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PHYSICALLY DEGENERATE SYSTEMS AND QUANTUM DYNAMICS

J. C. Slater

Abstract

By analogy with the mathematical definition of degenerate systems, it is suggested that systems which are interrupted before they have traversed a full period, or which are in an external field which varies greatly in the time of one period, be called physically degenerate. It is further suggested, in harmony with the ideas of Ehrenfest and Tolman, that such systems show *weak quantization,* the quantization becoming less and less complete as the degeneracy increases. In the case of partially degenerate systems, the values of the related action variable and of the energy are grouped more or less closely about the mean values which they would all have if the systems were completely quantized. As examples, these ideas are applied to several problems, such as *quantization in a small or rapidly changing magnetic field* (including Glaser's results for the change of diamagnetic susceptibility of some gases with pressure, experiments by Breit and Ellett and by Wood and Ellett on depolarization, and the experiment of Gerlach and Stern in which atoms are projected into a strong field), absorption in the higher lines of the principal series of an alkali (including a discussion of *quantization in hyperbolic and parabolic orbits*), and the continuous x-ray spectrum. It is then pointed out that this assumption demands the *existence of quantum forces* which have not been previously considered in quantum theory and whose action is to stabilize the stationary states, bringing the action variables and energy rapidly nearer and nearer to the proper values as time goes on. The suggestion is made that these forces are responsible for the large change of energy and action variables during a quantum transition. From this point of view the *adiabatic theorem* appears in a simple light; when the external parameters vary too rapidly, the quantization becomes poor, the quantum forces become strong and put the atom into a quantized state again. In any atom but hydrogen, quantum forces must be continuously acting to oppose the interchange of energy and momentum between electrons and to keep each electron quantized. These forces thus may prove to be important in the solution of problems of the quantum dynamics of the constitution of atoms, though they must be considered in connection with the dynamics of the oscillators.

THE quantum theory can hardly continue to deal with periodic systems alone, and the natural approach to the study of non-periodic motion is through those systems which are nearly but not quite periodic. The quantum conditions as at present stated apply only to periodic motions; it is natural to suppose that nearly but not quite periodic systems are nearly but not quite quantized. One is thus led to the study of weak quantization. The most interesting contributions to this problem have been made by Ehrenfest[1] and his collaborators. In the present paper certain aspects of the problem are discussed from a somewhat different angle from that of Ehrenfest and Tolman, although the underlying ideas are very similar, and, passing beyond their results, an attempt is made to draw certain conclusions regarding quantum dynamics.

Part I

Degenerate multiply periodic systems are ordinarily taken to be those in which one or more of the fundamental or combination frequencies are zero for all values of the momenta. In case the vanishing frequencies are combination tones, it is always possible by a change of co-ordinates to make them fundamentals, so that only this case need be considered. Intimately connected with the degeneracy is the failure of the ordinary quantum condition for the variable whose frequency vanishes. For the quantum condition involves an integral about a complete cycle, which is defined only by the motion of the system, and a degenerate co-ordinate, having zero frequency, does not traverse a cycle in any finite time. Thus, for example, an atom cannot be quantized in space unless it is in an external field, for otherwise the frequency of precession of the direction of the angular momentum, one of the fundamental frequencies, is zero, since no torque acts and the axis points in an invariable direction. Then we do not know what a complete cycle for this co-ordinate is; since the axis is fixed, the direction about which it would precess is undefined, and there is no unique way of applying a quantum condition to the orientation. Once there is an external field, however, and the axis does precess in a periodic manner, a cycle is defined and the conditions can be applied.

This statement of the situation seems to imply a distinction between the case where the frequency is strictly zero, and the case where it has any value different from zero. Such a criterion is mathematical rather than physical. In physics one meets with distinctions according as dimensionless quantities are small or large compared with unity. By considering the problem of degeneracy in this light, it can be put in a much more comprehensible form. Instead of considering the mathematical degeneracy of a variable when its frequency is zero, we shall introduce the idea that it is physically degenerate in proportion as the ratio of its

[1] Ehrenfest and Breit, Zeits. f. Phys. **9,** 207 (1922); Ehrenfest and Tolman, Phys. Rev. **24,** 287 (1924).

frequency to some fixed quantity of the dimensions of a frequency is small compared with unity.

