The Quantum Theory of Many-Particle Systems

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EDITOR

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OF
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PREFACE

The latter part of the decade of the forties and the early part of the decade of the fifties revealed the great fruits that were reaped in quantum field theory through the progress and advancements made in the area of perturbation theory. Great insights were gained in the problems of Quantum Electrodynamics, the problems of Mesodynamics, and the questions attending the interactions of various particle fields. Many problems that had previously been placed aside due to the inadequacies of computational technique were approached anew with modern weapons and experimentally verifiable numerical results were obtained. In areas where exact numerical results were still beyond achievement, qualitative information was obtained with regard to the nature of the solutions.

Stimulated by the success of the techniques of diagrammatic perturbation theory, attention was turned to several of the persistent and stalwart problems of statistical mechanics—problems that had been described by Feynman as "cities under siege completely surrounded by knowledge but themselves isolated and unassailable." These included superconductivity and superfluidity. In addition to these two questions, the problems surrounding the elucidation of the behavior of nuclear matter served to focus the attention of those who had previously been concerned solely with quantum field theory upon the structure of statistical mechanics.

It was, however, the "two cities" of superfluidity and superconductivity that stimulated the union of statistical mechanician and field theorist in a revitalized attack upon the problem of a statistical mechanics of interacting systems. This collection begins with a theoretical explanation of the first of these "cities" and ends with an attempt at elucidation of the second.

The student who first approaches this subject finds himself in a woods of mathematical methods, manipulations, expansions, partial summations and what appears to be a chaos of graphical abstractions. We hope that this collection of papers may aid the student and research worker in finding some order in the diversity of literature on this subject.

The order of the papers is in the first instance historical and in the second along the lines of methodology and the application of these methods to various problems.

The first group of papers serves to introduce the reader to one of the physical problems whose nature one seeks to elucidate and to the method of perturbation theory that might serve as a tool in this respect.

The first paper in this collection is a contribution by R. P. Feynman to the atomic theory of liquid helium. In order to compute the thermodynamic behavior of helium at low temperatures it is necessary to know the form of the energy spectrum for the low-lying states of the system. The form of the energy spectrum and the nature of the low-lying states were conjectured by Landau to be phonons and rotons. Landau went further and gave a microscopic or atomic explanation of the so-called two-fluid model. In this first paper Feynman exhibits a variational wave function for the helium system. From this wave function the shape of the energy spectrum is deduced. Feynman discovers that the lowest portion of the energy spectrum varies directly as the magnitude of the momentum vector. The states for which this is true are called phonon states. The states immediately above these are the states of quadratic dependence upon the momentum. These are the roton states of Landau.

Feynman has thus adduced evidence for the general features of the wave function of the helium system and theorectically derived the Landau energy spectrum. This energy spectrum is then used to calculate the thermodynamic properties of liquid helium. The parameters are fitted by use of the experimentally determined structure function. Discrepancies observed between the parameters so obtained and those same parameters experimentally determined indicate the necessity for an improved variational wave-function. The element that has been neglected is the interaction between the quasi-particle configurations or excitations. It is just these interactions that give rise to what has been termed the backflow problem. This paper by Feynman serves as an excellent introduction to the physical aspects of the liquid helium problem.

Although the arguments of Feynman and others give qualitative physical insight into the many-body problem, what is yet called for is an *a priori* deduction that begins with a specific model and proceeds to rigorously derive these results quantitatively through mathematical solution of the Schroedinger equation or some equivalent quantum mechanical scheme. It is clear that this cannot be done except through some type of perturbation theory.

The next three papers serve to illustrate the development of a form of perturbation theory capable of dealing with many-particle systems in which the interactions are strong. These papers are by Brueckner, Brueckner and Gammel, and Goldstone. They contain in essense a derivation of the so-called linked cluster expansion theorem for the ground state energy of a many-particle system. Calculation of the ground state energy permits the deduction of the properties of nuclei and the zero-temperature thermodynamic properties of many-particle systems.

The "linked cluster" expansion is a manner of rearranging and collecting terms in perturbation expansion in order to prevent the occurrence of divergencies and to assess the contribution of all terms of a given order. Goldstone has invented a graphical representation of the perturbation terms. This is an adaptation of the diagrammatic method of Feynmann to the many-body problem. It is discovered that the graphs that contribute to the energy are closed graphs having no loose ends, the contributions of the energy being additive in that one sums over single graphs that are connected or completely linked and not in two or more disconnected pieces.

