The values of $g_\perp$ are very near the theoretical value of $4g$, the slightly lower value for the trichloride possibly being due to the influence of the doublet for which $J_z = \pm\frac{3}{2}$. Such an effect suggests that the splitting of the ground level of Cm^{3+} is smaller in the trichloride than in the ethylsulfate, a result analogous to that for Gd^{3+} in the two crystals.[3] This is also suggested by a number of weak, highly anisotropic, lines in the spectrum of the trichloride, some of which may arise from transitions between higher components of the ground level. These are now being investigated.

The present work, by showing the spurious nature of the earlier observations, eliminates what had become a serious difficulty in the theory; at the same time, it provides an important datum, namely, the Landé g value of the ground level of Cm^{3+} that should be valuable in fixing the degree of intermediate coupling both for Cm^{3+} and, by extrapolation, for later members of the actinide series.

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Weak-Coupling Rate Equations and Initial Conditions*

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Irreversible rate equations for the diagonal and off-diagonal elements of the density matrix are derived in the weak-coupling, long-time approximation for two types of crystal perturbations—electrons scattering from random impurities, and spin-spin interactions. No initial random phase assumption on the density matrix is necessary in the derivation using the random perturbation. For the spin-spin interactions, a "partial" initial random phase assumption is introduced and used in a natural way. It is shown, alternatively, that if one takes into account the very extensive cancellation of terms for the vast majority of unperturbed energy states, no initial restrictions need be placed on the majority of the density matrix elements. In all three cases the equations obtained are the same, being Pauli equations for the diagonal density matrix elements, but simpler relaxation-oscillation equations for the off-diagonal elements.

I. INTRODUCTION

THERE has been considerable interest in the past several years in developing rate equations describing irreversible behavior in many-body systems. The most complete of such equations are the so-called "generalized master equations," which have been obtained by Prigogine and Résibois,[1] Van Hove,[2] Janner,[3] and Swenson.[4] The Prigogine-Résibois equations, and the equations obtained earlier by the Prigogine group,[1] apply to gases with interaction, and describe the evolution in time of the diagonal and off-diagonal elements of the density matrix in the quantum-mechanical case. Special initial conditions, but not the random phase assumption, are used. The Van Hove-Janner-Swenson equations apply to any system but describe the time-dependence of the quantities $U_{ij}U^\dagger_{ji}$ ("transition probabilities") and $U_{ij}U^\dagger_{ki}$ ("interference terms"), where $U(t) = \exp(-iH't/\hbar)$ is the time evolution operator, H' is the total Hamiltonian, and subscript indices denote

matrix elements in an unperturbed energy representation. The initial conditions for the transition probabilities and interference terms are given by the definition of $U(t)$.

The equations mentioned above have the following common property. In spite of the different initial conditions, the density matrix elements, transition probabilities, and interference terms all have Markoffian, irreversible behavior in the weak-coupling, long-time limits.[2,3,5] Specifically, they all are given by Pauli equations.[6]

The purpose of this paper is to examine the role of initial conditions, and the form of the irreversible rate equations, for two specific but quite different interactions in crystals. We derive rate equations for the density matrix elements in the $\lambda^2 t$ limit (defined below). In each case the Pauli equation obtains for the diagonal density matrix elements but not for the off-diagonal density matrix elements. The first example treats a random perturbation, and it is shown that no initial random phase assumption on the density matrix is necessary. The second example treats spin-spin interactions, and we show that either of two methods may be used to

[1] I. Prigogine and P. Résibois, Physica 27, 629 (1961). This paper contains references to the earlier work of the Prigogine group.
[2] L. Van Hove, Physica 23, 441 (1957).
[3] A. Janner, Helv. Phys. Acta 35, 47 (1962).
[4] R. J. Swenson, J. Math. Phys. 3, 1017 (1962).
[5] P. Résibois, Phys. Rev. Letters 5, 411 (1960).
[6] L. Van Hove, Physica 21, 517 (1955).

obtain a description of irreversible behavior. In the one case, since a complete random phase assumption is too restrictive, we introduce and use in a natural way a *partial* random phase assumption. Alternatively, we show that if one takes into account the very extensive cancellation of terms for the vast majority of unperturbed energy states, no conditions need be placed on the initial values of the majority of the density matrix elements. Philippot[7] has recently discussed the role of random phase assumptions[8] and initial conditions.

