product,” since the term we are integrating  $\rho$  against is the product of  $A$  and  $B$ . Because we’ve defined  $A$  and  $B$  such that the results of measurements yield the values  $+1$  and  $-1$ , the product for any given value of  $\lambda$  will always be either  $+1$  (meaning that the two particles would both be measured to be pointing either in the selected directions  $\mathbf{a}$  and  $\mathbf{b}$  or in directions opposed to them) or  $-1$  (meaning that the directions of  $\sigma_1$  and  $\sigma_2$  would be measured to be opposed, whether because  $\sigma_1$  would *not* be measured to point in direction  $\mathbf{a}$  and  $\sigma_2$  would be measured to point in direction  $\mathbf{b}$  or because  $\sigma_1$  would be measured to point in direction  $\mathbf{a}$  and  $\sigma_2$  would *not* be measured to point in direction  $\mathbf{b}$ ). Since it is a weighted sum of all the positive and negative terms,  $P(\mathbf{a}, \mathbf{b})$  is thus a measure of the *correlation* between the spin-direction of the two particles relative to the angles  $\mathbf{a}$  and  $\mathbf{b}$ .]

This should equal the quantum mechanical expectation value, which for the singlet state is

$$\langle \boldsymbol{\sigma}_1 \cdot \mathbf{a} \boldsymbol{\sigma}_2 \cdot \mathbf{b} \rangle = -\mathbf{a} \cdot \mathbf{b}.^{10} \quad (3)$$

But it will be shown that this is not possible.

Some might prefer a formulation in which the hidden variables fall into two sets, with  $A$  dependent on one and  $B$  on the other; this possibility is contained in the above, since  $\lambda$  stands for any number of variables and the dependences thereon of  $A$  and  $B$  are unrestricted. In a complete physical theory of the type envisaged by Einstein, the hidden variables would have dynamical significance and laws of motion; our  $\lambda$  can then be thought of as initial values of these variables at some suitable instant.

\* \* \*

#### IV. Contradiction

The main result will now be proved. Because  $\rho$  is a normalized probability distribution,

$$\int d\lambda \rho(\lambda) = 1, \quad (12)$$

and because of the properties (1),  $P$  in (2) cannot be less than  $-1$ . It can reach  $-1$  at  $\mathbf{a} = \mathbf{b}$  only if

$$A(\mathbf{a}, \lambda) = -B(\mathbf{a}, \lambda) \quad (13)$$

except at a set of points  $\lambda$  of zero probability. Assuming this, (2) can be rewritten

$$P(\mathbf{a}, \mathbf{b}) = - \int d\lambda \rho(\lambda) A(\mathbf{a}, \lambda) A(\mathbf{b}, \lambda). \quad (14)$$

It follows that if  $\mathbf{c}$  is another unit vector

$$\begin{aligned} P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c}) &= - \int d\lambda \rho(\lambda) [A(\mathbf{a}, \lambda) A(\mathbf{b}, \lambda) - A(\mathbf{a}, \lambda) A(\mathbf{c}, \lambda)] \\ &= \int d\lambda \rho(\lambda) A(\mathbf{a}, \lambda) A(\mathbf{b}, \lambda) [A(\mathbf{b}, \lambda) A(\mathbf{c}, \lambda) - 1],^{11} \end{aligned}$$

using (1), whence

$$|P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c})| \leq \int d\lambda \rho(\lambda) [1 - A(\mathbf{b}, \lambda) A(\mathbf{c}, \lambda)].^{12}$$

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<sup>10</sup>[As for the left-hand side, the angle brackets denote an average, that of the product of the results of the measurements described in the previous note, taken for many pairs of electrons. As for the right-hand side, since  $\mathbf{a}$  and  $\mathbf{b}$  are unit vectors, their dot product can take on any value from  $-1$ , when they are pointing in opposite directions, to  $+1$ , when they are pointing in the same direction. Again, for any two unit-length vectors spanning an angle  $\theta$ , their dot product is equal to  $\cos \theta$ . The minus sign denotes the theoretical expectation that the spins will be opposed. So, if  $\mathbf{a}$  and  $\mathbf{b}$  point in the same direction, the result will be  $-\cos 0^\circ = -1$ . A key move for the experiment will be to take measurements in directions that are neither opposed nor identical, since they will involve components the theory says are in the indeterminacy relation. In this usage, then, the dot product is meant perfectly literally.]

<sup>11</sup>[Since  $A(\mathbf{b}, \lambda) A(\mathbf{b}, \lambda) = 1$  for any  $\mathbf{b}$  and any  $\lambda$ .]

<sup>12</sup>[The introduction of the inequality depends on two points. The definition of  $A$  in (1) implies that the average value of  $A(\mathbf{a}, \lambda) A(\mathbf{b}, \lambda)$  can range from  $-1$  to  $+1$ ; furthermore,  $\rho(\lambda)[1 - A(\mathbf{b}, \lambda) A(\mathbf{c}, \lambda)] \geq 0$ . This and the previous footnote are based on David J. Griffiths (*Introduction to Quantum Mechanics*, Upper Saddle River, NJ: Pearson Prentice Hall, 2005), 437.]