These results can be achieved without the introduction of graphical representation by applying partial summation techniques to the perturbation expansion. By use of these techniques Brueckner shows that there are no contributions to the energy of a many-particle system by unlinked clusters. Brueckner shows by direct evaluation that, at least up to fourth order, the contributions from unlinked terms cancel. In the paper with Gammel the energy expansion is applied to numerically calculate some of the properties of nuclear matter.

In the description of large quantum mechanical systems one is naturally lead to the question of the behavior of the dynamical variables characteristic of the system in the limit of large volume. Are the variables volume dependent or volume independent in the asymptotic limit? An important advance in understanding this problem was made by Hugenholtz. In adapting graphical techniques to a perturbation theory of the resolvent operator, Hugenholtz was able to study the volume dependence of the perturbed energy levels of a many-body system. Through an analysis of diagrams that contribute to the matrix elements a complete separation was made between the extensive and intensive contributions of the perturbed energy and energy shifts for the problem of a Fermi gas with two-body interaction. This paper by Hugenholtz

gives a very good resumé of the techniques of Van Hove and also an introduction to the use of diagrammatic techniques in partial summations.

The next paper by Bloch contains a derivation of the ground state energy of an interacting quantum system. Developing a graphical repesentation of the contributing terms, Bloch unfolds another form of the linked cluster expansion. The formal similarity between the ground state energy expansion and the expansion of the partition function at finite temperature permits the construction of a linked cluster expansion for the Helmholz free energy. This is explored in later papers by Bloch and DeDominicis.

In spite of the appearance of numerous formal expansion schemes, one appears to be still a long way from a numerical calculation of the properties of liquid helium that is based upon a realistic interatomic potential function. There has been progress, however, in obtaining numerical results for a simplified model of helium that one obtains by omitting the attractive nature of the interactor and considering only the hard sphere personality of the interatomic potential. The hope is that the qualitative character of these results will persist when the attractive nature is introduced.

In a brilliant series of papers, the hard sphere boson system is studied exhaustively by Huang and Yang, and by Lee, Huang, and Yang. Using a pseudopotential method, the eigenvalues and eigenfunction are calculated and from these the thermodynamics of the system follows. The authors verify rigorously the conjectures of Landau and the qualitative deductions of Feynman.

Further studies by Wu reveal that one can extend the pseudopotential method further to yield higher terms in the low-density expansion of the ground state energy of a Bose system with hard sphere potential. It is found by Wu that the expansion is not a power series in $(a^3\rho)^{\frac{1}{2}}$ but contains logarithmic terms as well. Limitations of the pseudopotential method are assessed by considerations relating to the three-body problem.

As is well known, in the latter day developments in quantum electrodynamics Green's function methods played a dominant role. Realizing the formal connection between Green's function methods of quantum field theory and the density matrix formulation of quantum statistics, Matsubara formulated Feynman's method for quantum statistical mechanics and was the first to introduce Green's function methods for the non-

zero case. In addition to the general reformulation of statistical mechanics of interacting particles, application was made to the problem of electron-phonon interaction. Apart from the historical value of having pointed the way, this paper by Matsubara contains valuable theorems on con-tractions and commutations of operators that are adaptations of theorems derived previously by Anderson in quantum field theory.

In earlier papers of this volume one has seen the treatment of the boson gas through diagonilization of model Hamiltonians. The next paper in this volume contains a Green's function treatment of the boson system at zero temperature. Hugenholtz and Pines make essential use of the Green's function in the resolution of the difficulties associated with the depletion of the zero momentum states. These authors exhibit the general series expansion of the energy of the boson system. This ground state energy calculation contains the next order term beyond that of Lee and Yang and compares with the result of Wu.

The next step in understanding the boson problem is the generalization of formalisms to the non-zero temperature case. Advancements along these lines were seen earlier in the work of Bloch and DeDominicis; however, the periodicities that characterize the mathematical properties of the Green's function present them as suitable objects for developing the physics of a non-zero, temperature-interacting, many-body system.