It is easy to find a fixed quantity having the dimensions of frequency with which to compare the frequency itself. Degenerate systems are of interest principally for two reasons, their lack of quantization under ordinary conditions, and the failure of the quantum conditions to be preserved when the system is carried adiabatically through a degenerate case. We recall that the explanation of the failure of quantization was that the variable never traversed a cycle. It seems reasonable to say that a system is physically degenerate if its variable has had time to go through only a part of a cycle. The fraction of a cycle which has been passed through since any given instant is the product of the frequency and the length of time which has elapsed, or the ratio of the frequency to the reciprocal of that time. It is then very reasonable to define a physically degenerate system as one in which one of the frequencies is small compared with $1/T$, where T is the length of time in which the motion has been going on. If the motion has been progressing since the atom entered its stationary state, then the average value of T is the average life in the state, or $1/T$ is the probability of leaving the state in unit time, which has the dimensions of a frequency.

Degenerate systems are of particular importance, also, in the application of the adiabatic theorem; for as an external parameter is varied slowly, the quantum conditions are continually satisfied, except in the very important case in which the system passes through a degenerate state. For the theorem to hold, the external parameter must vary so slowly that it remains approximately constant over one period; but if one of the fundamental frequencies becomes very small, a period of that frequency is very large, and if the external parameter changes at any reasonable rate it will change decidedly during one period, so that the conditions of the theorem are not met. Evidently, in this case, a definition of physical degeneracy is immediately provided: A system is physically degenerate if the external field changes so fast that the adiabatic theorem does not hold. This amounts to saying that the product of the relative change in the parameter per unit time, and the time of one period, is large; or that the ratio of the frequency to the relative change of the parameter per unit time is small. This is the same kind of condition we had before; but now T is the reciprocal of the relative change of the external parameter per unit time; that is, it is the time in which the parameter changes by an amount comparable with itself. If, for example, the parameter varies periodically, $1/T$ is a small constant times the frequency of variation.

Suppose that physical degeneracy be defined as just suggested, for the two cases of interrupted motion and of motion in a varying field. We then meet the problem of quantization. The conventional statement is that mathematically degenerate systems are not quantized; undegenerate ones are. This, again, is an unphysical sort of definition; and we amend it to say that the completeness of quantization approaches zero with the quantity νT, ν being the frequency in question; that is, the quantization is less and less complete in proportion as the system is more and more degenerate physically. This statement covers both cases we have considered. We ask more closely as to the meaning of the completeness of quantization. When quantization of a particular co-ordinate is complete, all systems have one or another of a set of definite values for the phase integrals, or action variables, connected with that co-ordinate; when there is no quantization, the various systems have values of the related action variable which are spread in a uniform fashion over a large range of values. An intermediate state of quantization would be one in which, while all systems do not have precisely the same values of the action variables, still they are grouped more or less closely about the mean values. Thus it is to be supposed that, as νT increases, the systems, having for $\nu T=0$ all values of the action variable associated with the frequency ν, have their values of action cluster closer and closer together until finally for $\nu T=$ infinity, all have precisely the same value. Now the energy of a system is a function of the action variables; so that, if, with incomplete quantization, there are systems with many values of the action variables, there are also systems with a variety of energies. Thus, as νT increases, the energies draw closer and closer together, if we leave out of account the effect which the incomplete quantization of other variables would have on the energy. This diffuseness of energy values results, if we apply Bohr's frequency condition, in a diffuseness of the resulting spectral lines; and this may be connected with the diffuseness in the spectrum of the oscillators producing the radiation, on account of their finite time of oscillation. This connection will not, however, be discussed in the present paper.

