

## Practice and Theory of the Modulation of Geiger Counters

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Experiments are described in which the behavior of Geiger-Müller counters under conditions of low frequency and high frequency modulation was studied. The modulation was obtained by the superposition of an a.c. voltage wave upon the d.c. counting threshold. It was found that for frequencies up to about 500 kc such modulation could be successfully carried out. An analysis of the results of these experiments shows that for some counters the breakdown process can be ascribed to the liberation of electrons from the cathode by positive ion impact, while for other counters the photoelectric liberation of electrons from the cathode is predominant in the mechanism of the breakdown. Counters have been constructed for which there is evidence that both of these processes occur in the same counter. The theory of high frequency modulation of counters is discussed.

### INTRODUCTION

OF the neutron speed experiments to date, those of Dunning, Pegram, and co-workers,<sup>1</sup> and of Alvarez<sup>2</sup> have given satisfactory results in the region of thermal velocities. Both of these methods, however, are at a disadvantage when it comes to the measurement of the speeds of neutrons with energies greater than a fraction of a volt. In the rotating disk method of Dunning it is the limitation of the speed with which the disks can be rotated which imposes this restriction. In Alvarez' work the modulation of the receiver was accomplished by alternately blocking and unblocking the amplifier which passed the pulses from the ionization chamber to the recorder. It is probable that the upper limit of the applicability of this method would be reached at such a modulation frequency that the period of the modulation cycle becomes comparable with the breakdown time of the ionization chamber.

The work reported here was undertaken for the purpose of establishing whether the direct electrical modulation of Geiger counters is possible at high frequencies. This was done with a particular view to the use of such counters as modulated receivers in neutron speed measurements beyond the limits of the methods already mentioned. From an analysis of the various theories<sup>3, 4</sup> of mechanisms in gas discharges it

seems plausible to expect that high frequency modulation should be possible.

In modulation work the counter is maintained at a steady d.c. voltage equal to the counting threshold. Upon this is superposed an a.c. voltage wave in such a way that the counter is swung alternately up onto the plateau and down below the threshold into the insensitive voltage region.

### EXPERIMENTS WITH LOW FREQUENCY MODULATION OF SOURCE AND COUNTER

As a preliminary to the investigation of counter behavior at high frequencies, the response of counters to low frequency modulation was studied in the range from 250 to 600 cycles per second. Even at the highest of these frequencies the breakdown time of the counter was less than the half-period of the modulation cycle, so that the breakdowns which occurred usually went to completion in the same half-cycle as their beginning.

An arrangement was devised for the simultaneous modulation of source and counter with variable phase. A square wave of 100 volts amplitude was obtained by means of a rotating commutator, and was impressed capacitatively onto the anode of the counter. The modulation of the source consisted of the covering and uncovering of an old radon tube by the passage of the teeth of a rotating sector disk on the same motor shaft with the commutator, so that the source was alternately shielded from and exposed to the counter.

The results of this experiment are shown in

<sup>1</sup> Dunning, Pegram, Fink, Mitchell, Segrè, *Phys. Rev.* **48**, 704 (1935).

<sup>2</sup> L. Alvarez, *Phys. Rev.* **54**, 609 (1938).

<sup>3</sup> K. T. Compton and I. Langmuir, *Rev. Mod. Phys.* **2**, 123 (1930).

<sup>4</sup> L. Loeb, *Rev. Mod. Phys.* **8**, 267 (1936).

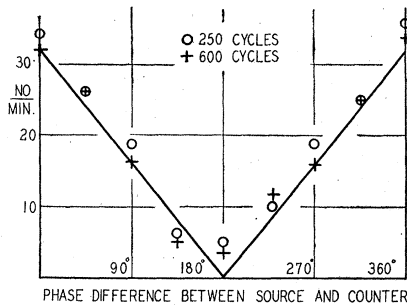


FIG. 1. Results of experiments on low frequency modulation of a typical counter and source, showing variation of counting rate with phase difference between source and counter.

Fig. 1, where the counting rates are given for two different frequencies as a function of the difference in phase between the passing of the counter voltage above the threshold and the uncovering of the source. These data have been corrected for the background and for the fraction of the rays which penetrated the teeth of the wheel. The figure shows graphically the dependence of the counting rate upon the phase difference between source and counter. The full line gives the counting rates expected from the value of the unmodulated d.c. rate with the source exposed. The results show that the low frequency modulation of Geiger counters has been accomplished.