Before pursuing the general theory of Green's functions, we present another example of their application to a physical problem. This is im-plicitly contained in the works of Hubbard, who treats the behavior of an electron gas in what has become a classical series of papers. The fundamental work of Gell-Mann and Brueckner on the electron gas is also presented for comparison with the Green's function technique.

As is well known, in contrast to the case of the electron gas, the interactions in nuclear matter are short range and strong. The next series of papers by Klein and Prange reveal the power of the Green's function technique in the study of infinite fermion systems at zero temperature. The generalization of the Green's function to finite temper-ature and their subsequent analytical properties are discussed.

The paper, *Theory of Many-Particle Systems* by Martin and Schwin-ger, is the first of a series that attempts to treat the subject from a unified nonperturbative point of view. The authors begin with a de-velopment of thermodynamics within the framework of a generating function defined over a complex field. A prescription is given for extracting the density of states. This formal function also generates,

via the method of steepest descents, expressions for the energy and number. By consideration of the time rate of change of the momentum density operator of a field $\psi(x)$ one arrives at the stress tensor for the interacting field.The average diagonal element of the stress tensor is identified as the pressure of the system. Contact is then made with the usual form of thermodynamics. Thus one is exposed to a very elegant and self-contained exposition of thermodynamics developed within the framework of a field theory and affected by the technique of a formal generating function. This constitutes the mathematical description of macroscopic properties.

The connection between the macroscopic properties and the microscopic detail of a system is contained in the Green's functions that characterize the system. These functions are defined for a microcanonical ensemble, however, in order to extract the properties of these functions the authors introduce a generating Green's function. The connection between the generating function and the Green's functions is indicated. The usefulness of the generating Green's functions lies in the deduction of the analytical properties of the temperature Green's functions. These generating functions have a periodicity in a kind of complex temperature time space. This periodicity facilitates fourier analysis and subsequent spectral representation. One of the more powerful and useful points of this paper is the deduction of analytical properties from the spectral representation. Martin and Schwinger indicate the properties of the spectral function in the general case and exhibit it for a noninteracting system. Spectral representations are studied for Bose-Einstein, and Ferni-Dirac systems.

The remaining sections of this paper deal with nonequilibrium or transport phenomena, determination of the Green's functions and formal solutions. To the reader interested in actually constructing the Green's functions for specific problems and the ultimate numerical calculation for results, there is an extensive development of the various approximation techniques that lend themselves to construction of these functions. Among the methods given is a Hartree type of approximation for the two particle Green's functions. This type of decomposition is generalized to higher n-particle Green's functions and a n-particle correlation function is introduced and studied. This particular approach to the approximation of the Green's functions has proven quite useful in the study of n-particle systems. Martin and Kadanoff have treated the problem of superconductivity through a study of the correlation func-

tion. Other studies strengthened by this correlation function are by Puff, in the problem of nuclear matter; and Parry, in the problem of Bose-Einstein condensation of liquid helium. These are studies of systems at equilibrium. A paper by McCumber studies the nonequilibrium problem of sound propagation.

Although we feel that the ideas and techniques contained in the Martin-Schwinger formalism have yet to be fully exploited, much progress has been made. The aforementioned papers are taken as examples of the Green's function technique of Martin and Schwinger.

Kadanoff and Martin base their treatment of superconductivity upon the analytical behavior of the correlation functions of a superconductor. They exhibit these correlation functions within the Hartree approximation and the equations that they satisfy. Green's functions for the superconductor are found within this approximation. A study of the temperature behavior of the poles of these reveals the mathematical manifestations of the instability which leads to the superconducting state. A correlation function description of the superconducting model of BCS and Bogalubov is described and their results are obtained. Later sections of this paper are concerned with the development of an approximation to the hierarchy of correlation functions that would satisfy the requirement of gauge invariance. Lifetimes of the elementary excitations and transport properties are treated in the last sections.

With this paper on the theory of superconductivity this volume comes to an end. It is the hope of the editor that this choice of collected papers may prove useful as a stepping stone for the reader to current developments in this rapidly moving area of physics.