A number of examples will illustrate the many applications of these ideas to familiar problems of quantum theory. Perhaps the most complete example is the problem of quantization in a magnetic field. Let us first consider a static magnetic field. Then T represents the length of life of a stationary state, or $1/T$ equals on the average the probability P of leaving the state. The frequency which may become degenerate is the frequency of precession; it is the Larmor frequency $eH/4\pi mc$ if the Zeeman effect is normal, or a small number times this if it is anomalous. This frequency vanishes with H, the external magnetic field. The associated action variable is the component of the angular momentum in the direction of H; and since the total angular momentum is independent of the field, this amounts to a constant times the cosine of the angle between the axis of the atom and H. Our statement is now that the strength of the quantization is measured by $(eH/4\pi mc)/P$, which equals the average number of cycles which the Larmor precession makes in the time of a stationary state. When, then, H is small, the quantization becomes poor. That is, the directions of the axes cease to be assigned to definite values, but are merely clustered about those values as most probable ones. In the limit, when H is zero, the emphasis on the "quantized" directions is completely lost, the distribution of directions being entirely at random; and the range of values of H in which the change occurs is that region where it is of the same magnitude as $4\pi mcP/e$. If, then, we are to take a constant field and increase P, the probability of leaving the stationary state, the direction of orientation becomes less and less quantized until finally it is not quantized at all. An interesting experimental application of this result appears to be the discovery of Glaser[2] on the change of the diamagnetic susceptibility of some gases with pressure. Glaser finds that the magnetic susceptibility of certain gases decreases from one definite value to another when the pressure is increased at constant magnetic field, the change coming in a rather sharply defined pressure range. This he interprets as a change from a quantized condition at lower pressures to a non-quantized one at higher pressures, the oriented molecules having a greater diamagnetic effect than those oriented at random. Now increasing the pressure increases the probability of collision, and it seems inevitable that a collision would disturb the periodicity of the precession, so that we can consider the time T to be the average time between collisions, and P the probability of collision. Then we see that increasing P should, in fact, decrease the completeness of quantization and hence the susceptibility. Further, the range of values of P in which the change should come for a given value of H, can be found from the formula above; and if we calculate by gas theory the pressures for which the probability of collision is of this order, we find closely the range of pressures actually determined experimentally by Glaser. It is also found by Glaser that the range of pressure, and hence P, increases with increasing magnetic field, as we should expect.

We may also consider the case of the quantization in a variable magnetic field. The simplest case is that of a periodically varying field. Here we shall expect the quantization to begin to fail, for constant H

[2] Glaser, Ann. der Phys. **75**, 459 (1924).

and increasing frequency of the field, when the frequency of the field approaches that of the Larmor precession, for the frequency of the field is of the same order as the relative change of the field in unit time. This case appears to find an application in the recent experiment of Breit and Ellett[3] on the depolarization of resonance radiation by an oscillating magnetic field. Wood and Ellett[4] find that the depolarizing effect of a steady field increases as its Larmor precession becomes of the same order of magnitude as the probability of leaving the excited state, so that this effect is apparently connected with the strength of the quantization of the excited state. Breit and Ellett then take a field which is just strong enough to depolarize, but have it of an oscillating frequency. So long as its frequency of vibration is small compared with the probability of leaving the state, it depolarizes; but when its frequency becomes greater than the probability, the depolarizing effect decreases. This would be interpreted by saying that in the first case the time T was the time of a stationary state, and hence unaffected by the field, while in the second case it was the shorter time in which the field remained approximately constant, which decreased in inverse ratio to the frequency. Since the Larmor frequency is kept throughout of the order of magnitude of the initial $1/T$, the depolarizing effect is unchanged until the stage is reached where the fluctuations of the field predominate over the probability of leaving the stationary state, in dequantizing effect. Then T and νT begin to decrease, and this seems to be what is necessary to destroy the depolarization. Thus this phenomenon is in harmony with the view that a limitation of T, either by variation of the external parameters or by limiting the life in the stationary state, has the same effect.

Another case of quantization in a magnetic field is the experiment of Stern and Gerlach.[5] Here silver or other atoms are produced with a considerable thermal velocity in a region of practically no magnetic field and are then shot suddenly into a strong and variable magnetic field. As they enter the field they are presumably unquantized, for the Larmor frequency in the stray fields they had previously been in was not great enough to produce quantization. An approximately constant

[3] Briet and Ellett, Phys. Rev. **25,** 888 (abstract) (1925).

[4] Wood and Ellett, Proc. Roy. Soc. A**103,** 396 (1923);
Eldridge, Phys. Rev. **24,** 234 (1924); and particularly Breit, Phil. Mag. **47,** 832 (1924). Breit (loc. cit., p. 840) adopts precisely the present point of view regarding the diffuseness of quantization in weak fields.

