Perturbation-Theoretical Approach to Magneto-Optical Phenomena in the Spectral Region of Zero Absorption

Alfred Nedoluha

Infrared Division, U. S. Naval Ordnance Laboratory, Corona, California

The effect of a weak magnetic field on a many-electron system in an isolated ground state is calculated by a perturbation-theoretical method. The calculation is based on the property of internal localization of both the one-particle density matrix and a certain two-particle Green's function of the system, and is performed in the independent-particle approximation. After splitting off phase factors, we derive recurrence relations for the expansion of the density matrix and Green's function in powers of the magnetic field strength H. From the density matrix one obtains the energy of the system, from the Green's function the magneto-optical coefficients. In an approximation linear in H the gyration vector is given explicitly; the contributions to polarizability tensor and energy vanish in this approximation. The gyration vector obtained is in agreement with the results derived (a) for small systems, accessible to nondegenerate one-particle perturbation theory, and (b) for ideal crystals, treated by Roth in a modified Bloch representation.

1. INTRODUCTION

DENSITY matrices and Green's functions provide a general approach to many-body problems. Such a "Green's-function method," as we shall call it for brevity, allows for taking the interaction among particles into account, and a large amount of literature exists about this subject.[1] If the interaction among particles is neglected, Green's-function methods remain, of course, valid; but an alternative is now offered by direct consideration of the one-particle states. An approach which is based on an individual investigation of the one-particle states (orbitals) we shall designate as the "orbital method."

For an independent particle model, the density matrices and Green's functions can be built up from the one-particle energy eigenfunctions and eigenvalues. Even then the Green's-function method may be of advantage, however, since density matrices and Green's functions may be easier to handle and calculate than the orbitals themselves.

We shall be concerned here with the effect of an applied magnetic field H on certain properties of a many-electron system in the independent particle approximation.[2,3] The system is assumed to possess an isolated (i.e., discrete and nondegenerate) ground state. The ground state is then separated from the first excited state by a finite energy $\hbar\omega_G$ (that is, $\omega_G \neq 0$). Prototypes of such systems are an atom or molecule with a nondegenerate ground state, and an ideal insulating crystal (we are concerned here only with the electrons; the

positions of the nuclei are assumed to be fixed). W hall see that for the ground state of such a system the effect of a weak magnetic field on the energy and on the optical properties in the spectral region of zero absorption (that is, for circular frequencies ω, with $\omega < \omega_G$) may be made the subject of a perturbation calculation. The energy may be obtained from the one-particle density matrix and the optical effects from a two-particle Green's function. Actually, it is the optical effects we are primarily interested in here, but since our calculation of the Green's function will require a knowledge of the density matrix as a prerequisite and since the energy of the system may thus be obtained as a by-product, we shall to some extent include the energy in our discussions.

Green's-Function versus Orbital Method

Let us compare the assets of the Green's-function method with those of the orbital method in their application to diamagnetism and magneto-optical dispersion effects. First we must notice an important difference between the energy of a system and the dispersion properties: The energy depends only on the occupied one-electron energy eigenstates, while dispersion involves essentially all states. An approach to magneto-optical dispersion effects by the orbital method requires, therefore, that all one-electron energy eigenstates in the presence of the magnetic field be calculable, a requirement which is usually hard to meet. A certain simplification occurs for ω close to ω_G, in which case the states close to the energy gap give the dominant contribution; this restricted set of states, as well as the set of occupied states for the determination of the energy of the system, is frequently easier to handle than the complete set. We shall illustrate this with the following two examples:

(a) For a small system, say a molecule,[4] an application of conventional perturbation theory on the low-

[1] T. D. Schultz, *Quantum Field Theory and the Many-Body Problem* (Gordon and Breach, Publishers, Inc., New York, 1964); also C. Kittel, *Quantum Theory of Solids* (John Wiley and Sons, Inc., New York, 1963). Further references will be found in these monographs.

[2] A brief account of the presented work may be found in the *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965), hereafter referred to as P.

[3] Some of the material of the present paper is discussed in greater detail in NAVWEPS Quarterly Reports Nos. 8171 (1963), 8183 (1964), 8192 (1964), and 8197 (1964), (unpublished), Foundational Research Projects, Naval Ordnance Laboratory, Corona, California.

[4] A perturbation theoretical treatment of Faraday rotation by molecules, using the orbital method, has been given by R. Serber, Phys. Rev. 41, 489 (1932).

lying orbitals should be fairly routine. A calculation of the ground-state energy of the system in the presence of the magnetic field then presents no major obstacles. Similarly, the one-electron states which dominate the magneto-optical behavior for ω close to ω_G should be calculable by perturbation theory. For these phenomena the orbital method will, therefore, run into no major difficulties. In a general calculation of magneto-optical dispersion effects, however, the highly excited states must also be considered—even the ionization continuum. For these states the system may no longer be considered "small," and to treat the applied magnetic field as a small perturbation usually will not be justified. A Green's-function method will then be required, at least from a methodical point of view.

(b) In large systems, like crystals, a straightforward perturbation approach for the one-particle energy eigenstates is hampered by the high (quasi-) degeneracy, quite similar to the case of the highly excited states in "small" systems mentioned above. For crystals, the translational symmetry allows a different kind of approach, which, for states close to a band edge, results in the effective mass approximation; an applied magnetic field can then be taken into account with relative ease.[5] To calculate the dominant contribution to magneto-optical effects for ω close to ω_G, the orbital method will therefore be adequate.[6] To determine, however, the energy of a crystal and magneto-optical dispersion effects in general, one has to know also the states in the interior of the energy bands. It is true that for these states an effective wave equation in the presence of a magnetic field can be established,[7] but an explicit determination of the energy eigenstates should be rather awkward.[8] This difficulty may be overcome by departing from a pure one-particle method. The normal diamagnetism of crystals has been discussed by many authors[9] who, in one way or another, make use of a density matrix and either apply an effective wave equation or expand the energy of the crystal directly in powers of $\mathbf{H}$. The situation is similar for magneto-optical effects: Faraday rotation in crystals to first order in the magnetic field strength has been calculated by Roth[10] for arbitrary frequencies, by making use of an effective Hamiltonian and the trace of a certain opera-

tor. One might say that this last feature amounts essentially to the introduction of some kind of a Green's-function procedure.

Scope, Purpose, and Contents

Evidently, density matrices and Green's functions—sometimes in a hidden form—have been used before in connection with our problem, but it seems to us that no full advantage has been taken of these functions and, particularly, that the characteristic feature that makes them so useful for our purpose has not been pointed out. This characteristic feature is the property of internal localization, which will be discussed later in this paper. In much of the previous work that employs an expansion of energy and magneto-optical effects in powers of $\mathbf{H}$, it is not easy to see why such an expansion is sometimes justified and sometimes not. (The expansion breaks down for the de Haas–van Alphen effect and the oscillatory magneto-optical effects.) It will turn out that it is the property of internal localization of the density matrix and Green's function which is crucial for the possibility of such an expansion (be it convergent or asymptotic).

It seems to us that, quite generally, whenever the behavior of a system can be expanded in powers of $\mathbf{H}$, this should be traceable to the internal localization of some density matrix or Green's function of the system. To show this for the energy and the magneto-optical effects for $\omega < \omega_G$ of a many-fermion system in an isolated ground state is the subject of this paper. Another case for which our point can easily be proven is that of the energy of a system of particles obeying Boltzmann statistics; the density matrix of such a system at a given temperature may be obtained from the Bloch equation by integration over the inverse temperature,[11] starting from $T = \infty$, for which temperature the density matrix reduces essentially to the Dirac delta function which has perfect internal localization. Such a kind of theory could be used to extend our present work to temperatures greater than zero, assuming that the tails of the hole distribution below and the electron distribution above the energy gap can be approximated by Boltzmann distributions; but we shall leave such an extension for a future, more general approach.

The purpose of this paper is primarily a methodological one. Consequently we shall strip the theory of all features which are nonessential to our method; the electron spin will be ignored, and we shall be interested only in frequencies less than the gap frequency.[12] Also, we do not strive for mathematical rigor; on the contrary, many of our estimates will be of a highly intuitive nature. Nevertheless we hope to present reasonably convincing evidence as to the justifiability of our method and expect that, with the necessary mathematical

[5] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955); J. M. Luttinger, *ibid.* **102**, 1030 (1956).

[6] For recent work in this direction see I. M. Boswarva and A. B. Lidiard, Proc. Roy. Soc. (London) **A278**, 588 (1964); also J. Halpern, B. Lax, and Y. Nishina, Phys. Rev. **134**, A140 (1964).

[7] E. Brown, Phys. Rev. **133**, A1038 (1964), where further references will be found; also G. Eilenberger, Z. Physik **175**, 445 (1963).

[8] Further complications may be introduced by the fact that for higher energy bands the problem of band degeneracy becomes increasingly severe and the spread of the Wannier functions increasingly large; again this is analogous to the behavior of "small" systems at higher energies.

[9] For recent work in this field see A. Morita, Y. Abe, and H. Yamazaki, J. Phys. Soc. Japan **18**, 341 (1963); J. E. Hebborn, J. M. Luttinger, E. H. Sondheimer, and P. J. Stiles, J. Phys. Chem. Solids **25**, 741 (1964).

[10] L. M. Roth, Phys. Rev. **133**, A542 (1964).