The mathematical analysis is very similar to that of Van Hove[6] and so we shall in most instances indicate the techniques only very briefly. The starting point is the quantum-mechanical Liouville equation

$$-i\hbar d\rho(t)/dt = [\rho(t), H'],$$

where ρ is the density matrix. The formal solution for $\rho(t)$ is

$$\rho(t) = U(t)\rho(0)U^\dagger(t). \tag{1}$$

With the Hamiltonian written as $H' = H + \lambda V$, where H is the unperturbed part, λV is the perturbation, and λ characterizes the size of the perturbation, the evolution operator $U(t)$ may be expanded as

$$U(t) = e^{-iHt/\hbar} + \sum_{n=1}^{\infty} (-i\lambda/\hbar)^n$$

$$\times \int_0^t dt_n \cdots \int_0^{t_2} dt_1\, e^{-iH(t-t_n)/\hbar} V \cdots$$

$$\times V e^{-iH(t_2-t_1)/\hbar} V e^{-iHt_1/\hbar}. \tag{2}$$

An alternate and very convenient expansion of $U(t)$ is one in terms of its diagonal part.[6] However, we shall not use that expansion explicitly. We choose V so that it has no diagonal elements in the unperturbed energy representation; that is, all diagonal elements of H' comprise H. The $\lambda^2 t$ limit is defined by the conditions $\lambda \to 0$, $t \to \infty$, $\lambda^2 t$ finite. Only those terms which do not vanish in this limit are retained.

II. RATE EQUATIONS FOR ELECTRON-IMPURITY PERTURBATIONS

In this section, we consider perturbations corresponding to the interaction of independent electrons with randomly located impurities. This interaction was considered by Kohn and Luttinger[9] in obtaining a steady-state solution to the Liouville equation. The random nature of the perturbation necessitates an addi-

tional averaging over the positions of the impurities. This feature allows the derivation of the rate equations for the density matrix elements without use of a random phase assumption.

The normalized eigenfunctions for a free electron in a cubical volume $\Omega = L^3$ with periodic boundary conditions are

$$\psi_k = \Omega^{-1/2} \exp(i\mathbf{k}\cdot\mathbf{r}).$$

The allowed values of $k_\alpha (\alpha = x, y, z)$ are $2\pi n_\alpha/L$, with n_α any integer or zero. The electron interacts with each of $\mathfrak{N}$ randomly located scatterers at positions $\mathbf{r}_i$, with a finite range potential $\varphi(\mathbf{r}-\mathbf{r}_i)$. The matrix elements of λV are thus

$$\lambda V_{kk'} = \Omega^{-1}\Phi_{kk'} \sum_j \exp[-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_j],$$

where

$$\Phi_{kk'} = \int d\mathbf{r}\, \varphi(\mathbf{r}) \exp[-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}].$$

The matrix elements of H are

$$H_{kk} = \hbar^2 k^2/2m + (\mathfrak{N}/\Omega)\int d\mathbf{r}\, \varphi(\mathbf{r}).$$

The statistical properties of V may be illustrated by the second-order terms

$$\lambda^2\langle (VAV)_{kk'}\rangle = \delta_{kk'}c\Omega^{-1}\sum_{k''}|\Phi_{kk''}|^2 A_{k''k''}, \tag{3}$$

and

$$\lambda^2\langle (VBV)_{kk'}\rangle = c\Omega^{-1}\sum_{k''}|\Phi_{kk''}|^2 B_{k'',k''+k'-k}, \tag{4}$$

where $c = \mathfrak{N}/\Omega$ is the density of impurities, A is a diagonal operator, and B is an operator with off-diagonal elements. The bracket symbol $\langle\ \rangle$ represents an average over the positions of the impurities.

Equation (3), when referred to infinite volume, exhibits the diagonal singularity property, first discussed by Van Hove.[6] The properties (3) and (4) have been used by Prigogine and Toda[10] in a derivation of rate equations for time-averaged density matrix elements. They obtained Pauli equations for the off-diagonal elements, whereas, in the $\lambda^2 t$ limit, we do not.