The second term on the right is  $P(\mathbf{b}, \mathbf{c})$ , whence

$$1 + P(\mathbf{b}, \mathbf{c}) \geq |P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c})| \quad (15)$$

Unless  $P$  is constant, the right hand side is in general of order  $|\mathbf{b} - \mathbf{c}|$  for small  $|\mathbf{b} - \mathbf{c}|$ . Thus  $P(\mathbf{b}, \mathbf{c})$  cannot be stationary at the minimum value ( $-1$  at  $\mathbf{b} = \mathbf{c}$ ) and cannot equal the quantum mechanical value (3).<sup>13</sup>

\* \* \*

## V. Generalization

The example considered above has the advantage that it requires little imagination to envisage the measurements involved actually being made.... [F]or at least one quantum state, the "singlet" state ... the statistical predictions of quantum mechanics are incompatible with separable predetermination.

## VI. Conclusion

In a theory in which parameters are added to quantum mechanics to determine the results of individual measurements, without changing the statistical predictions, there must be a mechanism whereby the setting of one measuring device can influence the reading of another instrument, however remote. Moreover, the signal involved must propagate instantaneously, so that such a theory could not be Lorentz invariant. Of course, the situation is different if the quantum mechanical predictions are of limited validity. Conceivably they might apply only to experiments in which the settings of the instruments are made sufficiently in advance to allow them to reach some mutual rapport by exchange of signals with velocity less than or equal to that of light. In that connection, experiments of the type proposed by Bohm and Aharonov, in which the settings are changed during the flight of the particles, are crucial.

## REMARKS

Bell's "note" demonstrates a contradiction, and like any *reductio ad absurdum*, therefore, demonstrates that an inconsistency lurks somewhere in the premises it is testing. He seems to identify one as the source of the problem when he writes:

It is the *requirement of locality*, or more precisely that the result of a measurement on one system be unaffected by operations on a distant system with which it has interacted in the past, that creates the essential difficulty.

However that may be, the import of his argument has been interpreted variously, with many identifying the idea of complete determinacy or "hidden" variables as the essential problem. A main goal of these remarks is to clarify its logical structure. Afterwards, we will confirm by means of experiment the "statistical predictions of quantum mechanics" that are in contradiction with the sort of "local hidden variables theory" that is developed in the course of Bell's argument, though in a form different from the one he envisages, using photon polarization instead of electron spin.

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<sup>13</sup>[See the Remarks after the paper for discussion of this and the previous sentence.]

As for the argument, in section II, Bell reformulates EPR's proposal in the experimentally suggestive terms formulated by Bohm and Aharonov. The essential feature is the same, namely, two particles with a known relation (in this case, that their spins are opposed) are produced by a process predicted by quantum mechanics, one that happens to send the particles away from each other, such that their individual states might be measured separately. Just as in the case of ordinary polarization that Dirac discusses, the description that quantum mechanics gives of these particles involves a superposition of states, leading to a merely probabilistic prediction of the outcome. In the case of particles that stand in the uncertainty relation,<sup>14</sup> EPR show that the quantum-mechanical description does not contain enough information to tell how either will react; as they conclude, "the wave function does not provide a complete description of the physical reality."

This is where Bell's reformulation comes in, with the definitions of the measurement results  $A$  and  $B$  and the expectation value of their product  $P$  in equations (1) and (2), all in terms of the "more complete specification of the state" embodied in the term  $\lambda$ . The predictions of quantum mechanics are embodied in equation (3), which here plays a role analogous to that of Bohr's considerations (see note 4 in Chapter 16, page 187), concerning the momentum relation between the spatially separated systems (the relation that allows a measurement on one to reveal something about the state of the other). A hybridization of the two accounts could be said to occur in equation (13), the special case where the orientations of the detectors ( $a$  and  $b$ ) are the same, such that the dot product in equation (3) yields the value  $-1$ . Bell exploits this case to set a further specification on the functions  $A$  and  $B$ : whatever else they may say, they must be such that for the *same* angle, they predict numerically opposed results.  $A(a, \lambda)$  must equal the negative of  $B(a, \lambda)$ . As a result, equation (14) recasts equation (2)—the equation that indicates how to calculate the correlation of the two measurements—in a form that combines the statistical predictions of quantum mechanics with the idea that the measurements are independent and determined in advance by  $\lambda$ . At this point, the deed is done: locality and determinacy have been represented mathematically. The introduction of a third angle and a few simple substitutions and rearrangements will yield Bell's inequality, equation (15), which, we will demonstrate, stands in contradiction with the experimentally verified predictions of equation (3).