[11] A. H. Wilson, Proc. Cambridge Phil. Soc. **49**, 292 (1953).

[12] Particularly for small systems there will exist, in addition, other nonabsorbing regions, but, for simplicity, we shall confine our considerations to $\omega < \omega_G$.

effort, our arguments could be put on a more rigorous basis.

We shall derive here recurrence relations for an expansion of the density matrix and Green's function in powers of the magnetic field strength. To illustrate our method it will suffice to calculate from these recurrence relations the first-order terms, i.e., the terms linear in $\mathbf{H}$. There is no contribution to the system energy linear in $\mathbf{H}$. All magneto-optical effects for $\omega < \omega_G$ may be expressed by a polarizability tensor $\boldsymbol{\alpha}$ and a gyration vector $\mathbf{G}$. The first-order contribution to $\boldsymbol{\alpha}$ disappears, but $\mathbf{G}$ is nonvanishing in this order and determines the Faraday rotation. An explicit expression for the gyration vector to first order in the magnetic field strength will be given; agreement with the orbital method and with Roth's work[10] will be shown.

2. DENSITY MATRIX AND GREEN FUNCTIONS

Let us consider a system of N electrons in a potential field $V(\mathbf{r})$. The electron spin will be ignored. We shall give various definitions and general relations concerning density matrices and Green's functions for an independent-particle model, first in the absence and then in the presence of an applied magnetic field $\mathbf{H}$.

Definitions for $H=0$

An electron in an energy eigenstate k is to have an energy $\mathcal{E}_k = \hbar\omega_k$ and is described by a wave function $\phi_k(\mathbf{r})$ obeying

$$\mathcal{3C}_0(\mathbf{r})\phi_k(\mathbf{r}) = \mathcal{E}_k\phi_k(\mathbf{r}), \tag{2.1}$$

with

$$\mathcal{3C}_0(\mathbf{r}) = \mathbf{p}^2/2m + V(\mathbf{r}), \quad \mathbf{p} = -i\hbar\boldsymbol{\nabla}. \tag{2.2}$$

The energy eigenfunctions are assumed to form a complete orthogonal set, normalized to unity over the whole system.

We assume that the system is in its ground state and that this ground state is isolated with an energy gap $\mathcal{E}_G = \hbar\omega_G \neq 0$. If we enumerate the one-particle energy eigenstates such that $\omega_k \leq \omega_l$ for $k < l$, then the states 1 through N will be occupied and all others empty.

The one-particle density matrix we shall be interested in is of the form

$$\rho_0(\mathbf{r},\mathbf{r}') = \overset{o}{\underset{k}{\sum}} \phi_k^*(\mathbf{r})\phi_k(\mathbf{r}'), \tag{2.3}$$

which is also known as Dirac zero-temperature density matrix.[13] The superscript o of the summation sign indicates summation over all occupied states, while the subscript 0 of ρ refers to the absence of any applied magnetic field. If the density matrix is known, the ground state of the system is completely described.[14]

Of further interest to us will be the function

$$G(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)$$

$$= \overset{o}{\underset{k}{\sum}}\overset{u}{\underset{l}{\sum}} [\hbar(\omega_{lk}-\omega)]^{-1}\phi_k^*(\mathbf{r})\phi_l(\mathbf{r}')\phi_k(\mathbf{r}'')\phi_l^*(\mathbf{r}'''),$$

$$(\omega < \omega_G). \tag{2.4}$$

Here $\omega_{lk} = \omega_l - \omega_k$ and the superscripts o and u of the summation signs indicate summation over all occupied and unoccupied states, respectively. This function is closely related to various types of Green's functions and, for brevity and for lack of a better name, we shall likewise call it a Green's function.

The connection of (2.4) with the double-time two-particle Green's functions of statistical physics[15] we shall illustrate on the example of the retarded Green's function

$$G_r(t_1,t_2) = (i/\hbar)\theta(t_1-t_2)\langle[A(t_1),B(t_2)]\rangle, \tag{2.5}$$

with

$$A(t_1) = \phi^\dagger(\mathbf{r},t_1)\phi(\mathbf{r}',t_1), \quad B(t_2) = \phi^\dagger(\mathbf{r}''',t_2)\phi(\mathbf{r}'',t_2). \tag{2.6}$$

Here the ϕ are wave functions in second quantization; θ is the step function; the square brackets indicate the commutator, and the angular brackets the average which, in our case, corresponds to the expectation value over the ground state of the system. The Green's function (2.5) depends then on time only through $t = t_1 - t_2$. Its Fourier transform[16] is related to (2.4) for $0 < \omega < \omega_G$ by

$$G_r(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)$$

$$= G(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) + G(\mathbf{r}''',\mathbf{r}'',\mathbf{r}',\mathbf{r};-\omega). \tag{2.7}$$

Relations to other kinds of double-time two-particle Green's functions are discussed in Ref. 3.

Projections

The function (2.4) can be connected with Green's functions in a somewhat different manner by applying the concept of projections, which will be useful later in this paper. The expansion of an arbitrary function

$$F(\mathbf{r},\mathbf{r}') = \sum_{k,l} c_{kl}\phi_k^*(\mathbf{r})\phi_l(\mathbf{r}') \tag{2.8}$$

can be split up in the form

$$F(\mathbf{r},\mathbf{r}') = \overset{2}{\underset{s,t=1}{\sum}} F_{st}(\mathbf{r},\mathbf{r}'). \tag{2.9}$$

The subscripts s and t indicate the range of summation for k and l, respectively, where a subscript value of 1 stands for a summation over all occupied states, and a value of 2 for a summation over all unoccupied states.

[13] N. H. March and A. M. Murray, Phys. Rev. **120**, 830 (1960).
[14] P.-O. Löwdin, Phys. Rev. **97**, 1474, 1490 (1955).

[15] V. L. Bonch-Bruevich and S. V. Tyablikov, *The Green's Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam 1962).
[16] This Fourier transform is 2π times that given in Ref. 15.

The functions $F_{st}(\mathbf{r},\mathbf{r}')$ are called the orthogonal projections[14] of $F(\mathbf{r},\mathbf{r}')$ on the corresponding subspaces of representation space. In supermatrix notation we may denote F_{11}, F_{22} as diagonal terms and F_{12}, F_{21} as cross terms.

As an important example, consider the Dirac δ function, which may be written as

$$\delta(\mathbf{r},\mathbf{r}') = \sum_k \phi_k^*(\mathbf{r})\phi_k(\mathbf{r}'). \qquad (2.10)$$

Obviously, the cross terms of this function are zero, while the diagonal terms δ_{11} and δ_{22} are equal to the density matrix ρ_0 defined in Eq. (2.3) and its complement $\bar{\rho}_0$, respectively. The density matrix and its complement act as projection operators:

$$\int\int \delta_{ss}(\mathbf{r},\mathbf{r}'')F(\mathbf{r}'',\mathbf{r}''')\delta_{tt}(\mathbf{r}''',\mathbf{r}')d\mathbf{r}''d\mathbf{r}'''$$
$$= F_{st}(\mathbf{r},\mathbf{r}'), \quad (s,t=1,2). \qquad (2.11)$$

The concept of projections may easily be applied also to functions of more than two variables. Of particular importance to us will be functions of four variables which we expand according to

$$F(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''')$$
$$= \sum_{k,l,m,n} c_{klmn}\phi_k^*(\mathbf{r})\phi_l(\mathbf{r}')\phi_m(\mathbf{r}'')\phi_n^*(\mathbf{r}'''). \qquad (2.12)$$

Such a function may be written as[17]

$$F(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''') = \sum_{s,t,u,v} F_{stuv}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}'''), \qquad (2.13)$$

where the subscripts s, t, u, v characterize the ranges of k, l, m, n in the expansion (2.12).

Consider now the function

$$\mathcal{G}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) = \sum_{k,l} [\hbar(\omega_{lk}-\omega)]^{-1}\phi_k^*(\mathbf{r})$$
$$\times \phi_l(\mathbf{r}')\phi_k(\mathbf{r}'')\phi_l^*(\mathbf{r}'''). \qquad (2.14)$$

This function obeys the differential equation

$$[\mathcal{K}_0^*(\mathbf{r}) - \mathcal{K}_0(\mathbf{r}') + \hbar\omega]\mathcal{G}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)$$
$$= -\delta(\mathbf{r},\mathbf{r}'')\delta(\mathbf{r}''',\mathbf{r}'), \qquad (2.15)$$

and deserves, therefore, to be called a Green's function. Actually, this Green's function is not completely defined by (2.14) because of the singularities occurring in the summation for pairs of states with $\omega_{lk}-\omega=0$. However, we shall be interested only in two projections of $\mathcal{G}$, namely $\mathcal{G}_{1212}$ and $\mathcal{G}_{2121}$. For $-\omega_G<\omega<\omega_G$, both of these projections are well-defined because the occurring ω_{lk} have ω_G as a lower bound for their magnitudes. Obviously,

$$\mathcal{G}_{1212}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) = G(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega),$$
$$\mathcal{G}_{2121}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) = -G(\mathbf{r}''',\mathbf{r}'',\mathbf{r}',\mathbf{r};-\omega). \qquad (2.16)$$

The retarded Green function in Eq. (2.7) is the difference between these two terms.