We consider first the rate equations for the off-diagonal elements. Let the nth order term in the expansion (2) of $U(t)$ be denoted by $U_n(t)$. The essential characteristics of the general term in the expansion of $\rho(t)$ by means of Eqs. (1) and (2), are illustrated by the second-order terms. One such term is, for $\mathbf{k}\neq\mathbf{k}'$,

$$[U_2(t)\rho(0)U_0^\dagger(t)]_{kk'}$$

$$= -(\lambda^2 c/\hbar^2\Omega)\rho_{kk'}(0)e^{-i\omega_{kk'}t}\sum_{k''}|\Phi_{kk''}|^2$$

$$\times \int_0^t dt_2 \int_0^{t_2} dt_1 \exp[i\omega_{kk''}(t_2-t_1)], \tag{5}$$

where $\omega_{kk'} = (k^2 - k'^2)\hbar/2m$, and Eq. (3) has been used. As $\Omega \to \infty$, the summation is replaced by integration

[7] J. Philippot, Physica **27**, 490 (1961).

[8] The phrase "random phase assumption" may be used in more than one sense. We apply it here only to the phases of the probability amplitudes for the eigenstates forming the basis representation, that is, to the density matrix elements. In some of the above references, it is also applied to the phases appearing in the perturbation matrix elements. These two types of phases are not related.

[9] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957); **109**, 1892 (1958).

[10] I. Prigogine and M. Toda, Mol. Phys. **1**, 48 (1958).

according to the scheme

$$\sum_{k''} \rightarrow (\Omega/8\pi^3)\int d\mathbf{k}''.$$

Carrying out the time integrations in Eq. (5), one obtains in the $\lambda^2 t$ limit

$$[U_2(t)\rho(0)U_0^\dagger(t)]_{kk'} = -\tfrac{1}{2}\lambda^2 t \tilde{W}_k \rho_{kk'}(0)e^{-i\omega_{kk'}t}, \quad (6)$$

where

$$\tilde{W}_k = \frac{c}{8\pi^3}\int d\mathbf{k}'' \,|\Phi_{kk''}|^2\frac{2}{\hbar^2}\Big[\pi\delta(\omega_{kk''})+iP\Big(\frac{1}{\omega_{kk''}}\Big)\Big], \quad (7)$$

and $\delta(\omega)$ and $P(1/\omega)$ are the delta and principal-value functions, respectively.

The second-order term $[U_1(t)\rho(0)U_1^\dagger(t)]_{kk'}$, however, has a different character. Using Eqs. (2) and (4), one obtains

$$[U_1(t)\rho(0)U_1^\dagger(t)]_{kk'}$$
$$= (\lambda^2 c/\hbar^2\Omega)e^{-i\omega_{kk'}t}\sum_{k''}|\Phi_{kk''}|^2\rho_{k''k'''}(0)$$

$$\times \int_0^t dt_1 \int_0^t dt_1' \,\exp[i\omega_{kk''}t_1 + i\omega_{k'''k'}t_1'], \quad (8)$$

with $\mathbf{k}''' \equiv \mathbf{k}''+\mathbf{k}'-\mathbf{k}$. Now if all values of $\mathbf{k}''$ in Eq. (8) could contribute in the $\lambda^2 t$ limit, a volume-independent term similar to Eq. (6) would result. However, only those values of $\mathbf{k}''$ satisfying $k^2-k''^2=k'^2-(\mathbf{k}''+\mathbf{k}'-\mathbf{k})^2$ can make a $\lambda^2 t$ contribution. That is, for infinite volume, the allowed range of integration over say k_z'', for given k_x'' and k_y'', is infinitesimal, and the contribution from Eq. (8) vanishes.