So much for an account of the arc of the argument. The all-too-brief sentences following equation (15), detailing the contradiction, require significant elucidation, which will take up the remainder of this subsection. At this point, Bell might simply have chosen some values for the angles  $a$ ,  $b$ , and  $c$  that would make the values equation (3) predicts for the expectation values  $P(a, b)$ ,  $P(a, c)$ , and  $P(b, c)$  violate the inequality. Arguably, there is something more satisfying in demonstrating a more general result: showing that for a whole *range* of possible values, the inequality is violated. He accomplishes this by pointing out that when  $b$  and  $c$  are close (or in his words, "for small  $|b - c|$ "), the left-hand side of (15) is expected according to equation (3) to be "stationary" at the value 0. (What he actually talks about is  $P(b, c)$  being stationary at  $-1$ , but since this is added to the constant 1, it amounts to the same.) If the left-hand side is stationary at a minimum of 0 when  $b$  and  $c$  are close, this means qualitatively that its

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<sup>14</sup>A mathematically precise way of specifying which physical quantities stand in that relation is developed in later chapters of Dirac's *Principles of Quantum Mechanics*, and it is this formalism, that of "non-commuting observables" that EPR refer to in their 1935 paper.

graph in that region is "flat." By contrast, Bell points out, the right-hand side "is . . . of order  $|\mathbf{b} - \mathbf{c}|$ ," the absolute value of the difference between the two angles; the graph of this, too, reaches a minimum of 0 when the angles are equal, but instead of being flat, is "pointy." In the region around 0, the graph that is pointy inevitably lies *above* the graph that is flat, but the right-hand side is meant to be less than or equal to the left, if the inequality holds. Thus, Bell's words in section IV about  $P(\mathbf{b}, \mathbf{c})$ —that it "cannot be stationary" and "cannot equal the quantum mechanical value"—have the silent proviso "while equation (15) holds and  $P(\mathbf{a}, \mathbf{b})$  and  $P(\mathbf{a}, \mathbf{c})$  have their quantum-mechanical values."

A quantitative derivation of this contradiction follows. For the left-hand side of (15), since  $P(\mathbf{b}, \mathbf{c})$  by (3) ought to equal  $-\mathbf{b} \cdot \mathbf{c}$ , we can put  $1 - \cos(\mathbf{b} - \mathbf{c})$ . The right-hand side is trickier, and will require a few approximations and interpolations. First, we will apply equation (3) to get the expected value of the products:  $P(\mathbf{a}, \mathbf{b}) = -\cos(\mathbf{a} - \mathbf{b})$  and  $P(\mathbf{a}, \mathbf{c}) = -\cos(\mathbf{a} - \mathbf{c})$ . Accordingly, we rewrite the right-hand side of (15) as

$$|P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c})| = |- \cos(\mathbf{a} - \mathbf{b}) + \cos(\mathbf{a} - \mathbf{c})|. \quad (15a - \text{RHS})$$

Now, the argument of the rightmost term  $(\mathbf{a} - \mathbf{c})$  can be rewritten as  $(\mathbf{a} - \mathbf{b}) + (\mathbf{b} - \mathbf{c})$ . According to the rule for the cosine of a sum of angles,  $\cos(F + G) = \cos F \cos G - \sin F \sin G$ . Hence,

$$\cos[(\mathbf{a} - \mathbf{b}) + (\mathbf{b} - \mathbf{c})] = \cos(\mathbf{a} - \mathbf{b}) \cos(\mathbf{b} - \mathbf{c}) - \sin(\mathbf{a} - \mathbf{b}) \sin(\mathbf{b} - \mathbf{c}).$$

You may already be familiar with the small-angle approximation for the sine function,  $\sin x \approx x$ , used in Junior Lab in discussing the motion of the pendulum. There is an analogous approximation for cosine,  $\cos x \approx 1 - \frac{x^2}{2}$ . Therefore, using both for the terms involving  $(\mathbf{b} - \mathbf{c})$ ,

$$\cos(\mathbf{a} - \mathbf{b}) \cos(\mathbf{b} - \mathbf{c}) - \sin(\mathbf{a} - \mathbf{b}) \sin(\mathbf{b} - \mathbf{c}) = \cos(\mathbf{a} - \mathbf{b})[1 - (\mathbf{b} - \mathbf{c})^2/2] - \sin(\mathbf{a} - \mathbf{b})(\mathbf{b} - \mathbf{c}).$$

Substituting this back into our (15a – RHS) above, we get

$$|- \cos(\mathbf{a} - \mathbf{b}) + \cos(\mathbf{a} - \mathbf{b}) - \cos(\mathbf{a} - \mathbf{b})(\mathbf{b} - \mathbf{c})^2/2 - \sin(\mathbf{a} - \mathbf{b})(\mathbf{b} - \mathbf{c})|. \quad (15b - \text{RHS})$$