The $\mathcal{G}_{stst}$ obey differential equations which are the

[17] Throughout this paper the subscripts s, t, u, v have the range 1, 2.

corresponding projections of (2.15). They have the important property that the cross terms of the solution of the inhomogeneous differential equation

$$[\mathcal{K}_0^*(\mathbf{r}) - \mathcal{K}_0(\mathbf{r}') + \hbar\omega]g(\mathbf{r},\mathbf{r}') = f(\mathbf{r},\mathbf{r}') \qquad (2.17)$$

may be given in the form

$$g_{st}(\mathbf{r},\mathbf{r}') = -\int\int \mathcal{G}_{stst}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)$$
$$\times f(\mathbf{r}'',\mathbf{r}''')d\mathbf{r}''d\mathbf{r}''', \quad (s\neq t), \qquad (2.18)$$

as may readily be verified.

Definitions for $H\neq 0$

In the presence of an applied magnetic field the one-particle energy eigenstates will be characterized by Greek letters. An energy eigenfunction will be designated by $\psi_\kappa(\mathbf{r})$ and obeys

$$\mathcal{K}(\mathbf{r})\psi_\kappa(\mathbf{r}) = \mathcal{E}_\kappa\psi_\kappa(\mathbf{r}). \qquad (2.19)$$

In Coulomb gauge

$$\mathcal{K}(\mathbf{r}) = \mathcal{K}_0(\mathbf{r}) + (e/mc)\mathbf{A}\cdot\mathbf{p} + (e^2/2mc^2)\mathbf{A}^2. \qquad (2.20)$$

We shall assume the magnetic field $\mathbf{H}$ to be uniform and write the vector potential in the form $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{H}\times\mathbf{r}$. The density martix and the Green's function are designated by ρ and Γ and are defined according to Eqs. (2.3) and (2.4), but made up now from energy eigenfunctions and eigenvalues in the presence of $\mathbf{H}$.

Relations for ρ and Γ can be established similarly to those for ρ_0 and G. A word of caution is required, however: The projection of a function depends on the underlying set of orthogonal functions; in this paper, projections will always be understood with respect to the ϕ_k, that is, with respect to the set of one-particle energy eigenfunctions for $\mathbf{H}=0$.

3. INTERNAL LOCALIZATION

We shall give here a short discussion of the internal localization of the density matrix and the Green's function. It will suffice to consider the case where $\mathbf{H}=0$; in the presence of an applied magnetic field a similar treatment would be possible. The problem of internal localization could be approached systematically by an iteration procedure (see Ref. 3) rather similar to the one that will be developed in Secs. 4 and 5 for taking the effect of an applied magnetic field into account. Such an approach, however, would go beyond the scope of our present paper, and we shall confine ourselves to a straightforward derivation of upper bounds for the mean-square internal diameters of $|\rho_0|^2$ and $|G|^2$.

Density Matrix

We shall be interested in the dependence of $\rho_0(\mathbf{r},\mathbf{r}')$ on $(\mathbf{r}-\mathbf{r}')$. This difference might be considered as the

argument of something like an internal structure of ρ_0. The internal localization of ρ_0 may be characterized by the integrals

$$d^{(\nu)}(\hat{\kappa}) = (1/N) \int \int |\hat{\kappa} \cdot (\mathbf{r} - \mathbf{r}')|^\nu |\rho_0(\mathbf{r}, \mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}',$$
$$(\nu \geq 0), \quad (3.1)$$

where $\hat{\kappa}$ is a unit vector. Because of $d^{(0)} = 1$, Eq. (3.1) represents the mean νth power of the internal diameter of $|\rho_0|^2$ in the direction $\hat{\kappa}$. For brevity, we shall refer to $d^{(\nu)}$ also as the νth moment.

It will be illuminating to discuss the internal localization of ρ_0 for some special cases. If we consider any quantum-mechanical system of finite extension in a state where all the fermions are bound to that system, then the density matrix made up from these bound one-particle states is internally localized in a trivial manner. This property of internal localization is connected to the discreteness of the ground state by the usual identification of bound states with discrete energy levels. If the decay of the bound wave functions outside the system is of an exponential kind, as may be expected for most practical cases, then $d^{(\nu)}$ will exist, i.e., be of finite magnitude, for each finite $\nu \geq 0$. The numerical order of magnitude of $d^{(\nu)}$, however, will depend critically on the kind of system under consideration:

(a) For an atomic system the diameter of any low-energy electron orbit will be of the order of the Bohr radius, which obviously will also characterize the internal diameter of ρ_0.

(b) For a large system the situation becomes more interesting. Although the internal diameter of ρ_0 can essentially be no larger than the size of the system, it may be much smaller. For illustration, take an ideal crystal of infinite size. No "trivial" internal localization occurs in this case because the energy eigenfunctions are no longer localized to any finite region in space. Nevertheless, the density matrix of a crystal in an isolated ground state may easily be seen to be internally localized. The condition of an isolated ground state means that the crystal has to be an insulator. The $\mathcal{E}_G$ corresponds to the forbidden energy gap between the top of the highest valence band and the bottom of the lowest conduction band. The one-particle energy eigenfunctions are the Bloch waves. Expressing the Bloch waves by Wannier functions $a_n(\mathbf{r})$ and taking into account that the summation in (2.3) extends over full bands, one finds readily

$$\rho_0(\mathbf{r}, \mathbf{r}') = \sum_{n}^{o} \sum_{\mathbf{R}} a_n^*(\mathbf{r} - \mathbf{R}) a_n(\mathbf{r}' - \mathbf{R}). \quad (3.2)$$

The summation over n goes over all occupied bands, that over $\mathbf{R}$ over all lattice points. From the properties of the Wannier functions[18] we conclude that the internal

---

[18] W. Kohn, Phys. Rev. **115**, 809 (1959); E. I. Blount, Solid

localization of ρ_0 is of an exponential kind[19]; $d^{(\nu)}$ will exist then as above.

(c) For comparison, let us finally consider an ideal free fermion gas in infinite space. In this system the ground state is not discrete. It will be sufficient to consider the one-dimensional case. The one-particle energy eigenfunctions of the system are of the form e^{ikx}. Under the assumption that in the ground state of the gas all states are occupied up to $|k| = K$, the density matrix becomes

$$\rho_0(x, x') = [\pi(x - x')]^{-1} \sin[K(x - x')]. \quad (3.3)$$

For every given $K > 0$ the density matrix therefore goes to zero for $|x - x'| \to \infty$, but $d^{(\nu)}$ (for $\nu \geq 1$) does not exist, i.e., it becomes infinite for this model. Such a kind of "weak" internal localization will prove insufficient for a perturbation expansion with respect to an applied magnetic field.

The above examples offer reassurance that for a system in an isolated ground state the density matrix actually does possess the property of internal localization. Nevertheless, it is somehow unsatisfying that we should have to rely on the individual properties of one-particle states to investigate the internal localization of ρ_0. At least for $\nu = 2$, an upper bound for (3.1) can easily be established on more general grounds. Calculating $d^{(2)}(\hat{\kappa})$ by substitution of (2.3) in Eq. (3.1) and applying the closure property yields

$$d^{(2)}(\hat{\kappa}) = (2/N) \sum_{k}^{o} \sum_{l}^{u} (\hat{\kappa} \cdot \mathbf{r}_{kl})(\hat{\kappa} \cdot \mathbf{r}_{lk}). \quad (3.4)$$

Comparing this with the Thomas-Reiche-Kuhn f-sum rule

$$(2m/\hbar) \sum_{k}^{o} \sum_{l}^{u} \omega_{lk}(\hat{\kappa} \cdot \mathbf{r}_{kl})(\hat{\kappa} \cdot \mathbf{r}_{lk}) = N, \quad (3.5)$$

and taking into account that the occurring ω_{lk} have ω_G as a lower bound, we arrive at

$$d^{(2)}(\hat{\kappa}) \leq \hbar/m\omega_G. \quad (3.6)$$

As a typical case of a large energy gap, take that occurring for an hydrogen atom in its ground state. There we have $\omega_G = \frac{3}{4}\omega_I$, where $\omega_I = \hbar/2ma_0^2$ is the ionization frequency of the hydrogen atom and $a_0 = \hbar^2/me^2$ the Bohr radius; the right-hand side of (3.6) then becomes equal to $(8/3)a_0^2$. Smaller gaps, such as usually occur in crystals, will allow larger internal diameters.

Instead of comparing Eq. (3.4) with the f-sum rule,

State Phys. **13**, 305 (1962); D. S. Bulyanitsa and Yu. E. Svetlov, Fiz. Tver. Tela **4**, 1339 (1962) [English transl.: Soviet Phys.— Solid State **4**, 981 (1962)].