#### EXPERIMENTS WITH HIGH FREQUENCY MODULATION OF COUNTER ALONE

Suppose the normal d.c. plateau counting rate of a Geiger counter is determined with the supply voltage maintained at some value on the plateau, and with a steady source of radiation at some convenient distance. If now the d.c. voltage is made equal to the threshold and the counter is modulated with an a.c. voltage wave, the new counting rate determined should be about one-half the d.c. plateau rate, one-half because with modulation the counter voltage is on the plateau for about half the total time, and below the threshold for the other half. This halving of the normal d.c. counting rate is thus an expected consequence of successful modulation, and can accordingly be used to trace the behavior of counters in their response to modulation of this sort. In the experiments to be reported now the counters to be tested were

modulated as described, and this halving of the plateau counting rate was looked for. The apparatus used in this work is illustrated schematically in Fig. 2.

In order to include as wide a frequency range as possible, two complete variable frequency oscillators were constructed. One, for frequencies from 500 cycles to 50 kc per second, was built with a two-stage amplifier in the same unit. The other, for frequencies from 50 kc to 10 mc per second, gave sufficient voltage to use directly without amplification. Both were of the regular Hartley type. The sweep frequencies of a cathode-ray oscillograph were calibrated by the Lissajous figure method, and were used whenever needed for the determination of oscillator frequencies. The d.c. voltage for the counter was supplied by a conventional power pack and filter circuit operated from a constant-voltage motor-generator. In the determination of counting rates, the breakdowns of the counter were observed in an Edelman string electrometer.

In order that an oscillograph analysis<sup>5, 6, 7</sup> of the breakdown phenomena could be made, a single-stage amplifier unit was used, as indicated in the figure. The discharge current of the counter, flowing through the grid resistance of the amplifier tube, gave the voltage pulses to the grid. In the case of a.c. modulation of the counter, the charging current through the capacity of the counter was sufficient to cause a trace of the modulation wave to appear on the screen of the oscillograph. Thus it was possible to observe not only the breakdowns themselves,

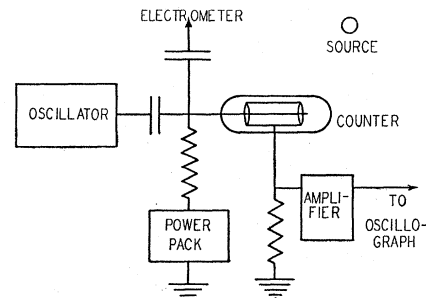


FIG. 2. Schematic arrangement of apparatus in experiments on high frequency modulation of counters.

<sup>5</sup> W. E. Ramsey and M. R. Lipman, *Rev. Sci. Inst.* **6**, 121 (1935).

<sup>6</sup> W. E. Danforth, *Phys. Rev.* **46**, 1026 (1934).

<sup>7</sup> P. B. Moon, *J. Sci. Inst.* **14**, 189 (1937), bibliography.

but the time of their occurrence during the cycle as well.

In the course of this investigation a great many counters were constructed and tested. A description will now be given of one of the most successful of these, to be hereafter referred to as counter *A*, followed by a report of its behavior at various modulation frequencies. Fig. 3 shows the details of its construction. The cathode was a brass cylinder 20 mm long and 11 mm inside diameter. A 12-mil tungsten wire 20 mm long between the bead and the end of the glass holder, served as the anode. Before the final filling, the cathode surface was oxidized by heating in air. The counter was filled with tank argon with an estimated admixture of from  $\frac{1}{2}$  percent to 1 percent of air to a total pressure of 6 cm. The d.c. counting rate characteristic showed a nearly flat plateau of about 150 volts' width. In modulation work a wave amplitude of 100 volts' peak from the axis was used: this was sufficient to carry the counter well up onto the plateau during the peak half-cycle. For the various frequencies the counting rates *C*, in counts per minute, along with the oscillograph observations, are given below, each figure representing the counting of at least 200 breakdowns. The d.c. plateau counting rate under the conditions of this experiment was 47 counts per minute.