Now, since  $\mathbf{a}$  and  $\mathbf{b}$  are just some constant angles, the terms  $\cos(\mathbf{a} - \mathbf{b})/2$  and  $\sin(\mathbf{a} - \mathbf{b})$ , also, are just some constants  $X$  and  $Y$  ranging from  $-1/2$  to  $+1/2$  and from  $-1$  to  $+1$  respectively. It follows that we can rewrite the right-hand side of (15) as a function of  $\mathbf{b} - \mathbf{c}$ ,

$$|P(\mathbf{a}, \mathbf{b}) - P(\mathbf{a}, \mathbf{c})| = |X(\mathbf{b} - \mathbf{c})^2 + Y(\mathbf{b} - \mathbf{c})|. \quad (15c - \text{RHS})$$

This contains one term that is linear in  $\mathbf{b} - \mathbf{c}$  and one that is quadratic in  $\mathbf{b} - \mathbf{c}$ . For small values of  $|\mathbf{b} - \mathbf{c}|$ , much less than 1, the linear term ( $Y(\mathbf{b} - \mathbf{c})$ ) will dominate and the quadratic term (much, much smaller) can effectively be disregarded. This is what justifies Bell in his assertion that "the right hand side is in general of order  $|\mathbf{b} - \mathbf{c}|$  for small  $|\mathbf{b} - \mathbf{c}|$ ."

For illustration, we take the case in which  $\mathbf{a} - \mathbf{b}$  is equal to  $45^\circ$ , and graph the left and right hand sides of Bell's equation (15) for values of  $\mathbf{b} - \mathbf{c}$  near 0.

The left-hand side ( $1 + P(\mathbf{b}, \mathbf{c})$ ) is the "smooth" curve, stationary at its minimum when  $\mathbf{b} = \mathbf{c}$ . The right-hand side is the V-shape that resembles the graph for  $|\mathbf{b} - \mathbf{c}|$ , and resembles it most when  $|\mathbf{b} - \mathbf{c}|$  is small. The same basic shape is visible for different



values of  $a$  and  $b$ . For comparison, below is the graph of the case in which  $a - b$  is equal to  $22.5^\circ$ .

Farther away from 0, the graph looks less like that of the absolute value function, but near 0, it still has the characteristic pointiness due to the predominance of the linear term in  $|b - c|$ . Both graphs show the contradiction between the inequality (15), derived from both the local hidden variables theory and the quantum-mechanical anti-correlation expressed in (13), and the quantum-mechanical result in equation (3). Equation (15), therefore, does not count as what Bell means in section VI by "a theory in which parameters are added to quantum mechanics to determine the results of individual measurements, *without changing the statistical predictions.*" Equation (1), upon which (15) is based, includes those added parameters and *also* the "vital assumption" that the function  $B$ , specifying the result for the measurement of particle 2, "does not depend on the setting  $a$  of the magnet for particle 1, nor  $A$  on  $b$ ." The final result (15), however, contradicts those predictions expressed in (3).

### The Same Thing, Otherwise

We will demonstrate the quantum-mechanical violation of Bell's inequality experimentally, using photons and not electrons as our particles, and polarization rather than spin as our measurement of interest. In Bell's and EPR's thought-experiments, the paired particles are in some way connected. In our experiment, we depend on the (obscure) mechanism of spontaneous parametric down-conversion to produce pairs of photons that will exhibit the behavior a local hidden-variables theory implies is impossible. We have relied on this mechanism to produce pairs of photons before, but now we require them to be in a special state (akin to the "singlet spin state") that requires a different arrangement of our equipment.

In particular, we use a pair of down-conversion crystals oriented at  $90^\circ$  to each other, and pass laser light through them at a  $45^\circ$  angle to both, so that each can respond to the component of that light that is oriented along their relevant axes, producing a cone of pairs of photons. The two cones must be aligned spatially and in terms of their

phase (by a “compensating crystal”) by means of a process that the lab director can attest is lengthy and finicky.<sup>15</sup> The result of all this careful alignment is that, where the cones overlap, two paths are formed from the down-conversion crystals to the detectors. Along these paths are projected pairs of photons in a special state that has the same character as the particles in all our authors’ thought experiments: a state which quantum mechanics describes as indeterminate but linked. Bell imagined testing two electrons produced according a process quantum mechanics says should give them indeterminate but opposed spin directions. Our apparatus produces photons that exhibit indeterminate but correlated polarization: when measured along a certain axis, they exhibit the same direction of polarization.