[19] In recent work by J. des Cloizeaux, Phys. Rev. **135**, A685, A698 (1964) the exponential character of the density matrix for an insulating crystal has been shown directly, without the detour over the Wannier functions. Actually, the density matrix occurs there as the more fundamental quantity.

one can derive with[20]

$$\mathbf{p}_{kl} = im\omega_{kl}\mathbf{r}_{kl} \tag{3.7}$$

the inequality

$$d^{(2)}(\hat{\kappa}) \le (2/m^2\omega_G{}^2 N)\sum_k{}^o (\mathbf{p}^2)_{kk}. \tag{3.8}$$

If we assume that the average kinetic energy per electron is $\lesssim \hbar\omega_I$ (which is equal to the kinetic energy of an electron in the ground state of the hydrogen atom), then we obtain

$$d^{(2)}(\hat{\kappa}) \lesssim (4\hbar/m)\omega_I\omega_G{}^{-2}. \tag{3.9}$$

Through this inequality is weaker than (3.6) and its derivation less rigorous, we shall prefer it in later applications. The reason is that (3.9) seems more indicative of the range of exponential decay of the density matrix than inequality (3.6) which is rather sensitive with respect to the particular definition (3.1) of $d^{(2)}$. While in our applications there will be attached to each density matrix $\rho_0(\mathbf{r},\mathbf{r}')$ at most a linear factor $(\mathbf{r}-\mathbf{r}')$ and no higher powers, nevertheless these factors will occur in expressions more complicated than (3.1). We shall feel safer than by resorting to the more "robust" inequality (3.9). Obviously, this distinction is relevant for small energy gaps only; for large gaps, that is $\omega_G \approx \omega_I$, inequalities (3.6) and (3.9) essentially agree.

Green's Function

The internal localization of the Green's function (2.4) may be characterized by the quantities

$$d^{(\mu,\nu)}(\hat{\kappa},\hat{\lambda};\omega) = e^{(\mu,\nu)}(\hat{\kappa},\hat{\lambda};\omega)/e^{(00)}(\omega), \tag{3.10}$$

with

$$e^{(\mu,\nu)}(\hat{\kappa},\hat{\lambda};\omega) = \int \cdots \int |\hat{\kappa}\cdot(\mathbf{r}-\mathbf{r}'')|^\mu |\hat{\lambda}\cdot(\mathbf{r}'''-\mathbf{r}')|^\nu$$

$$\times |G(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)|^2 d\mathbf{r}\cdots d\mathbf{r}''',$$

$$(\mu, \nu \ge 0), \tag{3.11}$$

where $\hat{\kappa}$ and $\hat{\lambda}$ are arbitrary vectors of magnitude unity. For $\mu = \nu = 0$ the quantity $e^{(\mu,\nu)}$ is independent of $\hat{\kappa}$ and $\hat{\lambda}$ and we therefore omit these vectors in the argument of $e^{(00)}$.

According to its definition $d^{(00)}$ is unity, while $e^{(00)}$ is found as

$$e^{(00)}(\omega) = \sum_k{}^o \sum_l{}^u [\hbar(\omega_{lk}-\omega)]^{-2}. \tag{3.12}$$

For $\mu = 0$, $\nu = 2$, one obtains, by invoking the closure property, applying (3.7), and performing some algebraic

manipulations,

$$d^{(02)}(\hat{\kappa},\hat{\lambda};\omega) \le 8\hbar^2/m\epsilon(\omega). \tag{3.13}$$

Here use has been made of Eq. (3.12) and an upper bound $1/\epsilon(\omega)$ has been introduced according to

$$\hat{\lambda}\cdot(\mathbf{pp})\cdot\hat{\lambda}/2m\hbar^2(\omega_{lN}-\omega)^2 \le 1/\epsilon(\omega), \quad (l>N). \tag{3.14}$$

The question arises if such an $\epsilon(\omega)>0$ exists. At least for cases of practical interest, the answer seems to be in the affirmative. The matrix elements of the momentum products over $2m$ in inequality (3.14) have the corresponding expectation value of the kinetic energy of a particle as an upper bound; because of the quadratic energy denominators we expect that the left-hand sides of these inequalities will have their maxima in the vicinity of the energy gap. Estimating the kinetic energy in this region as $\lesssim \hbar\omega_I$ again, we obtain

$$\epsilon(\omega) \gtrsim \hbar(\omega_G-\omega)^2/\omega_I. \tag{3.15}$$

In a similar manner we may estimate $d^{(20)}$ and arrive at

$$\left.\begin{array}{r} d^{(02)}(\hat{\kappa},\hat{\lambda};\omega) \\ d^{(20)}(\hat{\kappa},\hat{\lambda};\omega) \end{array}\right\} \lesssim \frac{8\hbar\omega_I}{m(\omega_G-\omega)^2}. \tag{3.16}$$

For $\omega = 0$ this upper bound agrees essentially with that in (3.9).

We want to emphasize that the mean-square internal diameters of the density matrix and Green's function may stay much smaller, of course, than their upper bounds. This is particularly true as far as the singular behavior of the inequalities (3.16) for $\omega \to \omega_G$ is concerned. Consider, e.g., an insulating crystal with one or more conduction and valence bands. The conduction bands are assumed to have their minima at $\mathbf{k}=0$ and to be degenerate there; a corresponding assumption is made for the maxima of the valence bands. Let us assume furthermore that, as is usually the case, the matrix elements of the momentum operator within and between the conduction bands disappear for $\mathbf{k}=0$ and similarly for the valence bands. If all bands are now parabolic in the vicinity of $\mathbf{k}=0$, it is easy to see that $e^{(00)}(\omega)$ will have no singularity for $(\omega_G-\omega) \to +0$, while $d^{(02)}$ and $d^{(20)}$ will have only logarithmic singularities.

4. PERTURBATION THEORY FOR THE DENSITY MATRIX

From the definition of the density matrix ρ, we find that it obeys the ultrahyperbolical "Schrödinger equation"

$$[\mathcal{H}^*(\mathbf{r})-\mathcal{H}(\mathbf{r}')]\rho(\mathbf{r},\mathbf{r}')=0 \tag{4.1}$$

and the idempotency condition

$$\int \rho(\mathbf{r},\mathbf{r}'')\rho(\mathbf{r}'',\mathbf{r}')d\mathbf{r}'' = \rho(\mathbf{r},\mathbf{r}'). \tag{4.2}$$

These equations are not yet in an appropriate form

---

[20] Equation (3.7), which enters also in a derivation of the f-sum rule, is known to hold if the two energy eigenfunctions involved (a) have the property that at least one of them disappears sufficiently rapidly for $|\mathbf{r}|\to\infty$, or (b) are the Bloch waves of an infinite crystal.

for a perturbation approach because for large orbits the terms containing the vector potential $\mathbf{A}(\mathbf{r})$ may not be considered as small. This difficulty may be overcome by defining a phase factor

$$\gamma(\mathbf{r},\mathbf{r}') = \exp[-ie/2\hbar c)\mathbf{H}\cdot(\mathbf{r}\times\mathbf{r}')] \qquad (4.3)$$

and performing the transformation

$$\rho(\mathbf{r},\mathbf{r}') = \gamma(\mathbf{r},\mathbf{r}')\tau(\mathbf{r},\mathbf{r}'). \qquad (4.4)$$

The phase factor introduced is the same as that used by Sondheimer and Wilson[21] in the treatment of the diamagnetism of free electrons.

The function τ is found to obey the equations

$$[\mathcal{H}_0(\mathbf{r})-\mathcal{H}_0(\mathbf{r}')]\tau(\mathbf{r},\mathbf{r}')$$
$$- (e/2mc)\mathbf{H}\cdot[(\mathbf{r}-\mathbf{r}')\times(\mathbf{p}-\mathbf{p}')]\tau(\mathbf{r},\mathbf{r}')=0 \qquad (4.5)$$

and

$$\int \exp[Q(\mathbf{r},\mathbf{r}',\mathbf{r}'')]\tau(\mathbf{r},\mathbf{r}'')\tau(\mathbf{r}'',\mathbf{r}')d\mathbf{r}''=\tau(\mathbf{r},\mathbf{r}'), \qquad (4.6)$$

where

$$Q(\mathbf{r},\mathbf{r}',\mathbf{r}'') = (ie/2\hbar c)\mathbf{H}\cdot(\mathbf{r}\times\mathbf{r}'+\mathbf{r}'\times\mathbf{r}''+\mathbf{r}''\times\mathbf{r}). \qquad (4.7)$$

The sum of cross products in the last equation may also be written as $(\mathbf{r}-\mathbf{r}'')\times(\mathbf{r}'-\mathbf{r}'')$, and we see that the position vectors occurring explicitly in Eqs. (4.5) and (4.6) are combined now in the form of differences. This, together with the internal localization of τ, furnishes the basis to our perturbation approach.