The generalization to arbitrary order for the off-diagonal elements of $\rho(t)$ is simple. One sees that it is never possible to couple V's from opposite sides of $\rho(0)$ because of the restrictions placed upon the intermediate states, as in Eq. (8). Hence U and $U^\dagger$ make $\lambda^2 t$ contributions separately. Further, since the $\lambda^2 t$ contributions to $[U_n(t)]_{kk'}$ come only from the pairing of adjacent V's, n must be even, and $\mathbf{k}'$ must equal $\mathbf{k}$. A typical term of order $2n$ is

$$[U_{2n-2r}\rho(0)U_{2r}^\dagger]_{kk'}$$
$$= \rho_{kk'}(0)e^{-i\omega_{kk'}t}\frac{(-\lambda^2 t\tilde{W}_k/2)^{n-r}(-\lambda^2 t\tilde{W}_{k'}^*/2)^r}{(n-r)!r!}.$$

On summing r from 0 to n, and n from 0 to ∞, one obtains the final result

$$\rho_{kk'}(t) = \rho_{kk'}(0)\exp[-i\omega_{kk'}t - \tfrac{1}{2}\lambda^2 t(\tilde{W}_k + \tilde{W}_{k'}^*)], \quad (9)$$

where $\tilde{W}_{k'}^*$ is the complex conjugate of $\tilde{W}_{k'}$, defined by Eq. (7).

Equation (9) is the off-diagonal solution to the Liouville equation in the $\lambda^2 t$ limit, for a perturbation characterizing an electron scattering from randomly located impurities. The motion is simple oscillation and relaxation. The real part of the exponent is $\tfrac{1}{2}(W_k+W_{k'})$, apart from the $\lambda^2 t$, where W_k, defined by

$$W_k \equiv \mathrm{Re}\{\tilde{W}_k\} = \int d\mathbf{k}'' \,(c/8\pi^3)|\Phi_{kk''}|^2(2\pi/\hbar^2)\delta(\omega_{kk''}),$$

is the total transition probability per unit time out of, or into, state ψ_k. Thus $\rho_{kk'}(t)$ relaxes at a rate equal to the average total transition rate out of states ψ_k and $\psi_{k'}$.

The rate equations for the diagonal density matrix elements are obtained in a similar way. Consider, for example, the fourth-order term containing

$$V_{kk_1}V_{k_1k_2}\rho_{k_2k_3}(0)V_{k_3k_4}V_{k_4k},$$

where $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$, and $\mathbf{k}_4$ are to be summed over. When the average over impurities is taken, only three classes of terms remain, for which (1) $\mathbf{k}_3=\mathbf{k}_2=\mathbf{k}$; (2) $\mathbf{k}_3=\mathbf{k}_2$, $\mathbf{k}_4=\mathbf{k}_1$; (3) $\mathbf{k}_3=\mathbf{k}_2$, $\mathbf{k}_4=\mathbf{k}-\mathbf{k}_1+\mathbf{k}_2$. Only classes (1) and (2) contribute in the $\lambda^2 t$ limit. Note that in all three cases, only the diagonal elements of $\rho(0)$ appear. This is a general result, in any order; that is, the diagonal elements of $\rho(t)$ depend only on the diagonal elements of $\rho(0)$. This being the case, the subsequent analysis becomes identical to that of Van Hove,[6] and we need not reproduce it here. In the $\lambda^2 t$ limit, the diagonal elements satisfy the Pauli equation

$$d\rho_{kk}(t)/dt = \sum_{k'} W_{kk'}[\rho_{k'k'}(t)-\rho_{kk}(t)], \quad (10)$$

where $W_{kk'}$ is the transition probability per unit time, given by

$$W_{kk'} = 2\pi\hbar^{-2}c\Omega^{-1}|\Phi_{kk'}|^2\delta(\omega_{kk'}).$$

The Pauli equation for the diagonal density matrix elements, and Eq. (9) for the off-diagonal density matrix elements, are thus obtained without a random phase assumption on the density matrix, and in fact without any statement at all about initial conditions. This, however, is not surprising, because of the random nature of the perturbation. Two systems with the same initial condition but with different distributions of impurities will evolve differently in time. When an average is taken over all such systems, it is clear that the initial condition is unimportant.