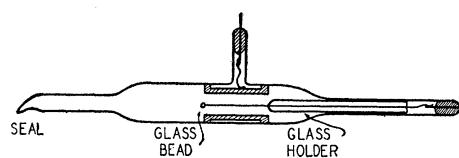


FIG. 3. Details of construction of counter *A*.

a normal breakdown pulse. All breakdowns were of normal size. All breakdowns went to completion.

Among the counters studied in this way there were others whose reactions were so strikingly different in many ways from those of counter *A* that a detailed report of the observations made upon a typical one of these others, to be referred to hereafter as counter *B*, seems justified. Because it was intended for use later in soft x-ray work, this counter was one of several made with a thin glass window at one end. The anode wire of 20-mil unoxidized tungsten, supported at one end by a glass holder, extended for a short distance axially along the center of the cathode cylinder. This latter was of copper, 20 mm long, and of 9 mm inside diameter. The cathode surface was prepared according to a treatment described by Neher.<sup>8</sup> The filling gas was a mixture of 98 percent tank argon and 2 percent air at a pressure of 6 cm prepared and admitted to the counter by means of an apparatus designed for the purpose.

In preliminary experiments with this counter unmodulated a very striking phenomenon was observed, which appeared also in several of the other counters studied. As the d.c. voltage was raised above the threshold the voltage drop at each breakdown, as observed by the amplitude of the kicks in the electrometer, increased, being of a magnitude approximately proportional to the difference between the operating voltage and the threshold. At a particular point on the counting plateau, however, a very well-defined voltage was reached above which all the electrometer kicks were very much larger than expected, and where the breakdown time of the counter suddenly changed from the order of  $10^{-3}$  sec. to the order of  $10^{-4}$  sec. The counting rate remained practically unaltered as the voltage was raised across this "transition" value,

- 500 cycles:  $C=18$ . All counts came during the peak half-cycle on the counter. Breakdowns starting late in the half-cycle were "choked off" before they could run to their normal completion.
- 2700 cycles:  $C=17$ . At this frequency all breakdowns were more or less choked off, depending on whether they started early or late in the peak half-cycle.
- 10 kc:  $C=15$ . The choking off was very pronounced at this frequency. Electrometer "kicks" were too small to observe with much reliability in counting.
- 25 kc: Electrometer kicks were too small to observe. All breakdowns observed in the oscillograph came during the peak half-cycle on the counter. The "tails" of the breakdown traces extended beyond the point where the counter voltage went below the threshold.
- 50 kc: Breakdowns began to carry over into succeeding cycles. They always started, however, during a peak half-cycle on the counter. Electrometer kicks were still very small: discharges apparently did not go to completion even though they did carry over a few cycles.
- 150 kc:  $C=26$ . 550 kc:  $C=28$ . 1 mc:  $C=29$ . 5 mc:  $C=35$ . The envelope of all the breakdown humps on the oscillograph screen for one discharge resembled closely

<sup>8</sup> L. Strong, *Procedures in Experimental Physics* (Prentice-Hall, 1938), Chapter 7.

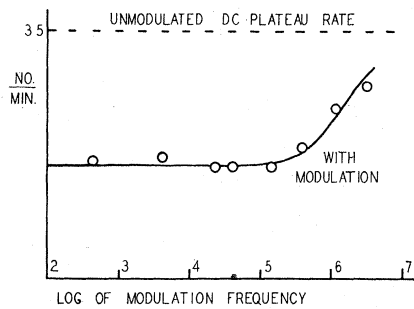


FIG. 4. Results of experiments on high frequency modulation of counter *A*, showing halving of the d.c. plateau counting rate for frequencies up to about a million cycles per second.

which in counter *B* came about 60 volts above the ordinary threshold. In modulation experiments where the wave amplitude did not exceed 60 volts, this counter in all points of behavior resembled closely counter *A*. For modulation wave amplitudes of around 150 volts' peak from the axis, however, the counter was above the transition voltage during most of the peak half-cycle, and it is for this condition that the following report is given. The normal unmodulated d.c. plateau counting rate under the conditions of this experiment was 35 counts per minute.