[5] For general description of method, see Gerlach and Stern, Ann. der Phys. **74,** 673 (1924).

field is then suddenly applied to them; its magnitude is of the order of 12,000 gauss, so that its Larmor frequency is of the order of 1.7×10^{10} per sec. At any subsequent instant, then, the time T will be the time which has elapsed since entering the field, or the time in which the field where the atom is changes by a considerable fraction of itself, whichever is smaller, and the strength of quantization will depend on νT or $1.7\times10^{10}T$. If, then, T is large compared with 6×10^{-11} sec., the atom will be well quantized. Now the velocity of the atom is the thermal velocity, of the order of 5×10^{4} cm/sec., so that if the field is 5 cm long, it takes 10^{-4} sec. to traverse it. This, then, is the order of the time required for the field at the atom to change by a large fraction of itself, so that the process is perfectly adiabatic as far as the change of the field is concerned, except, perhaps, at the very beginning, when the atom suddenly enters the field. The quantization would be expected to be good except for the insignificant time of the order of 6×10^{-11} sec. just at the beginning.

Quantization in a magnetic field forms the best example of a degenerate system as it is the most familiar, but many other less familiar cases are no less significant. For example, suppose we are considering hydrogen atoms in various excited states. Corresponding to each total quantum number, there are, if the relativity precession be considered, states with various azimuthal quantum numbers. If each atom existed an infinite time in its stationary state, they would all have precisely one or another of the "allowed" values of angular momentum; but now suppose the life of the stationary states to be decreased, by increasing the pressure or by some other method; then the ratio of the relativity precessional frequency to the probability of leaving the state decreases. Thus the quantization decreases and the values of angular momentum and of the minor axes of the elliptical orbits are no longer confined to definite values but are distributed over all values, clustering, however, about these as means. Finally, as the life gets very short—so short that but a fraction of a complete precession is made in one stationary state—the angular momentum is distributed evenly over all possible values, with no clustering at all about the multiples of $h/2\pi$.

Another case is furnished by absorption in the higher lines of the principal series of an alkali. There the excited orbits are very eccentric and of frequency decreasing as the principal quantum number increases, until for an infinite quantum number the frequency becomes zero, the orbit becoming parabolic. But, in the limit, the life remains finite under ordinary circumstances, so that a point must be reached in the scale of ascending quantum numbers, above which the fundamental frequency is small compared with the probability of interruption, and the electron makes only a part of a circuit of its orbit before it is interfered with. At this point, then, the quantization must become diffuse, so that for greater values a continuous range of energies and angular momenta is possible. As we pass to the parabolic orbit, the tendency to quantize completely disappears. This case differs from the previous ones in that here all variables become degenerate, the largest frequency vanishing and periodicity ceasing. When this stage is reached, it is a transition only of degree, not of kind, to the hyperbolic orbits, which may likewise be supposed to be interrupted after finite lengths of time; a finite part of a hyperbolic orbit is not different in kind from a finite part of an ellipse. It appears from this that hyperbolic orbits should show no indication of sharp quantization. This situation would find application in the related problems of the continuous absorption beyond the limit of the series, and the continuous x-ray spectrum. In the first case, the final orbit is supposed to be of hyperbolic type; hence its action variables and energy are distributed continuously, and by the frequency relation the absorption spectrum is continuous. In the second case, the initial state consists of a free electron and an ion or atom, so that the electron may be considered to be describing an orbit of generally hyperbolic nature; and the final orbit is presumably sometimes of the same kind, sometimes an elliptic, quantized orbit. As in the orbits of hyperbolic type, we should expect that there would be complete absence of quantization in any other completely non-periodic type of motion which appears as the limiting case of complete physical degeneracy. A free electron in a metal, for example, if it really bumps about from atom to atom, must be expected to show practically no quantization of the ordinary kind. An extension of the ideas described here seems to offer the most hopeful method of attack on the problems of non-periodic motion in the quantum theory.