III. RATE EQUATIONS FOR SPIN-SPIN INTERACTIONS

In this section we consider interactions between spin particles. For definiteness we give a specific, typical Hamiltonian, although to establish the argument it will not be necessary to write out the matrix elements in all their detail. We take the dipolar and exchange interactions plus an external magnetic field term (Zeeman energy):

$$H' = \sum_{i<j} D_{ij}[\mathbf{S}^i\cdot\mathbf{S}^j - 3(\mathbf{S}^i\cdot\mathbf{n}^{ij})(\mathbf{S}^j\cdot\mathbf{n}^{ij})]$$
$$- 2\sum_{i<j} J_{ij}\mathbf{S}^i\cdot\mathbf{S}^j - g\beta\mathcal{3C}\sum_j S_z^j. \quad (11)$$

Here D_{ij} and J_{ij} are the dipolar and exchange coupling parameters, respectively, $\mathbf{S}^i$ is the spin operator for particle i, $\mathbf{n}^{ij}$ is the unit vector from i to j, g is the spectroscopic splitting factor, β is the Bohr or nuclear magneton, $\mathcal{3C}$ is a magnetic field in the z direction, and the sums $\sum_{i<j}$ are over all pairs of particles. The number of spins is N.

This Hamiltonian, plus a possible Stark splitting term, is the basis for the usual treatment of spin-spin relaxation.[11] There it is common to take the Zeeman energy term, together with all the interaction terms commuting with it, as the unperturbed Hamiltonian, the remaining terms being chosen as the perturbation. However, we shall here take as the perturbation all the off-diagonal matrix elements of the Hamiltonian in the so-called free-spin representation, that is, the complete set of states formed as products of the eigenstates of the $S_z{}^i$. For simplicity we discuss only spin-$\frac{1}{2}$ particles.

As seen by taking matrix elements of Eq. (11), there are two classes of perturbation matrix elements, corresponding to the single-flip and double-flip processes. ($S_z{}^i$ only multiplies the state of particle i by a coefficient, whereas $S_x{}^i$ and $S_y{}^i$ also "flip" the state.) Let $|\theta\rangle$ represent an arbitrary product of free-spin states. By $|j\theta\rangle$ we will mean the state differing from $|\theta\rangle$ only by the flip of spin j, with similar meanings for $|jk\theta\rangle$, etc. A single-flip perturbation matrix element can be written in the form

$$\langle\theta|V|j\theta\rangle=\sum_{k(\neq j)}g(\theta;j,k), \qquad (12)$$

and is the sum of $N-1$ terms, corresponding to the number of pairs of one particle with all the others. There are N such matrix elements. A double-flip matrix element may be written

$$\langle\theta|V|jk\theta\rangle=f(\theta;j,k); \qquad (13)$$

it contains only one term, corresponding to a given pair of particles. There are $\frac{1}{2}N(N-1)$ such matrix elements.

The perturbation so chosen has the diagonal singularity property, as we now indicate. One easily sees that $\langle\theta|V^2|\theta\rangle$ has of the order of N^3 terms (of which N^3 are single-flip terms and N^2 are double-flip terms), whereas $\langle\theta|V^2|j\theta\rangle$, $\langle\theta|V^2|jk\theta\rangle$, $\langle\theta|V^2|jkm\theta\rangle$, and $\langle\theta|V^2|jkmn\theta\rangle$ have of the order of N^2, N^2, N, and 1 terms, respectively, all other matrix elements of V^2 vanishing. Thus $\langle\theta|V^2|\theta'\rangle$ is larger by at least a factor of the order of N for $|\theta\rangle=|\theta'\rangle$ than otherwise.

Of course, the magnitude of a term decreases with increasing separation between the particles, but this does not change the relative orders in N of the matrix elements of V^2. There is, however, another reason for arguing that the classification of the matrix elements of V^2 strictly according to the number of terms they contain is unsatisfactory. Briefly, this is because many of the terms in a matrix element of V^2 can be positive or negative, and for most states $|\theta\rangle$, a very extensive cancellation of terms will occur, lowering the order in N.

[11] W. J. Caspers, Physica **26**, 778, 798, 809 (1960).

We shall examine the consequences of this effect later in the section.