- 500 cycles:  $C=16$ . Breakdowns always occurred during the peak half-cycle on the counter.
- 6400 cycles:  $C=17$ . Tails of the breakdown traces extended beyond the point where the counter voltage passed below the threshold. No choking off of the breakdowns was observed.
- 22 kc:  $C=15$ . Breakdowns carried over one reverse half-cycle into the next following peak half-cycle. There was no apparent growth of the discharge, however, beyond the peak half-cycle it started in. The first half-cycle hump was always the larger.
- 45 kc:  $C=15$ . At this frequency the breakdowns carried over several cycles, but always began during a peak half-cycle on the counter. As before, for a given discharge, the first breakdown hump was always the largest, suggesting that the discharge was completed during the peak half-cycle in which it started, and that the collection of the positive ions was responsible for the rest of the humps.
- 150 kc:  $C=15$ . 550 kc:  $C=19$ .  $1\frac{1}{2}$  mc:  $C=24$ . 5 mc:  $C=27$ . The envelope of all the half-cycle humps for a single breakdown resembled a normal d.c. breakdown pulse. Still no choking off of the magnitude of the breakdowns was observed.

The modulation behavior of counter *B* is summed up in the graph of Fig. 4, where the

counting rates are plotted against the logarithm of the modulation frequency. It is seen that in this counter the halving of the unmodulated d.c. plateau rate is present up to about a million cycles per second.

Among the various counters investigated there were two others, similar in construction and cathode treatment to counter *B*, and filled with mixtures of 1 percent and 5 percent, respectively, of ethyl alcohol vapor in tank argon, for which the transition voltages appeared to coincide with the threshold. In these counters the magnitude of the voltage jump at each breakdown as soon as the threshold had been exceeded was about 250 volts. The modulation results on these counters showed the halving of the d.c. plateau counting rate at all frequencies below 300 kc. There was no significant difference in the behavior of the two which could be traced to the difference in alcohol concentration.

#### EXPERIMENTS WITH HIGH FREQUENCY MODULATION OF SOURCE AND COUNTER

In order that the modulation behavior of counters might be tested under conditions similar to those of an actual particle speed experiment, a low voltage grid-controlled x-ray tube was designed for use as a modulated source of radiation for the high frequency testing of counters. The counting rates of modulated Geiger counters were then determined for the two cases, when the counters were in phase coincidence with, and in opposition to, the emission from the x-ray tube.

The construction of the x-ray tube is shown in Fig. 5. The filament of 12-mil tungsten wire

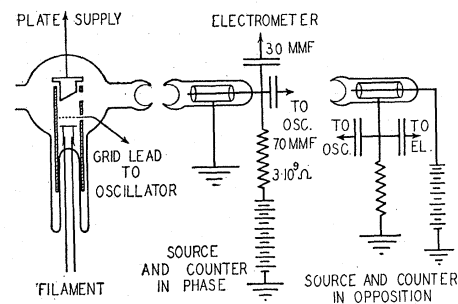


FIG. 5. Details of construction of x-ray tube, and connections in the counter circuit for in-phase and out-of-phase modulation of the counter.

was wound in a flat spiral just below the grid, which was of 40-mesh nickel gauze. A radiation-cooled piece of copper served as the anode. The whole assembly was surrounded by a metal sleeve which was grounded to the center tap of the filament winding. Because of the comparative ease with which grid control of the emission could be secured for low anode voltages, a power supply was designed which made use of a 6000-volt transformer. Thin glass windows were consequently required on the x-ray tube and Geiger counters to permit the passage of the soft rays thus obtained. In the operation of the x-ray tube it was found that more satisfactory modulation, especially at the higher frequencies, could be secured if the grid was so biased that the emission in each cycle was confined to a very short interval just at the middle of the positive half-cycle on the grid. For this purpose negative grid biases in the neighborhood of 20 volts smaller than the wave amplitudes were used.

The counter used in this experiment was similar to counter *B* with the one exception that the anode wire was much longer than the cathode and extended for some distance unshielded out of each end of the cylinder. The treatment of the cathode surface was the same as that already referred to.<sup>8</sup> The filling gas was a mixture of 1 percent tank oxygen in 99 percent tank argon at a pressure of 7 cm.

Figure 5 shows also the connections in the counter circuit for the cases when it was desired to have the counter in phase with, and in opposition to, the emission. In order to make sure that there was nothing inherent in the difference between the two circuit arrangements themselves which could affect the counting rate, the oscillator lead was grounded, and the unmodulated d.c. counting rate was taken for both cases. It was found to be the same. Throughout this experiment modulation waves of about 150 volts' amplitude were used.