Part II

The suggestion that the strength of quantization depends on νT carries an implication of greatest importance in regard to quantum dynamics. Assume a collection of atoms which at a given instant enter a stationary state, and suppose that none of them have anything to interfere with their periodicity for some time after that. Then, after a time T, the average strength of quantization will depend on νT; but this increases with the time, so that the quantization must become better and better as time goes on. That is, the energy and momentum of the various systems must cluster closer and closer about mean values with increasing time. As a necessary result, the energy and momentum of any individual atom must move closer and closer to the perfectly quantized value as time goes on. After a short enough time interval, any co-ordinate can be regarded as degenerate, while after a time of the order of a few vibrations of the principal frequency, the principal variables become properly quantized. This implies a mechanism by which the energy and action variables can be varied, wholly apart from classical mechanics, and varied in such a way as to bring them nearer and nearer to quantized values. Since the energy and momentum are generally considered to be changed only by the action of forces, it must be supposed that there is a quantum mechanism which exerts essentially a stabilizing force, pulling the systems into their properly quantized orbits. This is a conception very different from the conventional one, by which the quantum part of atomic dynamics is considered simply as a restriction on the constants of integration of the orbits. Nevertheless, it seems to be demanded by many things.

Perhaps the best example of the need of some such extra-mechanical force is seen in Stern and Gerlach's experiment where atoms from a region where there is no magnetic field, or at least where the magnetic field is so small and so rapidly changing that atoms will not be quantized in it, suddenly emerge into a strong field. They will be originally oriented in all directions, and hence will have all values of magnetic energy. Yet when the atoms are quantized—which in the experiment actually happens—they have definite values of energy, so that each must have gained or lost in the process of quantization, energy comparable with its whole magnetic energy. This is an amount much greater than can be gained or lost in this time by mechanical means. Einstein and Ehrenfest[6] have calculated the change of magnetic energy classically, on account of the radiation accompanying the Larmor precession, and find it of an order of magnitude altogether too small to account for the comparatively large and sudden change. This fact they consider a serious difficulty connected with the experiment, but it is a perfect example of the present theory, and the change of energy involved in orientation is to be thought of as produced by the quantum forces which we have introduced.

It is possible to apply the conception in a more ambitious way: to the dynamics of quantum transitions. As an atom enters a stationary state, we should expect according to our theory that its energy and action variables can have values anywhere inside a wide range. Is there any objection to supposing that they may have the values which they had as they left the last state? There does not seem to be. It seems permissible to suppose that the part of the change of stationary state

[6] Einstein and Ehrenfest, Zeits. f. Phys. **11,** 31 (1922).

which occurs instantaneously is not the change in energy and action variables, but the change in the orbit toward which the stabilizing forces impel the atom. If the atom is well quantized in an orbit, so that these forces are not active, and there is a sudden change in the orbit toward which the forces are acting, the atom will find itself very badly quantized, and the forces will suddenly commence to act violently. In the course of a few vibrations, however, any given action variable will be forced to approximately its proper value, which will be approached more and more closely as time goes on. On this view, the energy and action variables would change continuously; the two kinds of action, transitions and stationary states, which have previously been considered as entirely separate, would appear simply as two aspects of the same kind of dynamical action, the transitions being the periods when the quantum forces are very active, the stationary states when they are relatively quiescent. The lower a frequency is, the longer would take the transitional part of its motion, and for a frequency of the kind we have called degenerate, the variable would be always in a situation of transition, never reaching a real stationary state—whose characteristic would be the completeness of the quantization. In a system that is degenerate in all its variables, so that the orbit toward which the quantum forces impelled the motion changed in a time comparable with a period, the quantum forces would be continually active, never becoming quiescent, so that such a motion would be completely inexplicable on classical dynamics. The free electron in its interaction with an atom would be an example of this.

The adiabatic theorem, and the cases when it breaks down, appear in a simple light. If an external parameter varies slowly, then at any instant the variables have all gone through many vibrations since their periodicity was appreciably affected, so that the quantization is good, remains good, and the quantum forces remain small. The classical forces alone, as is known, are enough in this case to produce the changes in the orbit. As soon, however, as the external parameters vary too rapidly, the quantization ceases to be good, the quantum forces become strong and attempt to pull the atomic system back to its original stationary state or into some other. In this situation, the ordinary dynamical forces are known no longer to tend to keep the action variables constant, but to vary them, so that if only the classical forces acted, the system would become permanently unquantized if a parameter varied suddenly. With the quantum forces, however, the effect is much like a quantum transition and results in the atom going to a quantized state again. All intermediate stages between the adiabatic and the transition-like action would occur, with different grades of suddenness of change of the conditions.