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CONTENTS

Atomic Theory of the Two-Fluid Model of Liquid Helium

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(Received January 11, 1954)

It is argued that the wave function representing an excitation in liquid helium should be nearly of the form $\Sigma_i f(r_i)\phi$, where ϕ is the ground-state wave function, $f(r)$ is some function of position, and the sum is taken over each atom i. In the variational principle this trial function minimizes the energy if $f(r) = \exp(i\mathbf{k} \cdot \mathbf{r})$, the energy value being $E(k) = \hbar^2 k^2/2mS(k)$, where $S(k)$ is the structure factor of the liquid for neutron scattering. For small k, E rises linearly (phonons). For larger k, $S(k)$ has a maximum which makes a ring in the diffraction pattern and a minimum in the $E(k)$ vs k curve. Near the minimum, $E(k)$ behaves as $\Delta + \hbar^2(k-k_0)^2/2\mu$, which form Landau found agrees with the data on specific heat. The theoretical value of Δ is twice too high, however, indicating need of a better trial function.

Excitations near the minimum are shown to behave in all essential ways like the rotons postulated by Landau. The thermodynamic and hydrodynamic equations of the two-fluid model are discussed from this view. The view is not adequate to deal with the details of the λ transition and with problems of critical flow velocity.

In a dilute solution of He^3 atoms in He^4, the He^3 should move essentially as free particles but of higher effective mass. This mass is calculated, in an appendix, to be about six atomic mass units.

IN a previous paper,[1] II, a physical argument was given to interpret the fact that the excitations which constitute the normal fluid in the two-fluid theory of liquid helium were of two kinds. Those of lowest energy are longitudinal phonons. The main result of that paper was to give the physical reason for the fact that there can be no other excitations of low energy. It was shown that any others must have at least a minimum energy Δ. No quantitative argument was given to obtain this Δ nor to get an idea of the type of motion that such an excitation represents. In this paper we expect to determine Δ and the character of the excitations.

The physical arguments of II are carried a step further here to show that the wave function must be of a certain form. The form contains a function whose exact character is difficult to establish by intuitive arguments. However, the function can be determined, instead, from the variational principle as that function which minimizes the energy integral.

THE WAVE FUNCTION FOR EXCITED STATES

In II the exact character of the lowest excitation was not determined, but various possibilities were suggested. One is the rotation of a small ring of atoms. A second is the excitation of an atom in the local cage formed around it by its neighbors. Still a third is analogous to the motion of a single atom, with wave number k about $2\pi/a$, where a is the atomic spacing, the other atoms

FIG. 1. Typical configuration of the atoms. If an excitation represents rotation of a ring of atoms such as the six in heavy outline the wave function must be plus if they are in the α positions and minus if they are moved to the intermediate β positions.

[1] R. P. Feynman, Phys. Rev. **91**, 1291, 1301 (1953), hereafter called I, II, respectively.

moving about to get out of the way in front and to close in behind. It is not clear that they are really distinct possibilities, for they might be merely different ways of describing roughly the same thing.

We shall now try to find the form of the wave function which we would expect under the assumption that one or another of these possibilities is correct. It will turn out that all of the alternatives suggest the same wave function, at least to within a function $f(\mathbf{r})$, of position $\mathbf{r}$, which is determined only vaguely.

First, suppose that the excitation is the rotation of a small ring of atoms. The number of atoms in the ring is determined, according to II, by the condition that it is the smallest ring that can be considered to be able to turn easily as an independent unit in view of the interatomic forces. For illustrative purposes we suppose this means that there are six atoms in the ring.

We can describe the wave function for this excitation by giving the amplitude associated with every configuration of the atoms. Suppose Fig. 1 represents a typical configuration, the six atoms of the ring in question (say ring A) being indicated by heavy outline. We discuss how the amplitude changes as we rotate this ring, leaving the other atoms out of account for a moment. Suppose the wave function is positive, say $+1$, if the atoms are in the position shown by the full circles in Fig. 1, which we arbitrarily call the α position. Suppose all the six atoms move around together, and let the ring turn about 60°. The atoms then appear again in α position, although which is which has been changed, so the wave function, by the Bose statistics, is still $+1$. On the other hand, for a 30° rotation, if the atoms are located as indicated in the figure by dotted circles (β position), the wave function will change to -1 for the first excited state. We need only discuss the real part of the wave function—the imaginary part, if any, can be dealt with in a similar way. (Actually since we deal with an eigenstate of the energy, the real part of
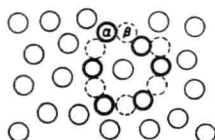
1