Because we are using photon polarization, our measurement scheme will have to be somewhat different. In particular, Bell’s function  $P$ , representing the average of the product of the results (+1 or -1) of the measurements of electron spin, will have to be redefined.  $A$  and  $B$  still represent, so to speak, a “yes or no” answer to the question put to each particle by the measuring device, but since our equipment only detects “yes” answers, we will express (2) in terms of experimentally feasible tests. Let  $A(\mathbf{a}, \lambda)$  be defined as equal to +1 when particle 1 is found to be polarized *parallel* to  $\mathbf{a}$  (which state we’ll denote as  $V_a$ ), and equal to -1 when particle 1 is found to be *perpendicular* to  $\mathbf{a}$  (which state we’ll denote as  $H_a$ , thinking of  $\mathbf{a}$  as “vertical” and its perpendicular as “horizontal”), and let  $B$  be defined similarly. We will call the probability that both particles are found to be polarized in the same direction as the specified measurement angles  $P_{VV}$ , the probability that the first is found to be polarized in the same direction as  $\mathbf{a}$  and the second perpendicular to  $\mathbf{b}$   $P_{VH}$ , and so forth for the other two possibilities. The probabilities of each possible outcome, then, are

$$\begin{aligned} P_{VV}(\mathbf{a}, \mathbf{b}) &= \int d\lambda \rho(\lambda) \frac{1 + A(\mathbf{a}, \lambda)}{2} \frac{1 + B(\mathbf{b}, \lambda)}{2} \\ P_{HH}(\mathbf{a}, \mathbf{b}) &= \int d\lambda \rho(\lambda) \frac{1 - A(\mathbf{a}, \lambda)}{2} \frac{1 - B(\mathbf{b}, \lambda)}{2} \\ P_{VH}(\mathbf{a}, \mathbf{b}) &= \int d\lambda \rho(\lambda) \frac{1 + A(\mathbf{a}, \lambda)}{2} \frac{1 - B(\mathbf{b}, \lambda)}{2} \\ P_{HV}(\mathbf{a}, \mathbf{b}) &= \int d\lambda \rho(\lambda) \frac{1 - A(\mathbf{a}, \lambda)}{2} \frac{1 + B(\mathbf{b}, \lambda)}{2}. \end{aligned}$$

Bell calls his equation (2) the “expectation value of the product,” and in order to avoid possible confusion, we will refer to this by the letter  $E$ , rather than  $P$ , which we’ve just used for the individual probabilities of various outcomes. The overall expectation value of the product of the measurements  $A$  and  $B$ , then, counting the correlations as positive and the anti-correlations as negative, is

$$E(\mathbf{a}, \mathbf{b}) = \int d\lambda \rho(\lambda) A(\mathbf{a}, \lambda)B(\mathbf{b}, \lambda) = P_{VV} + P_{HH} - P_{VH} - P_{HV}. \quad (\text{R1})$$

Effectively, what we have done is to factor  $E(\mathbf{a}, \mathbf{b})$  into four separate tests that we can perform directly, by setting up half-wave plates in front of our detectors, each of which

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<sup>15</sup>The process is described in detail in parts IV, V, and VI of Dehlinger, D. and Mitchell, M.W., “Entangled photons, nonlocality, and Bell inequalities in the undergraduate laboratory.” *Am. J. Phys.* **70** (9), 903–910 (2002).

has a horizontal polarization filter in front of it. The half-wave plates can be set so that light that has the polarization angle we want will have its polarization rotated to the horizontal. This is helpful for ensuring the maximum sensitivity of our detectors by reducing the possibility of deflection caused by ordinary linear polarizing filters. In any case, the result is the same: photons polarized in the specified directions and arriving at the detectors within our specified time window will be detected and counted as simultaneous.

In one last deviation from Bell, we do not test his version of the inequality directly, but another related one, derived on the same grounds, described here. Given four detection angles,  $\mathbf{a}$  and  $\mathbf{a}'$  for the first detector, and  $\mathbf{b}$  and  $\mathbf{b}'$  for the second, we define the quantity  $s$ , relevant to the degree of correlation in direction of polarization in any given pair of photons:

$$\begin{aligned} s &\equiv A(\mathbf{a}, \lambda)B(\mathbf{b}, \lambda) - A(\mathbf{a}, \lambda)B(\mathbf{b}', \lambda) + A(\mathbf{a}', \lambda)B(\mathbf{b}, \lambda) \\ &\quad + A(\mathbf{a}', \lambda)B(\mathbf{b}', \lambda) \\ &= A(\mathbf{a}, \lambda)[B(\mathbf{b}, \lambda) - B(\mathbf{b}', \lambda)] \\ &\quad + A(\mathbf{a}', \lambda)[B(\mathbf{b}, \lambda) + B(\mathbf{b}', \lambda)] \end{aligned} \quad (\text{R2})$$