Recurrence Relations

We shall expand τ in a power series in $\mathbf{H}$:

$$\tau(\mathbf{r},\mathbf{r}') = \sum_{\nu=0}^{\infty} \tau^{(\nu)}(\mathbf{r},\mathbf{r}'). \qquad (4.8)$$

Substituting this expansion in Eqs. (4.5) and (4.6), we may compare equal powers of $\mathbf{H}$ in each of these equations. The equations in zero order, or equivalently, for $\mathbf{H}=0$, are obviously satisfied by

$$\tau^{(0)}(\mathbf{r},\mathbf{r}') = \rho_0(\mathbf{r},\mathbf{r}'). \qquad (4.9)$$

For $\nu=1,\ 2,\ \cdots$ we obtain then certain recurrence relations. The cross terms of $\tau^{(\nu)}$ we shall calculate from Eq. (4.5) and the diagonal terms from (4.6). Comparison with Eq. (2.18) shows that the cross terms of the solution of (4.5) are given by

$$\tau_{st}^{(\nu)}(\mathbf{r},\mathbf{r}') = -(e/2mc)\int\int \mathcal{G}_{stst}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';0)$$
$$\times[\mathbf{H}\cdot(\mathbf{r}''-\mathbf{r}''')\times(\mathbf{p}''-\mathbf{p}''')]$$
$$\times\tau^{(\nu-1)}(\mathbf{r}'',\mathbf{r}''')d\mathbf{r}''d\mathbf{r}''', \qquad (s\neq t). \quad (4.10)$$

The product in Eq. (4.6) will give rise to a sum of terms from which the two terms containing $\tau^{(\nu)}$ can be separated; if we use (4.9) and form the diagonal parts according to (2.11), we obtain

$$\tau_{ss}^{(\nu)}(\mathbf{r},\mathbf{r}') = \mp \sum_{\kappa=0}^{\nu} \sum_{\lambda,\mu=0}^{\nu-1} \delta_{\nu,\kappa+\lambda+\mu}\frac{1}{\kappa!}\int\int\int [Q(\mathbf{r}'',\mathbf{r}''',\mathbf{r}^{iv})]^{\kappa}$$
$$\times\delta_{ss}(\mathbf{r},\mathbf{r}'')\tau^{(\lambda)}(\mathbf{r}'',\mathbf{r}^{iv})\tau^{(\mu)}(\mathbf{r}^{iv},\mathbf{r}''')$$
$$\times\delta_{ss}(\mathbf{r}''',\mathbf{r}')d\mathbf{r}''d\mathbf{r}'''d\mathbf{r}^{iv}. \qquad (4.11)$$

The upper sign stands for $s=1$, the lower sign for $s=2$. Because of time reversal symmetry, the $\tau_{st}^{(\nu)}$ obey the relation

$$\tau_{st}^{(\nu)}(\mathbf{r},\mathbf{r}') = (-1)^{\nu}\tau_{ts}^{(\nu)}(\mathbf{r}',\mathbf{r}). \qquad (4.12)$$

Equations (4.10) and (4.11) are recurrence relations from which, starting with (4.9), the $\tau^{(\nu)}$ can be successively calculated. The first-order term $\tau^{(1)}$ is given in Eq. P(9).[22] The expression in the first bracket there may be written as $\bar{\rho}_0(\mathbf{r}'',\mathbf{r}''')-\rho_0(\mathbf{r}'',\mathbf{r}''')$, where the $\bar{\rho}_0$ comes from $\tau_{11}^{(1)}$ and the $-\rho_0$ from $\tau_{22}^{(1)}$. In the second bracket the first Green's function originates from $\tau_{12}^{(1)}$, the second (including the minus sign) from $\tau_{21}^{(1)}$.

Estimates

To estimate the size of the $\tau_{st}^{(\nu)}(\mathbf{r},\mathbf{r}')$, let us consider the integrals

$$D_{st}^{(\nu)} = (1/N)\int\int |\tau_{st}^{(\nu)}(\mathbf{r},\mathbf{r}')|^2 d\mathbf{r}d\mathbf{r}'. \qquad (4.13)$$

In zero order we find $D_{11}^{(0)}=1$, while the other components vanish. As far as the diagonal parts of the first-order term are concerned, we consider the square root of the right-hand side of (3.9) as an approximate upper bound for each occurring factor of position vector differences and expect then,[23] for $s=t$,

$$D_{st}^{(1)} \lesssim (2\omega_C\omega_I/\omega_G^2)^2, \qquad (4.14)$$

where $\omega_C=eH/mc$ is the cyclotron frequency of a free electron and $H=|\mathbf{H}|$. In the cross terms of first order, we estimate the position vector difference as before, and the momentum operators as $\lesssim \hbar/a_0$. Substituting these cross terms in (4.13), one sees easily that each Green's function may contribute at most a factor $1/\mathcal{E}_G$, and the resulting upper bound for $D_{st}^{(1)}(s\neq t)$ is then, up to an irrelevant numerical factor of $\frac{1}{2}$, the same as in (4.14). From the combinations of density matrices and Green's functions occurring in the expression for $\tau^{(1)}$ and the fact that the upper bounds in (3.9) and (3.16) (for $\omega=0$) agree with each other, we shall expect the same upper bound to be approximately valid again for the mean-square internal diameter of $\tau_{st}^{(1)}$. Once the properties of $\tau^{(1)}$ have been established we may proceed along similar lines to an investigation of $\tau^{(2)}$, etc.

[21] E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) A210, 173 (1951).

[22] That is, Eq. (9) of P (Ref. 2).
[23] The internal diameter of $\bar{\rho}_0$ is obviously the same as that of ρ_0.

For our perturbation expansion for the density matrix to be useful we have to require $D_{st}^{(1)} \ll 1$; according to (4.14) this will be satisfied for magnetic fields weak enough that

$$\omega_C \ll \omega_G^2/\omega_I. \qquad (4.15)$$

It might be of interest to compare this condition for H with what we should anticipate from a consideration of the orbitals. Application of a magnetic field causes the edges of the energy gap to shift. The effect of the magnetic field on the ground state of the system will be expected to be obtainable by a perturbation theoretical approach if these shifts are small compared to the size of the energy gap.

For small systems like atoms or molecules, the diameter of the orbit of a one-particle state with an energy in the vicinity of the energy gap will be assumed to have the square root of the right-hand side of (3.9) as an upper bound. Estimating the magnitude of the momentum as $\lesssim \hbar/a_0$, we obtain from the term linear in H in the Hamiltonian (2.20) an edge shift $\lesssim \hbar\omega_C\omega_I/\omega_G$. This upper bound for the shift to be small compared to $\mathscr{E}_G$ requires $\omega_C \ll \omega_G^2/\omega_I$, which agrees with (4.15). The term in (2.20) quadratic in H yields a shift $\lesssim \hbar\omega_C^2\omega_I/\omega_G^2$; this results in the condition $\omega_C \ll (\omega_G^3/\omega_I)^{1/2}$, which is not stronger than (4.15).

For a crystal in an approximation linear in H, there are two contributions to the shift of a band edge: One is caused by the quasifree behavior of an electron and will be written as $eH/2m^*c$, where m^* is the effective electron mass; the other is due to its intracellular properties and is given by $\pm\frac{1}{2}g^*\beta H$ where g^* is the spectroscopic splitting factor and $\beta = e\hbar/2mc$ the Bohr magneton. Since both m/m^* and $\frac{1}{2}g^*$ are of the order ω_I/ω_G (or smaller), the resulting shift is $\lesssim \hbar\omega_C\omega_I/\omega_G$, which again leads to (4.15).

System Energy

Once the density matrix is known, the total energy of the system may easily be calculated from

$$E = \int [\mathscr{3C}(r')\rho(r,r')]_{r'=r}\,dr. \qquad (4.16)$$

Substitution of (4.4) gives the energy in the form

$$E = \int [\mathscr{3C}_0(r')\tau(r,r')]_{r'=r}\,dr, \qquad (4.17)$$

which no longer contains any large perturbations.

Substitution of (4.8) results in an expansion of E in powers of H. The terms of odd order disappear because of time-reversal degeneracy, as may be seen by use of (4.12).

5. PERTURBATION THEORY FOR THE GREEN FUNCTION

From the definition of Γ one can derive various equations satisfied by the Green's function. It will turn out that the inhomogeneous differential equation

$$[\mathscr{3C}^*(r) - \mathscr{3C}(r') + \hbar\omega]\Gamma(r,r',r'',r''';\omega)$$
$$= -\rho(r,r'')\bar\rho(r''',r'), \quad (5.1)$$

together with the homogeneous integral equations of the first kind

$$\int \bar\rho(r,r^{iv})\Gamma(r^{iv},r',r'',r''';\omega)\,dr^{iv} = 0, \qquad (5.2a)$$

$$\int \rho(r^{iv},r')\Gamma(r,r^{iv},r'',r''';\omega)\,dr^{iv} = 0 \qquad (5.2b)$$

is sufficient for a perturbation calculation of Γ. Here ρ is the density matrix in the presence of the magnetic field and $\bar\rho(r,r') = \delta(r,r') - \rho(r,r')$.

We define a function K by

$$\Gamma(r,r',r'',r''';\omega) = \gamma(r,r'')\gamma(r''',r')K(r,r',r'',r''';\omega), \qquad (5.3)$$

where the phase factors γ are given in (4.3). Substitution of (5.3) into (5.1) and (5.2) give for K the equations

$$\{\mathscr{3C}_0(r) - \mathscr{3C}_0(r') + \hbar\omega - (e/2mc)H\cdot[(r-r'')\times p - (r'''-r')\times p'] + (e^2/8mc^2)[H\times(r-r'')]^2$$

$$- (e^2/8mc^2)[H\times(r'''-r')]^2\}K(r,r',r'',r''';\omega) = -\tau(r,r'')\bar\tau(r''',r'), \quad (5.4)$$

$$\int \exp[Q(r,r'',r^{iv})]\bar\tau(r,r^{iv})K(r^{iv},r',r'',r''';\omega)\,dr^{iv} = 0, \qquad (5.5a)$$

$$\int \exp[Q(r^{iv},r''',r')]\tau(r^{iv},r')K(r,r^{iv},r'',r''';\omega)\,dr^{iv} = 0, \qquad (5.5b)$$

where $\bar\tau(r,r') = \delta(r,r') - \tau(r,r')$. As in Eqs. (4.5) and (4.6), the position vectors operating on K enter in the form of differences only; combined with the internal localization of ρ_0 and G, this furnishes the basis to our perturbation approach.