the wave function is an eigenfunction also.) For orientations intermediate between α, β the function is correspondingly intermediate between $+1$ and -1, but to simplify the remarks we describe it for just the configurations α, β. The wave function for excitation of this ring we call ψ_A. It is $+1$ if the A ring is at α, and -1 if at β, and does not depend on how other rings of atoms are oriented. We can describe this wave function as follows. Consider a function of position $\mathbf{r}$ in space, $f_A(\mathbf{r})$ which is $+1/6$ if $\mathbf{r}$ is at one of the six positions of the centers of the atoms for the α position of ring A, is $-1/6$ if it is at a β position, and is zero if $\mathbf{r}$ is at any other place in the liquid far from the A ring. Then consider the quantity $\sum_i f_A(\mathbf{r}_i)$ where the sum is taken over all the atoms, i, in the liquid. For a configuration of the liquid for which there are atoms at the six α positions the quantity is $+1$, while if six atoms are at a β position, it is -1. This suggests that we can write $\psi_A = \sum_i f_A(\mathbf{r}_i)$.

Actually this is incomplete because it does not correctly describe what happens if atoms in other parts of the liquid move. If ring A is in the α position, we wish the complete wave function to be $+1$ as far as this is concerned, but to drop to zero if two atoms overlap in other parts of the liquid, etc., just as for the ground state. That is, we expect (disregarding normalization)

$$\psi_A = \sum_i f_A(\mathbf{r}_i)\phi, \qquad (1)$$

where ϕ is the ground-state wave function, a function of all the coordinates. This takes care of another matter also. What happens if some atoms are on α and some on β? This should be of very small amplitude because we do not wish the atoms to overlap on account of the repulsions. This is not correctly described by $\sum_i f_A(\mathbf{r}_i)$, but the ϕ factor does guarantee such a behavior. It is small for such overlaps. Of course, if the ring contained many atoms it could readjust just a little and the ϕ would not prevent, for example, all those near one side of the ring being α, and those on the opposite side of the ring being β. We are not guaranteed that (1) will describe well the amplitude for such a configuration. In fact, it wouldn't be expected that a function of just one variable could describe the motion of several atoms. However, by the arguments of II the ring is supposed to be small, in fact, so small that one part of the ring cannot move independently of the rest. The ring is so small that if one atom is at α, there cannot be a large amplitude for finding atoms at β because of the interatomic repulsions. This is represented in (1) by the factor ϕ which falls if two atoms approach (see II for a full description of the properties of ϕ).

Not knowing the exact size and shape of the ring we cannot say what the exact function $f_A(\mathbf{r})$ should be. But at least we conclude in this case the excited-state wave function is of the form

$$\psi = \sum_i f(\mathbf{r}_i)\phi, \qquad (2)$$

where $f(\mathbf{r})$ is *some* function of position.

We might try to improve (1) by noting that, of course, the energy should be essentially the same if the excited ring were somewhere else in the liquid, say at B. The function

$$\psi_B = \sum_i f_B(\mathbf{r}_i)\phi \qquad (3)$$

would describe this if $f_B(\mathbf{r})$ is $+1/6$ for $\mathbf{r}$ at some one of the six α positions of some other ring B, and $-1/6$ for intermediate β positions, and zero elsewhere. Or we could locate the ring at still another position, etc. Any one atom might be thought of as belonging to more than one ring. This produces a kind of interaction between adjacent rings. Because of this interaction, a better wave function than (1) might be some linear combination of these possibilities, say $c_A\psi_A + c_B\psi_B + \cdots$. But we can still conclude that the form of the wave function is given by (2), but now, with the function $f(\mathbf{r}) = c_A f_A(\mathbf{r}) + c_B f_B(\mathbf{r}) + \cdots$, for any linear combination of functions of the form (2) is still of this form.

If the lowest excited state which we seek were something like the excitation of a single atom in a cage formed from its neighbors we would guess the wave function to be of the form (2) also. Because there would be a nodal plane across the cage, and we would take $f(\mathbf{r})$ to be positive if $\mathbf{r}$ is in the cage on one side of the plane, and negative if on the other, and to fall off to zero if $\mathbf{r}$ goes outside the cage. We do not care which atom is in the cage so the sum on i is taken over all atoms. Those which are outside the cage contribute nothing to the sum, because $f(\mathbf{r})$ is zero there. Further, there is no appreciable amplitude for there being more than one atom in the cage, because of the action of the factor ϕ which is very small if the atoms penetrate each other's mutual potential. The ϕ also takes care of the fact that the atoms in remote parts of the liquid behave independently of what the excited atom is doing, and act just as in the ground state. Further, linear combinations, representing the alternatives that the excited cage may be located at different places in the liquid, are still of the form (2).