The graph of Fig. 6 shows the relationship of the in-phase and out-of-phase counting rates for the different modulation frequencies. The ordinate represents the percent ratio of the out-of-phase to the in-phase rate. An inspection of the figure indicates that this Geiger counter could be used as a modulated receiver in a particle

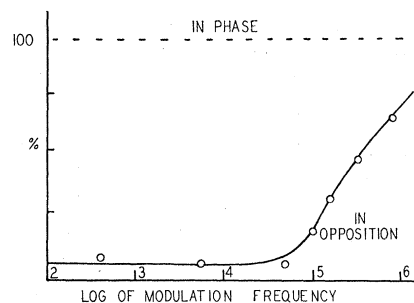


Fig. 6. Results of experiments on high frequency modulation of counter *B* with modulated x-rays.

speed experiment at a frequency perhaps as high as 500 kc.

#### DISCUSSION

The experiments show that the high frequency modulation of Geiger counters is practicable. If, as is suggested in the last section, a counter modulated at 500 kc is used as a receiver in a particle speed experiment at a distance of 1 meter from a modulated source, and in phase quadrature with it, the speed of a proton or neutron of about 10,000 electron-volts energy could be measured. The energy range over which this method should be useful is thus seen to be of an enormously greater extent than the range of from a few hundredths to a few tenths of a volt to which the methods (1) and (2) are restricted because of the limitations discussed.

Also, from a study of the results for counters *A* and *B*, several suggestions concerning the mechanism of the counter breakdown itself can be inferred. Of the various mechanisms which have been proposed in attempts to account for the operation of a counter, the ones which appear to be most favored by the evidence of these experiments are the positive ion process<sup>9</sup> and the photoelectric process.<sup>10, 11</sup> In the first of these the positive ions from the discharge migrate to the counter cathode and liberate electrons from it which cause further Townsend avalanches in the gas, leading to the continuation of the discharge. In the photoelectric mechanism some of the molecules involved in collisions with electrons in the avalanches are raised to spectro-

<sup>9</sup> A. von Hippel, *Zeits. f. Physik* **97**, 455 (1936).

<sup>10</sup> E. Greiner, *Zeits. f. Physik* **81**, 543 (1933).

<sup>11</sup> S. Werner, *Zeits. f. Physik* **90**, 384 (1934).

scopic levels short of complete ionization. In their radiative return to the ground state, light is emitted which by photoelectric absorption at the cathode ejects more avalanche-producing electrons which keep the discharge going.

#### THE POSITIVE ION MECHANISM

On the assumption of the positive ion process the explanation of high frequency modulation of counters is as follows. If an ionizing particle enters the counter during the half-cycle when the voltage is above the threshold, an ionization avalanche will occur in which enough positive ions are created to insure the liberation of several new electrons from the cathode when all the positive ions have been collected. Some of these will be liberated during the peak half-cycles of the succeeding modulation cycles when they in turn will produce more ionization and thus lead to the complete breakdown of the counter. On the other hand, an ionizing particle arriving during the half-cycle when the voltage is below the threshold will cause an avalanche in which too few positive ions will be created to insure the ejection of new electrons from the cathode, so that the discharge will probably proceed no farther than the first avalanche.

It appears from an argument based on several lines of evidence that the positive ion process is predominantly responsible for the breakdown mechanism of counter *A*. In the first place, under conditions of low frequency modulation a breakdown starting late in a peak half-cycle may yet be in progress when the counter voltage is carried below the threshold by the next alternation of the modulation wave. It is to be expected that such a breakdown will be choked off immediately. This choking off was actually observed for 500-cycle modulation of counter *A*: and it became more and more pronounced in its effect on the size of the breakdowns as the frequency was increased. On the assumption of the positive ion process, when the half-period of the modulation cycle becomes of the same order as the positive ion transport time, statistically only one avalanche should occur. As can easily be calculated<sup>12</sup> for a counter of this general

description, the positive ion transport time from the region of the anode, where the ionization is heaviest, to the cathode surface is about  $3.10^{-5}$  sec. The observed vanishing of the size of the breakdowns in the modulation experiments occurred somewhere between 25 kc and 50 kc, a frequency at least of the right order of magnitude to lend considerable support to the assumption of the positive ion process.