Recurrence Relations

Let us expand K in a power series in $\mathbf{H}$:

$$K(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) = \sum_{\nu=0}^{\infty} K^{(\nu)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega). \tag{5.6}$$

For the zero-order term we take

$$K^{(0)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) = G(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega). \tag{5.7}$$

Obviously G, as defined in Eq. (2.4), satisfies Eqs. (5.4) and (5.5) for $\mathbf{H}=0$. Substituting (5.6) and comparing equal powers of $\mathbf{H}$, we obtain then from Eqs. (5.4) and (5.5) certain sets of equations. To solve these equations in the form of recurrence relations for $K^{(\nu)}$ we have to decompose $K^{(\nu)}$ in its components according to (2.13). From Eq. (5.4) we get[17]

$$\sum_{u,v} K_{12uv}^{(\nu)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) = -\int\int G(\mathbf{r},\mathbf{r}',\mathbf{r}^{iv},\mathbf{r}^v;\omega)f^{(\nu)}(\mathbf{r}^{iv},\mathbf{r}^v,\mathbf{r}'',\mathbf{r}''';\omega)d\mathbf{r}^{iv}d\mathbf{r}^v, \tag{5.8}$$

with

$$f^{(\nu)}(\mathbf{r},\mathbf{r},'\mathbf{r}'',\mathbf{r}''';\omega) = (e/2mc)\mathbf{H}\cdot[(\mathbf{r}-\mathbf{r}'')\times\mathbf{p} - (\mathbf{r}'''-\mathbf{r}')\times\mathbf{p}']K^{(\nu-1)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) - (e^2/8mc^2)$$

$$\times\{[\mathbf{H}\times(\mathbf{r}-\mathbf{r}'')]^2 - [\mathbf{H}\times(\mathbf{r}'''-\mathbf{r}')]^2\}K^{(\nu-2)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) - \sum_{\mu=0}^{\nu}\tau^{(\mu)}(\mathbf{r},\mathbf{r}'')\bar{\tau}^{(\nu-\mu)}(\mathbf{r}''',\mathbf{r}'), \tag{5.9}$$

where for $\nu=1$ the second term on the right has to be omitted. Here $\tau^{(\nu)}$ is defined in (4.8), and the $\bar{\tau}^{(\nu)}$ are given by

$$\bar{\tau}^{(0)}(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r},\mathbf{r}') - \tau^{(0)}(\mathbf{r},\mathbf{r}') = \bar{\rho}_0(\mathbf{r},\mathbf{r}'),$$

$$\bar{\tau}^{(\nu)}(\mathbf{r},\mathbf{r}') = -\tau^{(\nu)}(\mathbf{r},\mathbf{r}'), \quad (\nu=1,2,\cdots). \tag{5.10}$$

In Eqs. (5.5) we split off the term with $\mu=\nu$ and obtain

$$\sum_{t,u,v} K_{2tuv}^{(\nu)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) = -\sum_{\kappa,\lambda=0}^{\nu}\sum_{\mu=0}^{\nu-1}\delta_{\nu,\kappa+\lambda+\mu}\frac{1}{\kappa!}\int[Q(\mathbf{r}'',\mathbf{r}^{iv})]^\kappa\bar{\tau}^{(\lambda)}(\mathbf{r},\mathbf{r}^{iv})K^{(\mu)}(\mathbf{r}^{iv},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)d\mathbf{r}^{iv}, \tag{5.11a}$$

$$\sum_{s,u,v} K_{s1uv}^{(\nu)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega) = -\sum_{\kappa,\lambda=0}^{\nu}\sum_{\mu=0}^{\nu-1}\delta_{\nu,\kappa+\lambda+\mu}\frac{1}{\kappa!}\int[Q(\mathbf{r}^{iv},\mathbf{r}''',\mathbf{r}')]^\kappa\tau^{(\lambda)}(\mathbf{r}^{iv},\mathbf{r}')K^{(\mu)}(\mathbf{r},\mathbf{r}^{iv},\mathbf{r}'',\mathbf{r}''';\omega)d\mathbf{r}^{iv}. \tag{5.11b}$$

Because of time-reversal symmetry the components of $K^{(\nu)}$ are related by

$$K_{stuv}^{(\nu)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)$$
$$= (-1)^\nu K_{uvst}^{(\nu)}(\mathbf{r}'',\mathbf{r}''',\mathbf{r},\mathbf{r}';\omega). \tag{5.12}$$

It is easy to see how Eqs. (5.8) and (5.11) complement each other; Eqs. (5.11) are unable to give a projection $K_{1212}^{(\nu)}$, which is provided, however, by Eq. (5.8). To obtain $K^{(\nu)}$ as a sum over all projections, we have to allow for the fact that Eqs. (5.11a) and (5.11b) overlap: the terms $K_{21uv}^{(\nu)}$ occur in each of these equations. Suppressing the arguments, we may write, for instance,

$$K^{(\nu)} = \sum_{u,v} K_{11uv}^{(\nu)} + \sum_{u,v} K_{12uv}^{(\nu)}$$
$$+ \sum_{t,u,v} K_{2tuv}^{(\nu)}. \tag{5.13}$$

Here the second term is given by Eq. (5.8) and the third term by (5.11a). The first term is a projection of Eq. (5.11b) and may be calculated from this equation by applying the appropriate projection operator.

Equations (5.8) and (5.11) are recurrence relations from which, starting with (5.7), the components of $K^{(\nu)}$ can be successively calculated. $K^{(1)}$ has been written out in Ref. 2.

Estimates

Investigating the size of the $K^{(\nu)}$, we could consider each component separately, as was done in the preceding section for the density matrix, but we shall confine ourselves to a discussion of

$$D^{(\nu)}(\omega) = \int\cdots\int|K^{(\nu)}(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)|^2$$
$$\times d\mathbf{r}\cdots d\mathbf{r}'''/e^{(00)}(\omega). \tag{5.14}$$

Here $e^{(00)}(\omega)$ is given in (3.12) and, trivially, one finds $D^{(0)}(\omega) = 1$. In an estimate of $D^{(1)}(\omega)$, one has to take into account that the magnitude of the Green's function and also its internal diameters depend on ω. For ω close to ω_G we shall expect then the dominant contribution to come from the double integral in $K^{(1)}$ (see Ref. 2). Substituting this double integral into (5.14), it is easy to see that each of the Green's functions containing $\mathbf{r}$ and $\mathbf{r}'$ as the first two arguments contributes at most a factor $1/(\mathscr{E}_G - \hbar\omega)$. We shall estimate the effect of each momentum operator by a factor $\lesssim \hbar/a_0$, and the position vector differences according to (3.16). This results in

$$D^{(1)}(\omega) \lesssim [2\omega_C\omega_I/(\omega_G-\omega)^2]^2. \tag{5.15}$$

From the remaining terms in $K^{(1)}$ those containing Q will make contributions to (5.14), the approximate upper bounds of which will be smaller by a factor $[(\omega_G-\omega)/\omega_G]^2$; those containing $\tau^{(1)}$ will lead to approximate upper bounds smaller by the square of this factor. If ω is not close to the gap frequency, i.e., if $(\omega_G-\omega)$ is of the same order of magnitude as ω_G, all these upper bounds will agree with each other and also with the upper bound for $D^{(1)}$ in (4.14).

For our perturbation expansion of the Green's function to be useful, requires $D^{(1)}(\omega)\ll1$. According to (5.15) this will be guaranteed if

$$\omega_C\ll(\omega_G-\omega)^2/\omega_I. \qquad (5.16)$$

One may ask again how this is compatible with the shift of the edges of the energy gap due to the magnetic field. We expect a necessary condition for a perturbation theoretical treatment of the Green's function to be that the edge shift is small compared to $(\omega_G-\omega)$, because otherwise ω_G would no longer be a useful approximation for the width of the energy gap in the presence of $\mathbf{H}$. The edge shift has been estimated in the preceding section to be $\lesssim \hbar\omega_C\omega_I/\omega_G$, which results in the condition $\omega_C\ll(\omega_G-\omega)\omega_G/\omega_I$. This inequality is weaker than (5.16); if the "expandability condition" (5.16) holds, the "edge shift condition" is satisfied *a fortiori*. It is possible, however, that the inequality (5.16) is unnecessarily stringent.

6. MAGNETO-OPTICAL PHENOMENA

We consider a macroscopically homogeneous system like a gas or a crystal in the presence of an applied static and homogeneous magnetic field. The system is assumed to possess a frequency region in which no absorption of electromagnetic radiation occurs. For an electromagnetic field with a frequency ω in that region, the dielectric displacement $\mathbf{D}$ may then be connected with the electric-field component $\mathbf{E}$ and its time derivative according to[24]

$$\mathbf{D}=\varepsilon\mathbf{E}+(1/\omega)\mathbf{G}\times\partial\mathbf{E}/\partial t. \qquad (6.1)$$

Here $\mathbf{G}$ is the gyration vector, and $\varepsilon=1+4\pi\alpha$ is the dielectric tensor, with α the polarizability tensor. In a system with cubic symmetry—important in practical application—the dielectric constant ϵ is a scalar, and $\mathbf{G}$ will have a nonvanishing component only along the direction of the applied magnetic field; this component we designate by G. The gyration vector leads to a Faraday rotation $\theta=\omega G/2c\bar{n}$, with $\bar{n}=\frac{1}{2}(n_++n_-)$, where $n_{\pm}=(\epsilon\pm G)^{1/2}$ is the index of refraction for right and left circularly polarized radiation, respectively. Our further considerations will not be restricted, however, to systems of any particular symmetry.