We will show that  $s$  can equal only  $-2$  or  $+2$ . Now, either  $B(\mathbf{b}, \lambda) = B(\mathbf{b}', \lambda)$  or  $B(\mathbf{b}, \lambda) = -B(\mathbf{b}', \lambda)$ , given that each can only equal  $+1$  or  $-1$ . Hence, of the two expressions in square brackets above, one must be  $0$  and the other  $2$  or  $-2$ . Since  $A$  can only be  $+1$  or  $-1$ ,  $s$  as a whole can equal only  $+2$  or  $-2$ , which is what was to be demonstrated. Let us define  $S$  as the average of  $s$  over a set of pairs of photons,

$$S(\mathbf{a}, \mathbf{a}', \mathbf{b}, \mathbf{b}') \equiv \langle s \rangle = \int d\lambda \rho(\lambda) s(\lambda, \mathbf{a}, \mathbf{a}', \mathbf{b}, \mathbf{b}'),$$

and notice that this amounts to an expression in terms of expectation values  $E$ .

$$S(\mathbf{a}, \mathbf{a}', \mathbf{b}, \mathbf{b}') = E(\mathbf{a}, \mathbf{b}) - E(\mathbf{a}, \mathbf{b}') + E(\mathbf{a}', \mathbf{b}) + E(\mathbf{a}', \mathbf{b}'). \quad (\text{R3})$$

Given what we showed about the allowable values for  $s$ , and recalling that  $\rho(\lambda)$  expresses the probability of every possible value of  $\lambda$ , such that  $\int d\lambda \rho(\lambda) = 1$ , we can be sure that

$$|S| \leq 2.<sup>16</sup> \quad (\text{R4})$$

For us, this is what will play the role of Bell's equation (15). It embodies the assumption that measurements on photon 1 depend on the setting of its detector ( $\mathbf{a}$ ) and some unknown parameters  $\lambda$  that together determine the result of the measurement, but not on the setting of detector 2, and vice versa. Unlike in Bell's original derivation, there is nothing here that assumes anything about the relation of the particles, as his equations (13) and (14) do.

In these derivations, almost all of our manipulations (apart from some trigonometry and approximations of trigonometric functions) have been simple multiplications, additions, and subtractions. Arguably, the most arcane thing in the whole affair is integrating against the probability distribution  $\rho(\lambda)$ , but even this is simply a way of saying, "whatever the various values of  $\lambda$  that determine the outcomes of our measurements may be, let us duly account for all of them, weighting the more likely more and the less likely less."

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<sup>16</sup>The derivation in these paragraphs is largely patterned after that found in Dehlinger and Mitchell, *op. cit.* After the authors of the paper in which it first appeared (Clauser, Horne, Shimony, and Holt), (R4) is referred to as the CHSH inequality.

## PRACTICUM

### The Equipment

- a *laser* that emits light at a wavelength of 405 nm,
- *mirrors* to direct the light in the right path,
- a *half-wave plate* (HWP), designed for 405 nm light, set to 45° so that the horizontally and vertically oriented down-conversion crystals will both receive light they can respond to,
- a *compensating crystal* (CC) which aligns the phase of the pairs emerging from the second down-conversion crystal with that of those emerging from the first,
- a pair of beta-barium borate *down-conversion crystals* (DC), rotated 90° relative to each other, to produce, by aid of the previous two components, photon *pairs* in an *indeterminate state* of linear polarization,
- two *half-wave plates* (HWP A/B), designed for 810 nm light, to rotate the polarization angles of the incoming photons,
- two *polarizing beam-splitters* (PBS) in front of the filters, set horizontally to allow suitably polarized light to enter the detectors,
- two wavelength *filters* in front of the detectors, to keep out stray photons, and
- two sensitive light *detectors* (A and B).



*Experimental setup for testing Bell's inequality.*

We will measure  $S$  using pairs of specially prepared photons, which (if all goes well) show a higher degree of correlation of polarization direction than that allowed by (R4). To do that, we will have to measure all the expectation values listed in (R3). We will measure each of those by measuring the probabilities of the four outcomes in (R1), two correlations (with a positive sign) and two anti-correlations (with a minus sign). All in all, then, we have to make 16 measurements. We shall measure these values using an initial set of angles that is calculated to produce the greatest deviation from the inequality, namely:

$$\mathbf{a} = 0^\circ \quad \mathbf{a}' = \pi/4 = 45^\circ \quad \mathbf{b} = \pi/8 = 22.5^\circ \quad \mathbf{b}' = 3\pi/8 = 67.5^\circ.$$

For each expectation value  $E$ , we will count coincidences with four different settings of the detectors, the original angles and their perpendiculars in all combinations. In what follows  $\mathbf{a}_\perp$  just means  $\mathbf{a} + 90^\circ$  (what above we called  $H_a$ ). To take an example at random, then, for  $E(\mathbf{a}, \mathbf{b}')$  we would take measurements for equal times of the number of coincidences for each of the four settings, score the correlations as  $+$  and the anti-correlations as  $-$ , i.e., tally them according to (R1), and finally divide that by the total number of coincidences for those four runs.