First we consider the classification of powers of V according to the number of terms in their matrix elements, regardless of any cancellation. The second-order term (in λ) of the form

$$\langle\theta|U_2(t)\rho(0)U_0{}^\dagger(t)|\theta'\rangle,$$

where $|\theta'\rangle$ may be equal to $|\theta\rangle$, contains the products

$$\langle\theta|V^2|\theta''\rangle\langle\theta''|\rho(0)|\theta'\rangle \qquad (14)$$

multiplied by time-dependent exponential functions, which we need not indicate explicitly. When the summation on $|\theta''\rangle$ is carried out over the five classes of non-vanishing matrix elements of V^2, given above, and if no restrictions are placed on the corresponding five sets of matrix elements of $\rho(0)$, it is seen that, the diagonal singularity condition notwithstanding, the classes of states $|jk\theta\rangle$, $|jkm\theta\rangle$, and $|jkmn\theta\rangle$, make contributions larger than those of the classes $|\theta\rangle$ and $|j\theta\rangle$ by a factor of N. The latter two each contribute about N^3 terms. Thus as $N\to\infty$, the terms which can give a $\lambda^2 t$ contribution, namely, $\langle\theta|V^2|\theta\rangle\langle\theta|\rho(0)|\theta'\rangle$, are negligible. The same effect occurs also in the second-order term

$$\langle\theta|U_1(t)\rho(0)U_1{}^\dagger(t)|\theta'\rangle,$$

as the reader can easily show, and in all higher order terms. Therefore, there is no possibility of describing irreversible behavior in the $\lambda^2 t$ limit if no restrictive conditions are placed on $\rho(0)$. This is not surprising, but it should be contrasted with the results of the previous section for random perturbations.

If we impose the random phase assumption, that is, assert that $\rho(0)$ is diagonal, then $\langle\theta|\rho(t)|\theta\rangle$ satisfies the Pauli equation in the $\lambda^2 t$ limit since Van Hove's derivation then applies directly. But the random phase assumption is clearly too strong a condition here, for it eliminates the possibility of describing the "transverse" magnetization or spin. That is, the ensemble averages of $\sum_i S_x{}^i$ and $\sum_i S_y{}^i$ are described by means of off-diagonal elements of the form $\langle\theta|\rho(t)|j\theta\rangle$, (or equivalently $\langle j\theta|\rho(t)|\theta\rangle$), and only these. We may say that in this case, and in most other cases, the "unperturbed" energy representation is not the "representation of the observables," and hence the random phase assumption is too restrictive.

However, we see that if a *partial* initial random phase assumption is used, corresponding to assuming random phases only between pairs of states which play no role in determining expectation values or ensemble averages of the dynamical observables, then, in the present case at least, irreversible rate equations in the $\lambda^2 t$ limit *can* be obtained. In the present case, the partial random phase assumption corresponds to setting all matrix elements of $\rho(0)$ equal to zero except those of the form $\langle\theta|\rho(0)|\theta\rangle$ and $\langle\theta|\rho(0)|j\theta\rangle$.

To illustrate, we consider the second-order term (14)

for the diagonal elements of $\rho(t)$. The summation over $|\theta''\rangle$, with $|\theta'\rangle = |\theta\rangle$, goes only over the classes of states $|\theta\rangle$ and $|j\theta\rangle$, which, as we have seen, each contribute about the same number of terms. Thus as $N \to \infty$, the $\lambda^2 t$ terms are not negligible compared to the remaining terms.

The complete diagonal density matrix element may be written, with the partial random phase assumption,

$$\langle\theta|\rho(t)|\theta\rangle = \langle\theta|U(t)|\theta\rangle\langle\theta|\rho(0)|\theta\rangle\langle\theta|U^\dagger(t)|\theta\rangle$$
$$+\sum_j \langle\theta|U(t)|j\theta\rangle\langle j\theta|\rho(0)|\theta\rangle\langle\theta|U^\dagger(t)|\theta\rangle$$
$$+\sum_j \langle\theta|U(t)|\theta\rangle\langle\theta|\rho(0)|j\theta\rangle\langle j\theta|U^\dagger(t)|\theta\rangle. \quad (15)$$

The summation on j goes over the N particles of the system. The diagonal singularity condition ensures that the first term on the right gives, in the $\lambda^2 t$ limit, the right side of the Pauli equation. The second and third terms can make no $\lambda^2 t$ contributions since they each contain a product of a diagonal matrix element of $U(t)$ [or $U^\dagger(t)$] with a nondiagonal matrix element of $U^\dagger(t)$ [or $U(t)$]. But also important is the fact that since $\langle\theta|U(t)|\theta\rangle$ is larger by a factor of N than $\langle\theta|U(t)|j\theta\rangle$, for any given order in λ, the three terms on the right in Eq. (15) are of the same order in N. Thus, the Pauli equation obtains for $\langle\theta|\rho(t)|\theta\rangle$ when the partial random phase assumption is used.