From semiclassical radiation theory, one obtains in the electric dipole approximation, for a system of volume V,

$$\alpha=\frac{e^2}{m^2\hbar V}\sum_\kappa^o\sum_\lambda^u\frac{\mathbf{P}_{\kappa\lambda}\mathbf{P}_{\lambda\kappa}+\mathbf{P}_{\lambda\kappa}\mathbf{P}_{\kappa\lambda}}{\omega_{\lambda\kappa}(\omega_{\lambda\kappa}^2-\omega^2)}, \qquad (6.2)$$

$$\mathbf{G}=-\frac{4\pi i e^2}{m^2\hbar\omega V}\sum_\kappa^o\sum_\lambda^u\frac{\mathbf{P}_{\kappa\lambda}\times\mathbf{P}_{\lambda\kappa}}{\omega_{\lambda\kappa}^2-\omega^2}, \qquad (6.3)$$

where $\mathbf{P}=\mathbf{p}+(e/c)\mathbf{A}$ is the kinetic momentum operator.

Polarizability Tensor

In (6.2) we make use of

$$\mathbf{P}_{\lambda\kappa}=im\omega_{\lambda\kappa}\mathbf{r}_{\lambda\kappa}, \qquad (6.4)$$

and it is then easy to see that the polarizability tensor may be written as

$$\alpha=-(2e^2/V)\int\Gamma_r(\mathbf{r},\mathbf{r},\mathbf{r}',\mathbf{r}';\omega)(\mathbf{r}-\mathbf{r}')(\mathbf{r}-\mathbf{r}')d\mathbf{r}d\mathbf{r}', \qquad (6.5)$$

where Γ_r is defined as in (2.7) but made up from Green's functions in the presence of $\mathbf{H}$. The position vectors enter the dyadic product only in the form of differences, which permits an expansion of α in powers of $\mathbf{H}$ by virtue of the internal localization of Γ. Because of (5.3), Eq. (6.5) remains correct if Γ_r is replaced by $K_r(\mathbf{r},\mathbf{r},\mathbf{r}',\mathbf{r}';\omega)$, where K_r is defined by

$$K_r(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)=K(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)$$
$$+K(\mathbf{r}''',\mathbf{r}'',\mathbf{r}',\mathbf{r};-\omega). \qquad (6.6)$$

A general method for the calculation of $K^{(\nu)}$ has been given in the preceding section and α in this sense is calculable up to arbitrary order in $\mathbf{H}$, but we are interested here only in first-order terms. However, in an expansion of α in powers of $\mathbf{H}$, the term linear in the magnetic field disappears, as do all other terms of odd order, because of (5.12). Consequently, we shall hereafter ignore α and concentrate on the gyration vector which is known to have a nonvanishing contribution linear in $\mathbf{H}$.

Gyration Vector

In the above expression for the gyration vector we could substitute (6.4) and, by application of the closure property, rewrite (6.3) to show the correct low-frequency dependence, i.e., proportionality to ω for $\omega\to0$, which gives a Faraday rotation proportional to ω^2.[6] For later comparison with other methods it will, however, be advantageous to retain $\mathbf{G}$ as given in (6.3), which leads to Eq. P(6).[25] Further substitution of

[24] J. Frenkel, Z. Physik **36**, 215 (1926).

[25] Notice that for frequencies in the nonabsorbing region the Fourier transform of the causal Green's function is identical with that of the retarded Green's function (2.5).

(5.3) yields

$$G = -(2\pi i e^2/m^2\omega^2 V)\int\int\{[\mathbf{p}'\times\mathbf{p}''+\tfrac{1}{2}(e/c)(\mathbf{H}\times(\mathbf{r}'-\mathbf{r}''))\times(\mathbf{p}'+\mathbf{p}'')]K_r(\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''';\omega)\}_{\mathbf{r}=\mathbf{r}',\mathbf{r}'''=\mathbf{r}''}d\mathbf{r}'d\mathbf{r}''. \quad (6.7)$$

Note again the dependence on $(\mathbf{r}'-\mathbf{r}'')$, which allows an expansion of G in powers of $\mathbf{H}$. In such an expansion the terms of even order in $\mathbf{H}$ disappear because of time-reversal symmetry. To obtain $G^{(1)}$, the contribution to G linear in $\mathbf{H}$, one has to act with the cross product of momentum vectors in (6.7) on $K_r^{(1)}$, and with the triple cross product on $K_r^{(0)}$, where $K_r^{(\nu)}$ is the term of order ν in an expansion of K_r in powers of the strength of the magnetic field; $K^{(0)}$ is given in Eq. (5.7), and $K^{(1)}$ in Ref. 2.

Relating to the existing literature, we wish to note that the possibility of expressing transport coefficients (of which the magneto-optical coefficients α and G are examples) by Green's functions is, of course, well known.[26] The novel feature here is the perturbation expansion of the Green's function with respect to the magnetic field and the consequent expansion of the magneto-optical coefficients.

For later applications it will be convenient to expand $K^{(\nu)}$ and $\tau^{(\nu)}$ according to (2.12) and (2.8), respectively.[27] Decomposing the gyration vector into a, b, and c terms,

$$G^{(1)} = G^{(1a)} + G^{(1b)} + G^{(1c)}, \quad (6.8)$$

and defining an operator ξ by its matrix elements

$$\xi_{kl} = \begin{cases} \mathbf{r}_{kl} & \text{for } k\leq N, \ l>N; \ \text{or } k>N, \ l\leq N; \\ 0 & \text{otherwise}, \end{cases} \quad (6.9)$$

we arrive, with the abbreviations

$$C = 2\pi i e^3/m^3 c\hbar^2\omega V, \quad (6.10)$$

$$\tau_{lk} = (\omega_{lk}^2 - \omega^2)^{-1}, \quad (6.11)$$

after some calculation and use of time-reversal symmetry, at

$$G^{(1a)} = -mC\left(\sum_k{}^o\sum_l{}^u - \sum_l{}^o\sum_k{}^u\right)\tau_{lk}\{\hbar(\mathbf{H}\times\xi_{kl})\times\mathbf{p}_{lk}+i\sum_n[(\mathbf{p}_{kl}\times\mathbf{p}_{ln})\mathbf{H}\cdot(\xi\times\xi)_{nk}-\sum_j(\mathbf{p}_{jl}\times\mathbf{p}_{ln})\mathbf{H}\cdot(\xi_{nk}\times\xi_{kj})]\}$$

$$-2C\left(\sum_k{}^o\sum_{l,n}{}^u - \sum_{l,n}{}^o\sum_k{}^u\right)(\tau_{lk}/\omega_{nk})(\mathbf{p}_{kl}\times\mathbf{p}_{ln})\mathbf{H}\cdot(\mathbf{p}\times\xi-\xi\times\mathbf{p})_{nk}, \quad (6.12a)$$

$$G^{(1b)} = -C\left(\sum_{k,n}{}^o\sum_l{}^u - \sum_l{}^o\sum_{k,n}{}^u\right)(\omega_{lk}+\omega_{ln})\tau_{lk}\tau_{ln}[(\mathbf{p}_{kl}\times\mathbf{p}_{ln})\mathbf{H}\cdot(\xi\times\mathbf{p})_{nk}-2\sum_j(\mathbf{p}_{kl}\times\mathbf{p}_{lj})\mathbf{H}\cdot(\xi_{jn}\times\mathbf{p}_{nk})], \quad (6.12b)$$

$$G^{(1c)} = (iC/m)\left(\sum_{k,n,j}{}^o\sum_l{}^u - \sum_l{}^o\sum_{k,n,j}{}^u\right)(\omega_{lk}\omega_{ln}+\omega_{lk}\omega_{lj}+\omega_{ln}\omega_{lj}+\omega^2)\tau_{lk}\tau_{ln}\tau_{lj}(\mathbf{p}_{kl}\times\mathbf{p}_{ln})\mathbf{H}\cdot(\mathbf{p}_{nj}\times\mathbf{p}_{jk}). \quad (6.12c)$$

The grouping into a, b, and c terms has been performed according to the possible singular behavior of the terms for $\omega\to\omega_G$: the a terms contain one factor τ_{lk}, the b terms two, the c term three. We say "possible singular behavior" because the occurrence of n such τ factors does not necessarily result in a pole of order n; depending on the behavior of the matrix elements involved, the pole could be of a lower order or there could occur no infinity at all.

The derived expressions for G, and particularly for $G^{(1)}$, are the main result of this paper. They hold for any system in an isolated ground state. Note that

Eqs. (6.12)—and the same is true for the energy representation of $\tau^{(1)}$ and $K^{(1)}$—contain no large terms in the sense that the matrix elements of ξ may be estimated from (3.7) and that the occurring τ_{lk} are bounded for given $\omega(<\omega_G)$. The matrix elements of $\mathbf{p}$ can, of course, become large, but—at least for cases of practical interest—we expect this to be accompanied by large energy differences and, therefore, small τ_{lk}, such that the high energy states should not cause any difficulties.

7. COMPARISONS

In this section we shall compare our result, Eqs. (6.12), first with that obtained from nondegenerate one-particle perturbation theory, then with that of

[26] An application of the Green's-function method to magneto-optical phenomena has been given by G. Ciobanu and L. Bányai, Phys. Status Solidi 3, 2299 (1963).