In the 25-kc oscillograph analysis it was seen that the tails of the breakdown traces extended over into the half-cycle when the voltage was below the threshold. This suggests that, even though the breakdowns were choked off when the counter voltage passed down through the threshold, the collection of the positive ions already present continued for a time which agrees in order of magnitude with the theoretically calculated transport time. It should be expected that if the frequency is increased still more, so that the half-period becomes somewhat shorter than the positive ion collection time, then the tails of the breakdowns will extend over into the next following peak half-cycle where any new electrons liberated from the cathode will cause the breakdown to continue. That this expectation is fulfilled at 50 kc, a frequency in qualitative agreement with that calculated theoretically, lends further support to the conviction that the positive ion process must predominate in this counter.

The normal breakdown time was observed for counter *A* to be about 1/1000 second, or about 30 positive ion transport times. In the normal breakdown of a counter, if the voltage is well up on the plateau, the various avalanches will begin to overlap, so that very soon after the initiation of a breakdown there may be several hundred avalanches in progress all at once. Because of this growth of the discharge the voltage across the counter falls far more rapidly than if the avalanches followed each other one at a time. The total breakdown time of this counter of about thirty positive ion transport times seems quite reasonable for a counter for whose action the positive ion process is responsible.

#### THE PHOTOELECTRIC MECHANISM

In the case of the predominance of the photoelectric mechanism the discharge of the counter

<sup>12</sup> J. Thomson, *Conduction of Electricity Through Gases* (Cambridge, 1928), Vol. I, p. 100.

should be very rapid. There is here practically no delay between one avalanche and the liberation of electrons from the cathode to start the next, so that the *actual* breakdown of the counter should be completed in a time of the order of 50 or 100 electron transit times, either by the discharging effect of the avalanche electrons themselves, or more probably by space charge formation within the counter. The further discharging effect of the collection of the positive ions out of the field will then occur, drawing out the *apparent* breakdown time to the order of a single positive ion transport time. If this process is predominant in a counter, then successful modulation should certainly be possible up to frequencies whose half-periods are comparable with the *actual* breakdown time of the counter, which may be as short as  $10^{-5}$  or  $10^{-6}$  second. At successively higher frequencies the choking off of the discharges might be expected to occur, until an ultimate limit for modulation is reached when the half-period becomes of the order of the transit time of an electron.

The behavior of counter *B* above its transition voltage seems to indicate the predominance of the photoelectric process. In modulation work there was no choking off of the breakdowns observed at any frequency. All the electrometer kicks were of the same size. It must be concluded that the mechanism responsible for the breakdown here is one which does its work and is finished in an extremely short time. Again, by the use of the oscillograph, the apparent breakdown time of this counter was found to be about  $1/6000$  second, even when the counter was discharging the parallel coupling capacity of 70 mmf at every breakdown, while the growth of the discharge to maximum current was too rapid to be timed at all by this method. It is difficult to see how so short a breakdown time could be explained on the assumption of the positive ion process. In the 45-kc oscillograph analysis, and even in that for 150 kc, there was no apparent growth of the discharge after the first half-cycle hump. This suggests that the discharge, insofar as the electron avalanches were concerned, was all completed in the half-cycle of its inception, and that the rest of the humps were due merely to the effect of the more leisurely col-

lection of the positive ions. This behavior is just what might be expected on the assumption of the photoelectric process.