The third possibility was only crudely described in II. It was noted that if the atoms were considered as roughly confined to cells, then a wave function representing the motion of an atom A could be $\exp(i\mathbf{k} \cdot \mathbf{r}_A)$, where $\mathbf{r}_A$ is the position of A, and it is assumed that as A moves about, the other atoms move around to make way for it so that the density is maintained roughly uniform. This would correspond in the liquid to a wave function

$$\exp(i\mathbf{k} \cdot \mathbf{r}_A)\phi, \qquad (4)$$

where ϕ is the ground-state wave functions of all the atoms including A. The factor ϕ does the equivalent of keeping the atoms in cells so that the density is nearly uniform no matter where $\mathbf{r}_A$ is. For small $\mathbf{k}$ this is a possibility only if atom A is different from the others and does not obey the Bose statistics. If the symmetry is taken into account then we must replace this by

2

the symmetrical sum

$$\sum_i \exp(i\mathbf{k}\cdot\mathbf{r}_i)\phi. \tag{5}$$

If ϕ had no large scale density fluctuations this would be no wave function at all, because there would be just as many atoms in the region where $\exp(i\mathbf{k}\cdot\mathbf{r})$ is positive as where it is negative and the sum cancels out.[2] This is in concert with the idea that the wave function cannot depend on where atom A is on a large scale. For if A moves a long distance and the others readjust to keep the density uniform, on a large scale (the scale $1/k$ for small k), the result is just equivalent to the interchange of atoms and the wave function cannot change as a consequence of the Bose symmetry. On the other hand, if while the atom moves from one position to that of its neighbor the wave function changes sign and returns, then (5) may be allowed. That is, something like (5) with k of order $2\pi/a$ may be a possibility. This again is of the form (2), but with $f(\mathbf{r})=\exp(i\mathbf{k}\cdot\mathbf{r})$. The argument just given for this alternative is admittedly not as complete as for the others, mainly because the original idea of what the state is, was based on such a crude model of atoms in cells. Insofar as the idea can be carried over to the case of the true liquid perhaps we can say the form (5), or (2) will represent it.

Since all the examples have led to the same form, we might expect that a more general argument could be made for the validity of (2). This is, in fact, possible starting from the general argument given in II to show why the excited states, other than phonons, can be expected to have an excitation. It was pointed out there that the excited-state function ψ must be orthogonal to the ground state. For some configuration, say α, of the atoms it acquires its maximum positive value. Then it will be negative for some other, say β, which represents some stirring from the α configuration without change of large scale density (to avoid phonon states). But stirring reproduces a configuration nearly like α although with some atoms interchanged. Thus it is hard to get the configuration β to be very far (in configuration space) from α to keep the gradient of ψ small in going from α to β.
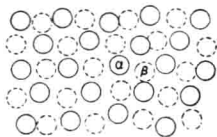

Fig. 2. In general the lowest excitation energy results if the configuration of atoms (solid circles) for which the wave function is most positive is as far as possible from that (dotted circles, β) for which it is most negative. All the β positions must be as far as possible from α positions, therefore.

[2] We shall see later that (5), for small $\mathbf{k}$, is actually a satisfactory wave function because ϕ does have the long wave density variations of the zero point motion of the sound field. We are trying to get excited states orthogonal to phonon states, and (5) for small $\mathbf{k}$ is not orthogonal. It is, in fact, just the wave function for such a phonon state. This is discussed later.