[27] $\tau^{(1)}$ and $K^{(1)}$ in energy representation are given in Ref. 3.

Roth[10] for a crystal. These comparisons are performed in more detail in Ref. 3.

Assuming that the effect of the applied magnetic field on each orbital may be obtained by nondegenerate perturbation theory one finds from Eq. (6.3), in first-order approximation,

$$G^{(1)} = -C[i\hbar(\sum_{k}^{o}\sum_{l}^{u}-\sum_{l}^{o}\sum_{k}^{u})(\tau_{lk}/\omega_{lk})(\mathbf{H}\times\mathbf{p}_{kl})\times\mathbf{p}_{lk}$$

$$+ (\sum_{k,n}^{o}\sum_{l}^{u}-\sum_{l}^{o}\sum_{k,n}^{u})(\omega_{lk}+\omega_{ln})\tau_{lk}\tau_{ln}(\mathbf{p}_{kl}\times\mathbf{p}_{ln})\mathbf{H}\cdot\mathbf{M}_{nk}-2(\sum_{k}^{o}\sum_{l,n}^{u}-\sum_{l,n}^{o}\sum_{k}^{u})(\tau_{lk}/\omega_{nk})(\mathbf{p}_{kl}\times\mathbf{p}_{ln})\mathbf{H}\cdot\mathbf{M}_{nk}], \quad (7.1)$$

where $\mathbf{M}$ is the angular-momentum operator. This is essentially the method applied by Serber[4] to Faraday rotation by molecules. On the other hand, after some manipulations one obtains the same expression by adding the contributions to $G^{(1)}$ in Eqs. (6.12). The results of the two methods agree therefore.

To compare our result with that of Roth for an ideal infinite crystal, we have to take (6.12) in crystal-momentum representation. The energy eigenfunctions are now the Bloch waves. Taking into account that the z component of the gyration vector is related to the xy component of the antisymmetric part of the conductivity tensor according to

$$G_z = (4\pi/\omega)\sigma_{xy}, \quad (7.2)$$

we may derive from (6.8) and (6.12) an expression for σ_{xy} which becomes identical with Roth's result if applying her Eq. (45)[10] to an insulating crystal at zero temperature and neglecting spin.

8. DISCUSSION

The problem posed for this work was to find a general approach to magneto-optical effects in the nonabsorbing region; the results achieved for small systems (treated by application of perturbation theory to each individual orbital) as well as those for insulating crystals (Roth[10]) should be contained as special cases. The required agreement of the gyration vector (6.12) with both the results of nondegenerate one-particle perturbation theory and Roth's method has been indicated in the preceding section.

It turned out, however, that the result of the nondegenerate orbital method represents not merely a special case of (6.12) but is identical with it whenever (3.7) holds, whether the application of nondegenerate perturbation theory is justified or not. In an extension of that, we are inclined to think that almost any formally correct perturbation approach based on an expansion in powers of $\mathbf{H}$ will give the correct final result.[28] This suggests consideration of our problem from two different angles:

From a pragmatic point of view it will be sufficient to obtain the correct result and to ignore the question of the justifiability of the method. One might as well then choose the simplest possible approach, which is probably that of nondegenerate perturbation theory applied to the one-particle energy eigenstates. This approach is formally possible, e.g., even for an infinite crystal: from Eq. (7.1) we may go to Eqs. (6.12), which in crystal-momentum representation lead to Roth's Eq. (45).[10] No new theoretical approaches are required then and all it takes is a rearranging of terms.

From a methodic-theoretical point of view, on the other hand, we wish to refrain from introducing any unwarranted assumptions and shall require the perturbation caused by the magnetic field to be small in every step of the calculation. Our Green's-function method, based on the internal localization of the density matrix and the Green's function, seems to satisfy this requirement both for small systems (atoms, molecules) and for crystals.

Atoms, molecules, and ideal insulating crystals are, of course, not the only systems covered by our theory. Another case of interest to which Eqs. (6.12) apply is that of an impurity atom in an insulating crystal. Faraday rotation due to a bound donor electron has so far been discussed only for a very simple model.[29]

The gyration vector can be calculated either from (6.7) or from (6.12). The first choice requires a knowledge of the density matrix and Green's function of the system (for $\mathbf{H}=0$), while the latter equations make direct use of the one-particle energy eigenstates (also for $\mathbf{H}=0$). The two methods are intimately related, since the density matrix and Green's function can be built up from the one-particle states. The primary obstacle in evaluating $G^{(1)}$ is represented by the fact that, even in the absence of the magnetic field, the complete set of orbitals—or, equivalently for (6.7), the exact expressions for density matrix and Green's function—are known only for the simplest physical models. A rigorous calculation of the magneto-optical coefficients is therefore out of the question at present. For ω close to ω_G, however, or if the energy gap itself

[28] Although we have performed no explicit calculations in this direction, we believe this to be true also for the energy of the system, i.e., for the problem of normal diamagnetism.

[29] I. M. Boswarva, R. E. Howard, and A. B. Lidiard, Proc. Roy. Soc. (London) **A269**, 125 (1962).

is small, the dominant contribution is usually given by the states in the vicinity of the gap, and the properties of these states are frequently well known. In the Green's function formalism these dominating states give rise to certain dominating expressions for the zero-magnetic-field density matrix and Green's function.

From the form of Eqs. (6.12) one might expect that for $\omega \rightarrow \omega_G$ the leading contribution to the gyration vector comes from (6.12c), but this is not necessarily so. Take, for example, a crystal model as discussed in the last paragraph of Sec. 3. Each one of the two matrix elements in the last cross product in (6.12c) becomes a homogeneous linear function of the components of $\mathbf{k}$ (for $\mathbf{k}$ small) and vanishes, therefore, for $\mathbf{k}=0$. This reduces the singularity of $\mathbf{G}^{(1c)}$ to that of $\mathbf{G}^{(1b)}$, i.e., proportionality to $(\omega_G-\omega)^{-1/2}$ for $(\omega_G-\omega) \rightarrow +0$. Actually, it is only the first term in (6.12b) which shows this kind of singularity, while the second term has no infinity in the indicated limit. For the crystal model under discussion, the dominant behavior of the gyration vector for frequencies close to the gap frequency is, therefore, determined by $\mathbf{G}^{(1c)}$ and the first term of $\mathbf{G}^{(1b)}$ in (6.12).

While in the present paper the Green's-function method has been introduced primarily for methodological reasons, Green's functions are of advantage also in the actual calculation of specific problems. In a treatment of magneto-optical effects in insulating crystals with multiple valence and conduction bands at frequencies close to the gap frequency it can be shown, e.g., that the dominating part of the Green's function may be written in a form which is covariant with respect to unitary transformations among the basis functions characterizing the edges of the valence bands or the conduction bands, respectively. This facilitates calculation of the dominating behavior of the gyration vector, and we anticipate reporting about this subject in a later paper.

The model on which our considerations have been based and the results we have derived can easily be extended and generalized. Explicit expressions for effects depending on higher powers of the magnetic field, like diamagnetism or Voigt effect, can readily be derived from our general formalism. An extension of our model to include spin effects is straightforward. Finally, by the very nature of our approach as a Green's-function method, it should lend itself—with appropriate modifications—to take particle interactions into account.

Superconductivity of Nb₃Ge

B. T. Matthias,* T. H. Geballe, R. H. Willens,† E. Corenzwit, and G. W. Hull, Jr.

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 1 March 1965; revised manuscript received 3 May 1965)

Evidence is presented to show that the maximum transition temperature of compounds with the β-W type structure ($A15$) occurs at the stoichiometric composition A_3B, when B is a nontransition element. The niobium-germanium A15-type compound, which normally forms with excess Nb, has a transition temperature of 6.9°K. It has been found that Nb₃Ge compounds prepared by rapid-quench techniques, in the presence of excess germanium, have transition temperatures as high as 17°K. This large increase in transition temperature is attributed to a closer approach to the stoichiometric 3:1 composition.

THIS paper reports experimental results which indicate that the maximum transition temperature of compounds with the β-W type structure ($A15$) generally occurs at the stoichiometric composition, A_3B. In this structure type the A atom is a transition metal of the 4th, 5th, or 6th column of the periodic table and the B atom is either a transition or a nontransition metal. The effect of varying the composition on the transition temperature has been reported for several A15-type compounds in which B is a nontransition metal.[1] These include V₃Si, V₃Ga, Nb₃Al, and

Nb₃Sn. It is always the stoichiometric compound which has the maximum transition temperature.

In order to illustrate the fact that the maximum T_c occurs at the ideal composition, the A15-type compound Nb₃Ge was investigated. This compound is isoelectronic with Nb₃Sn but its transition temperature is considerably lower. Geller[2] pointed out that the lattice constant of 5.168 Å for an Nb₃Ge compound as reported by Carpenter and Searcy[3] was larger than his predicted value of 5.12 Å and suggested that the β-W type phase did not have the correct stoichiometry. Carpenter[4] examined the composition range of Nb₃Ge and found

[1] B. W. Roberts, *Progress in Cryogenics*, edited by K. Mendelssohn (Academic Press Inc., New York, 1964), Vol. 4, p. 159.

[2] S. Geller, Acta Cryst. **9**, 885 (1956).

[3] J. H. Carpenter and A. W. Searcy, J. Am. Chem. Soc. **78**, 2079 (1956).

[4] J. H. Carpenter, J. Phys. Chem. **67**, 2141 (1963).