$$E(\mathbf{a}, \mathbf{b}') = \frac{N(\mathbf{a}, \mathbf{b}') + N(\mathbf{a}_\perp, \mathbf{b}'_\perp) - N(\mathbf{a}, \mathbf{b}'_\perp) - N(\mathbf{a}_\perp, \mathbf{b}')}{N(\mathbf{a}, \mathbf{b}') + N(\mathbf{a}_\perp, \mathbf{b}'_\perp) + N(\mathbf{a}, \mathbf{b}'_\perp) + N(\mathbf{a}_\perp, \mathbf{b}')}$$

For convenience, here is a sample table of all the settings and measurements, with space to record results. The example calculation above would be for rows 5 through 8. You will notice that the half-wave plates (listed as “hwp”) have to be set to half the desired angle. Perform 2 or 3 runs for each trial. Whichever you choose, perform the same number of equally timed runs for all 16 trials.

#		A	hwp	B	hwp	Counts (30 seconds)	$\pm$
1	$\mathbf{a}$ $\mathbf{b}$	0	0	22.5	11.25		+
2	$\mathbf{a}_\perp$ $\mathbf{b}$	90	45	22.5	11.25		-
3	$\mathbf{a}$ $\mathbf{b}_\perp$	0	0	112.5	56.25		-
4	$\mathbf{a}_\perp$ $\mathbf{b}_\perp$	90	45	112.5	56.25		+
5	$\mathbf{a}$ $\mathbf{b}'$	0	0	67.5	33.75		+
6	$\mathbf{a}_\perp$ $\mathbf{b}'$	90	45	67.5	33.75		-
7	$\mathbf{a}$ $\mathbf{b}'_\perp$	0	0	157.5	78.75		-
8	$\mathbf{a}_\perp$ $\mathbf{b}'_\perp$	90	45	157.5	78.75		+
9	$\mathbf{a}'$ $\mathbf{b}'$	45	22.5	67.5	33.75		+
10	$\mathbf{a}'_\perp$ $\mathbf{b}'$	135	67.5	67.5	33.75		-
11	$\mathbf{a}'$ $\mathbf{b}'_\perp$	45	22.5	157.5	78.75		-
12	$\mathbf{a}'_\perp$ $\mathbf{b}'_\perp$	135	67.5	157.5	78.75		+
13	$\mathbf{a}'$ $\mathbf{b}$	45	22.5	22.5	11.25		+
14	$\mathbf{a}'_\perp$ $\mathbf{b}$	135	67.5	22.5	11.25		-
15	$\mathbf{a}'$ $\mathbf{b}_\perp$	45	22.5	112.5	56.25		-
16	$\mathbf{a}'_\perp$ $\mathbf{b}_\perp$	135	67.5	112.5	56.25		+

## CONCLUSION

Since the first experimental verification that at least some specially prepared particles violate Bell’s inequality, there have been many developments and refinements. In the most significant recent tests, many of the “loopholes” that critics have pointed out over the years have been closed.<sup>17</sup> Reflection on the significance of this particular state of particles, which is commonly referred to as “entanglement,” has become a standard feature of discussions of the results of scientific inquiry into the behavior of electrons and photons and the quantum-mechanical theories that purport to explain it.

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<sup>17</sup>E.g., M. Giustina *et al.*, “Significant loophole-free test of Bell’s theorem with entangled photons,” *Phys. Rev. Lett.* **115** (2015), and B. Hensen *et al.*, “Loophole-free Bell inequality violation using electron spins separated by 1.3 km,” *Nature* **526**, 682–686 (29 Oct. 2015).



# APPENDIX: ESU, EMU, AND SI

## UNITS AND SYSTEMS OF MEASUREMENT

### MEASUREMENT OF ELECTRICAL AND MAGNETIC QUANTITIES

Before the adoption in 1960 of the International System of Units (usually abbreviated as SI, for *Système International*), scientists used two main systems of units for electric and magnetic quantities, depending on whether they were investigating primarily electromagnetic or electrostatic phenomena. For us, whose authors use these older units and whose measuring instruments use modern units, there is a practical necessity to be able to convert between them. But the differences and relations among these schemes of measurement also depend on the nature of electricity and reveal something about the difficulties inherent to the project of measurement.

The ESU (electrostatic) and EMU (electromagnetic) systems of units both define measures for charge, current, and electric potential. (The SI system, perhaps counter-intuitively, makes the measure of current fundamental.) In both systems, as well as in the International System, these units are named after early investigators of electrical phenomena: Coulomb, Ampere, and Volta. For practical purposes, all that is required is to know the ratios among the various systems of units, as given in the following table.