The lowest state would have the β configuration as far as possible from α. This means that in β as many atoms as possible are moved from sites (call them α positions) occupied by atoms in α. Hence β must be a configuration in which the atoms occupy sites (β positions) which are placed as well as possible between the α positions. (See Fig. 2.) In all these configurations, of course, the gross density must be kept uniform and the atoms should be kept from overlapping, to avoid high potential energy terms. If all atoms are on α positions ψ is maximum positive, and if all on β, maximum negative. The transition is made as smoothly as possible, and the kinetic energy thereby kept down, if for other configurations the amplitude is taken to be just the number of atoms on α positions minus the number on β positions. The number is just $\sum_i f(\mathbf{r}_i)$ where $f(\mathbf{r})$ is a function which is $+1$ if $\mathbf{r}$ is at an α position, and -1 if at a β position (and varies smoothly in between these limits as $\mathbf{r}$ moves about). It is of course a modulation to be taken on ϕ, because we wish to give small amplitude to configurations in which atoms overlap, etc., just as in the ground state. We are led, therefore, to (2). We can add the information that $f(\mathbf{r})$ must vary rapidly from plus to minus in distances of half an atomic spacing. That is, we expect that $f(\mathbf{r})$ will consist predominantly of Fourier components of wave number $\mathbf{k}$ of absolute magnitude $k=2\pi/a$.

In the above argument it is not self-evident that in going from the configuration of all atoms at α positions to that of all at β, the amplitude must be just linear in the number on α, N_α minus the number of β, N_β. Perhaps some other smooth function of this number, like $\sin[\pi(N_\alpha-N_\beta)/2N]$ might be better. However, for the majority of possible configurations N_α and N_β are nearly equal; in fact, for almost all, $(N_\alpha-N_\beta)/N$ is of order $\pm N^{-\frac{1}{2}}$. For such a small range of the variable, the function, whatever it is, ought to behave nearly linearly. If the wave function (2) is wrong for a very few special configurations it will not be important as we shall determine the energies by the variational method, and the special configurations will contribute only a small amount to the integrals because of their small share of the volume in configuration space.

THE EXCITATION ENERGY

We have concluded that a function of the form (2) should be a good approximation to the wave function of the excited state.[2a] The function $f(\mathbf{r})$ is known only imperfectly, however. We shall determine this function $f(\mathbf{r})$ by using the variational principle. The Hamiltonian of the system is

$$H=-(h^2/2m)\sum_i\nabla^2_i+V-E_0, \tag{6}$$

[2a] Wave functions of this form have been proposed before, for example by A. Bijl, Physica 7, 869 (1940). However, an argument establishing their validity for large $\mathbf{k}$ has been lacking, and it has not been clear that functions of other forms might not give much lower states.

3

where V is the potential energy of the system, and we measure energies above the ground-state energy E_0, so E_0 is subtracted in (6). Therefore the ground-state wave function satisfies

$$H\phi = 0. \qquad (7)$$

If we write

$$\psi = F\phi, \qquad (8)$$

where F is a function of all the coordinates, then we can verify, using (7), that

$$H\psi = H(F\phi) = -(\hbar^2/2m)\sum_i(\phi\nabla_i^2 F + 2\nabla_i\phi \cdot \nabla_i F) = \phi^{-1}(-\hbar^2/2m)\sum_i\nabla_i \cdot (\rho_N\nabla_i F), \quad (9)$$

where $\rho_N(\mathbf{r}^N) = \phi^2$ is the density function for the ground state, that is, the probability of finding the configuration $\mathbf{r}^N$ (we use $\mathbf{r}^N$ to denote the set of coordinates $\mathbf{r}_i$ of all the atoms, and $\int \cdots d^N\mathbf{r}$ to represent the integral over all of them).

The energy values come from minimizing the integral, (note ϕ is real)

$$\mathcal{E} = \int \psi^* H\psi d^N\mathbf{r}$$
$$= (\hbar^2/2m)\sum_i \int (\nabla_i F^*) \cdot (\nabla_i F)\rho_N d^N\mathbf{r}, \quad (10)$$

subject to the condition that the normalization integral,

$$\mathcal{I} = \int \psi^* \psi d^N\mathbf{r} = \int F^* F\rho_N d^N\mathbf{r}, \qquad (11)$$

is fixed. The energy is then $E = \mathcal{E}/\mathcal{I}$.