In the light of these results it is possible to make a speculation concerning the processes involved in bringing about the transition voltage in such a counter as this. Since at voltages below the transition voltage the magnitude and duration of the breakdowns occurring indicate the operation of the positive ion process, it is logical to conclude that the transition voltage is that at which the photoelectric process becomes predominant in the mechanism of the breakdown. This would explain the shortening of the breakdown time as the transition voltage is exceeded. On this view the transition voltage would be the threshold of the counter if the photoelectric process predominated at all voltages, as is apparently the case for the two alcohol-filled counters where the threshold and transition voltages are coincident. An explanation of the sudden increase in the magnitude of the voltage drop at each breakdown as the transition voltage is exceeded is suggested by some experiments of Werner<sup>8</sup> on gas-filled tubes of the Geiger counter form. In a circuit containing a discharge tube and variable voltage supply, Werner found that as the d.c. voltage across the tube is raised above the value at which a self-sustaining discharge occurs, which is the same as the threshold in a Geiger counter, the strength of the corona current increases very rapidly, and that as soon as a certain critical current is reached, the corona passes over into a glow discharge. In a circuit which includes a current-limiting resistance, this change is marked by a sudden decrease in the voltage across the tube itself to a value which corresponds to the normal cathode fall of the glow discharge, and which can be very much lower than the starting voltage of the corona. In a Geiger counter circuit, then, as the transition voltage is exceeded, the rapidity with which a breakdown proceeds under the photoelectric process may give a current of sufficient magnitude to cause the discharge to pass from the corona to the glow form. On this view the sudden increase in the size of the breakdowns is to be expected, for before a breakdown can be finished, the counter voltage must fall below the value which characterizes the glow.

In conclusion the author wishes to acknowledge his indebtedness to Professor J. A. Bearden, under whose direction this work was done, for his continued interest and many valuable sug-

gestions, to Professor James Franck for the original suggestion of the problem, and to Dr. D. R. Inglis for advice in the preparation of this manuscript.

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## A Method for Improved Calculation of Energies of Two-Electron Configurations from Hartree Functions

### Application to $2p^2$ Terms in O III

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A generalization of the method of the self-consistent field for two-electron configurations previously given by the author has now been simplified and improved in two ways. Firstly, it is now assumed that the radial functions are identical with the Hartree functions (or with simpler approximations to these), so that a considerable saving in labor results. Secondly, the core electrons are taken account of more accurately than in the original method. The final results are in general only valid if the valence electrons are

equivalent or if the difference in their azimuthal quantum numbers exceeds two; they do not involve a great deal of computation once the Hartree functions are known. Numerical calculations have been made for the normal state of helium (as a test of the method) and for the  $2p^2$  terms of O III. The improvement obtained with the present method, while not great, is significant; in particular, the separation ratio for the O III terms is markedly improved.

#### 1. INTRODUCTION

IN a recent paper,<sup>1</sup> a generalization of the method of the self-consistent field (s.c.f.) was given, applicable to the case of two-electron configurations in Russell-Saunders coupling, the core electrons being taken into account through a possible screening of the Coulomb field acting on the valence electrons.<sup>2</sup>

The generalization consists essentially in assuming for the wave function the form

$$\psi = \psi_0 \cdot X(x), \quad (1)$$

where  $\psi_0$  is a function of the form usually assumed in the s.c.f. method when the correct symmetry properties of the wave function are taken into account, and contains the two radial functions, while  $X(x)$  is an adjustable function of

$x = \cos(\mathbf{r}_1, \mathbf{r}_2)$ . The variational method is then applied, and yields differential equations for the two radial functions analogous to those of the s.c.f., together with a third equation for the function  $X$ . The assumption (1) is perhaps the most general one that can be made without introducing complications which would make the calculations intractable in many cases.

As developed in I, however, the method has two disadvantages. In the first place, the labor involved in carrying through numerical calculations would be considerable, particularly when exchange terms are taken into account. Secondly—and this is the more serious objection—the wave function (1) does not automatically satisfy the condition of being orthogonal to the wave functions of lower levels which have the same symmetry characteristics.<sup>3</sup> Since the effect of the

<sup>1</sup> A. F. Stevenson, Proc. Roy. Soc. **A160**, 588 (1937), referred to hereafter as I. The following correction may be noted: in Eq. (2), the sign in front of each of the square brackets should be  $-$  instead of  $+$ . What is really a special case of the method had been previously used by Breit, Phys. Rev. **36**, 383 (1930).

<sup>2</sup> The extension to the case where the core electrons are taken more accurately into account was also briefly indicated, but was not worked through in any detail.

<sup>3</sup> The orthogonality condition is automatically satisfied for levels with different symmetry characteristics on account of the transformation properties of the wave functions. The same nonorthogonality situation may arise in the s.c.f. method (with any number of electrons) if there are lower levels for which the electrons have the same azimuthal quantum numbers as in the configuration considered, since the corresponding radial functions will