SI units	EMU	ESU
1 coulomb	0.1 abcoulomb	$3 \times 10^9$ statcoulombs
1 ampere	0.1 abampere	$3 \times 10^9$ statamperes
1 volt	$10^8$ abvolts	1/300 statvolt

The dimensions of the units depend on which phenomenon is taken as definitive: the mutual attraction or repulsion of two charged bodies, or the magnetic field produced by charged bodies in motion. The former gives rise to the ESU system and the latter to the EMU system. The sizes of the units depend on the size of what are taken as the basic units of length, mass, and time. For ESU and EMU, those are the centimeter, the gram, and the second. The International System of Units differs in the size of its fundamental units for these dimensions, as it uses the meter, the kilogram, and the second. (Accordingly, these or related systems are sometimes referred to as CGS and MKS.) The derived SI units for, say, force and work, are defined with reference to the fundamental units: one newton is defined as the amount of force necessary to accelerate one kilogram of mass at the rate of one meter per second per second, one joule of work is done when a force of one newton acts on a body in the direction of its motion over a distance of one meter, and so forth.

As noted above, the International System makes one electrical quantity a “base unit,” namely, the unit of current, the ampere. It is a base unit in the sense that the other electrical quantities (e.g., charge, voltage, capacitance) are defined in terms of it. The ampere has been defined from 1946 until the present in terms of the effect discovered by Oersted, as “the constant current which, if maintained in two straight parallel

conductors of infinite length, of negligible circular cross-section, and placed 1 meter apart in vacuum, would produce between these conductors a force equal to  $2 \times 10^{-7}$  newtons per meter of length." At the time of this writing, the 26th General Conference of Weights and Measures is scheduled to vote (on Nov. 16, 2018) to redefine the ampere in terms of the elementary electrical charge, that carried by an electron (or proton). Thenceforward, the ampere will be defined

by taking the fixed numerical value of the elementary charge  $e$  to be  $1.602\,176\,634 \times 10^{-19}$  when expressed in the unit C, which is equal to A s.

The ampere, then, still nominally a base unit, is to be defined in terms of the coulomb, which is a quantity of charge specified by a definite *number* of elementary charges. The means by which this elementary charge is measured are unlike those of the electrostatic and electromagnetic systems of old. It relies on the physics of semiconductors, and the counter-intuitive quantum-mechanical behavior of individual electrons. A good source for further information is the Physical Measurement Laboratory, a major operating unit of the National Institute for Standards and Technology which develops and disseminates national standards for measurement of physical quantities.

### Electric Field Intensity and Electric Potential

Whichever system they use, our authors depend on being able to speak quantitatively about not only charge and current, but also *electric field intensity* and *electric potential*. A few notes about the dimension and measure of those quantities follow.

*Electric intensity* or *electric field strength* is expressed in terms of force per unit charge. The nameless unit is easily defined in the ESU and EMU systems: a field has strength 1 at a point if a charge of one statcoulomb (ESU) or 1 abcoulomb (EMU) placed there would experience a force of one dyne. Generally, within one of these systems of measurement, a field of strength  $E$  will exert a force  $F$  on a charge  $q$  numerically equal to  $F = Eq$ .

An especially convenient way of speaking about the intensity and extent of an electric field at once is as *electric potential* or *electric potential difference*, otherwise known as *voltage*. Except in the imaginary scenario necessary for a clear definition, a charge is never merely "placed" in an electric field; an actual charge feels a force, and responds by being accelerated. If we set up an electric field in a region of space—say, by charging two parallel plates with opposite charges—it can be useful to think about the quantitative measure of the electrical situation in that region in terms of how much kinetic energy a charged body would acquire in moving from one to another point within it. The electric potential difference between two locations in an electric field is equal to the work that would be done on a unit charge in moving from the one spot to the other. Potential is measured as work per charge. A feature of a "conservative" field of force (of which both the electric and the gravitational field are examples) is that the same difference in kinetic energy will result *no matter which path the body takes to get from the one point to the other*. Even if a charged body is compelled to take another path than the one it would if only subject to the electric force, the energy it gains due to the action of the field in going from one point to another (or, if opposed by the force, the work required to get it from the one point to the other), is uniquely specified by the potential difference between the two points multiplied by the quantity of the charge on the

body. This *path-independence* is characteristic of conservative fields of force and greatly simplifies many calculations.

In the ESU, EMU, and SI systems alike, the unit of electric potential difference is defined as the work done on or energy gained by one unit of charge in passing from one place to another in the field. In SI units, it takes 1 joule of work to move a charge of 1 coulomb across a potential difference of 1 volt.

Given that the intensity of the electric field  $E$  is measured as force per charge ( $f/q$ ), and work  $W$  is measured as force  $f$  acting over a distance  $s$ , we can see that for a uniform electric field, the potential difference ( $V = W/q$ ) between two points in it is simply the field strength  $E$  times the distance  $s$ .

$$E \cdot s = \frac{f}{q} \cdot s = \frac{f \cdot s}{q} = \frac{W}{q} = V.$$

In SI units, then, the dimension of electric field strength can also be expressed as *volts per meter*. In practical applications, it is often convenient to think of it in this way, and thus be able to calculate the strength of a uniform field given the voltage and the distance.

$$E = \frac{V}{s}.$$