The quantum forces which have been suggested may be applied, by virtue of one of their simplest properties, to some of the difficult problems of quantum dynamics. Their aim appears to be to get the atom in a quantized state, which is a multiply periodic motion with proper values for the action variables, and to keep it there; their action is roughly analogous to a sort of restoring force for atoms that stray from their proper orbit, so that they must be supposed to oppose any force which tries to remove the atom from a quantized orbit. Of course, in speaking of force, the word is used in the sense of generalized co-ordinates, and not as forces literally acting toward definite points of the path. In hydrogen, the coulomb forces and the relativity forces are capable of maintaining the atom in a multiply periodic, quantized orbit. Thus, when the atom remains in its stationary state, the quantum forces do not oppose the classical ones. Likewise they do not oppose external fields, such as constant or slowly changing magnetic or electric fields, which would also result in quantized orbits; but the radiation resistance, and the forces from external radiation fields, both do tend to change the atom's action variables. They must then be expected to be opposed by the quantum force, which will not allow them to affect appreciably the motion of the system. Since the quantum forces must be supposed capable of exerting powerful action, they are presumably able completely to counteract the effect of such forces. The reaction of such effects on the quantum forces appears in quite a different way, namely, in the induction of quantum transitions.

For any atom but hydrogen, if we consider only classical forces and consider each electron as a system by itself, to be quantized by itself, there are large classical forces tending to change the energy and action variables of each separate electron; for in the interaction of electrons, if it is classical, energy passes from one electron to another during the cycle. In such a system, then, powerful quantum forces are set up tending to oppose this interchange of energy, angular momentum, etc., between the various electrons, and tending to force the individual electrons into multiply periodic orbits, each quantized by itself. If the quantum forces succeed in this, they will still have to act all during the motion, opposing some of the classical forces. But the result will be exactly the kind of motion which we believe occurs in atoms—multiply periodic motion of the single electrons, with no interchange of energy or other quantities between the different parts of the atom in the course of the stationary state; that is, just the kind of motion we should have if each electron were in a central field. A hint is thus given of the direction in which to approach the problems of atomic dynamics, namely, the introduction of quantum forces, opposing some of the classical forces, and allowing only those to act which help to maintain each separate electron in multiply periodic motion. Only in the case of hydrogen do the forces necessary to do this become vanishingly small, so that only in this case can we expect the classical dynamics to provide a basis for discussing stationary states; and even in this case we cannot expect to discuss the stability of the orbits by classical mechanics.

In spite of the apparent hopefulness of this line of attack on quantum dynamics, it would be foolish to suppose that it was sufficient in itself to solve the problem; for it must be recalled that the dynamics of stationary states represents but one of the two aspects of atomic mechanics, the other being the dynamics of the oscillators, each connected with two stationary states. In hydrogen, the Bohr atom has shown that the dynamics can be discussed with great ease from the first standpoint, and this leads one to the conviction that such a treatment is possible in other cases also. But there are reasons for believing a discussion to be possible on the second basis also, and for thinking that that might be simpler than the first for complicated atoms; for the action of an external oscillating electric field of optical frequency on an atom is most simply treated by considering the oscillators directly, and in an atom of more than one electron, the field of one electron on another is probably of this form. Thus it seems reasonable to suppose that we could consider the dynamics of such an atom by treating the reactions of the oscillators connected with the various electrons on each other directly. Such an idea was in the mind of the author when he suggested a mechanism of oscillators to describe the reaction of an atom to light; it has occurred also to Born[7] and presumably to others. It seems probable that both of these methods of attack on quantum dynamics will prove fruitful, and will eventually be found to be related. The most useful method of procedure seems to be to work on both methods together, trying to fit them into a single consistent scheme, the connection between them being presumably in the nature of extensions of the frequency condition and the correspondence principle.

In a subject which has been thought about by as many physicists as this undoubtedly has, it is naturally impossible to claim much originality, in spite of the small amount which has been written about it specifically. I have had the pleasure of discussing certain parts of this paper with Dr. Breit, who holds very similar opinions to mine on most of the questions. My thanks are due, also, to Professor P. W. Bridgman for valuable suggestions regarding quantum dynamics, and to Professor E. C. Kemble and Dr. L. A. Turner for their criticisms.

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[7] Born, Zeits. f. Phys. **26**, 379 (1924).