In these expressions we must substitute

$$F = \sum_i f(\mathbf{r}_i). \qquad (12)$$

Consider the normalization integral first. It is

$$\mathcal{I} = \sum_i\sum_j \int f^*(\mathbf{r}_j)f(\mathbf{r}_i)\rho_N d^N\mathbf{r}.$$

For a fixed i and j we can integrate first over all of the other atomic coordinates. This integral on ρ_N gives the probability for finding the ith atom at $\mathbf{r}_i$ and the jth at $\mathbf{r}_j$; therefore

$$\mathcal{I} = \int f^*(\mathbf{r}_1)f(\mathbf{r}_2)\rho_2(\mathbf{r}_1,\mathbf{r}_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2, \quad (13)$$

where ρ_2 is the probability of finding an atom at $\mathbf{r}_1$ per cm³, and at $\mathbf{r}_2$ per cm³. These density functions can be defined in general by

$$\rho_k(\mathbf{r}_1',\mathbf{r}_2' \cdots \mathbf{r}_k') = \sum_i\sum_j \cdots \sum_n \int \delta(\mathbf{r}_i - \mathbf{r}_1')$$
$$\times \delta(\mathbf{r}_j - \mathbf{r}_2') \cdots \delta(\mathbf{r}_n - \mathbf{r}_k')\rho_N(\mathbf{r}^N)d^N\mathbf{r}. \quad (14)$$

For example, $\rho_1(\mathbf{r})$ is simply the chance of finding an atom at $\mathbf{r}_1'$, for the liquid in the ground state. This is independent of $\mathbf{r}$ and is the number density ρ_0 in the ground state. In the same way $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$ can be written as $\rho_0 p(\mathbf{r}_1-\mathbf{r}_2)$ where p is the probability of finding an atom at $\mathbf{r}_2$ per unit volume if one is known to be at $\mathbf{r}_1$. Except near the liquid surface it is a function of only the distance from $\mathbf{r}_1$ to $\mathbf{r}_2$, so (13) is

$$\mathcal{I} = \rho_0 \int f^*(\mathbf{r}_1)f(\mathbf{r}_2)p(\mathbf{r}_1-\mathbf{r}_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2. \quad (15)$$

The energy integral (10), with the substitution (12) becomes

$$\mathcal{E} = (\hbar^2/2m)\sum_i \int \nabla_i f^*(\mathbf{r}_i) \cdot \nabla_i f(\mathbf{r}_i)\rho_N d^N\mathbf{r}.$$

The integral of ρ_N over all atomic coordinates except $\mathbf{r}_i$ gives a result involving only $\rho_1(\mathbf{r}_i) = \rho_0$. Therefore we have simply

$$\mathcal{E} = \rho_0(\hbar^2/2m) \int \nabla f^*(\mathbf{r}) \cdot \nabla f(\mathbf{r})d^3\mathbf{r}. \quad (16)$$

The best choice of f is that which minimizes the ratio of (16) to (15). The variation with respect to f^* gives the equation

$$E \int p(\mathbf{r}_1-\mathbf{r}_2)f(\mathbf{r}_2)d^3\mathbf{r}_2 = -(\hbar^2/2m)\nabla^2 f(\mathbf{r}_1),$$

where the energy E is $\mathcal{E}/\mathcal{I}$. This has the solution

$$f(\mathbf{r}) = \exp i(\mathbf{k} \cdot \mathbf{r}), \qquad (17)$$

with the energy value

$$E(\mathbf{k}) = \hbar^2 k^2/2mS(k), \qquad (18)$$

where $S(\mathbf{k})$ is the Fourier transform of the correlation function,

$$S(\mathbf{k}) = \int p(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})d^3\mathbf{r}. \qquad (19)$$

It is a function only of k, the magnitude of $\mathbf{k}$.

It is readily verified that the solution is orthogonal to the ground state if we exclude $\mathbf{k} = 0$. In fact, the solutions for different values of $\mathbf{k}$ are orthogonal to each other. This is because they all belong to different eigenvalues, $\hbar\mathbf{k}$, of the total momentum operator

$$\mathbf{P} = (\hbar/i)\sum_i\nabla_i,$$

as is directly verified from (2) with (17), taking $\mathbf{P}\phi = 0$ since the ground state has zero total momentum.[3] Since

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[3] The argument is not rigorous because the momentum of the entire liquid can be changed without appreciable energy change by moving the center of gravity. This multiplies the wave function by a factor like $\exp(-i\hbar k N^{-1} \cdot \sum_i \mathbf{r}_i)$. This function is so different from (2), however, that the orthogonality is probably not destroyed.