The only off-diagonal density matrix elements of interest are of the form $\langle\theta|\rho(t)|j\theta\rangle$. Again, we illustrate the procedure with the second-order terms. Equation (14), with $|\theta'\rangle = |j\theta\rangle$, may be written when summed on $|\theta''\rangle$, again with omission of the time-dependent parts,

$$\langle\theta|V^2|\theta\rangle\langle\theta|\rho(0)|j\theta\rangle + \langle\theta|V^2|j\theta\rangle\langle j\theta|\rho(0)|j\theta\rangle$$
$$+\sum_{k(\neq j)} \langle\theta|V^2|jk\theta\rangle\langle jk\theta|\rho(0)|j\theta\rangle. \quad (16)$$

The first and third terms are of order N^3 and the second is of order N^2. Only the first term contributes in the $\lambda^2 t$ limit and is not negligible as $N \to \infty$.

However, the second-order term

$$\langle\theta|U_1(t)\rho(0)U_1^\dagger(t)|j\theta\rangle \quad (17)$$

makes *no* contribution in the $\lambda^2 t$ limit: Dropping the time-dependent terms again, we write Eq. (17) as

$$\sum_k \langle\theta|V|k\theta\rangle\langle k\theta|\rho(0)|\theta\rangle\langle\theta|V|j\theta\rangle$$
$$+\sum_{k(\neq j)} \langle\theta|V|k\theta\rangle\langle k\theta|\rho(0)|kj\theta\rangle\langle kj\theta|V|j\theta\rangle$$
$$+\sum_{k(\neq j)} \langle\theta|V|j\theta\rangle\langle j\theta|\rho(0)|kj\theta\rangle\langle kj\theta|V|j\theta\rangle \quad (18)$$

plus terms of lower order in N. Each of the three terms in Eq. (18) is of order N^3, that is, of the same order as the term in Eq. (16) making the $\lambda^2 t$ contribution. Only the first term in Eq. (18) can make a $\lambda^2 t$ contribution, but then only for $k = j$. [Note that the function $\exp(-i\omega_{\theta,j\theta}t)$, which multiplies every term in $\langle\theta|\rho(t)|j\theta\rangle$, is necessary for obtaining this $\lambda^2 t$ contribution.] The result is of order N^2 and hence negligible compared to the contributing term in Eq. (16).

The extension to arbitrary order parallels the derivation of the off-diagonal rate equations in the pre-

ceding section. With the partial random phase assumption, Eq. (1) becomes

$$\langle\theta|\rho(t)|j\theta\rangle = \sum_{\theta'} \langle\theta|U(t)|\theta'\rangle\langle\theta'|\rho(0)|\theta'\rangle\langle\theta'|U^\dagger(t)|j\theta\rangle$$
$$+\sum_{\theta'}\sum_k \langle\theta|U(t)|\theta'\rangle$$
$$\times\langle\theta'|\rho(0)|k\theta'\rangle\langle k\theta'|U^\dagger(t)|j\theta\rangle. \quad (19)$$

One can see that it is not possible to pair V's from opposite sides of $\rho(0)$, as in the above example, and thus that the $\lambda^2 t$ contributions come only from the diagonal elements of $U(t)$ and $U^\dagger(t)$. The noncontributing terms, for given order in λ, are of the same order in N as the contributing terms. Omitting the former, one can write Eq. (19) as

$$\langle\theta|\rho(t)|j\theta\rangle = \langle\theta|U(t)|\theta\rangle\langle j\theta|U^\dagger(t)|j\theta\rangle\langle\theta|\rho(0)|j\theta\rangle,$$

which reduces to the same rate equation as given by Eq. (9), the techniques of reduction being just the same as those leading to Eq. (9).

We turn now to the alternate classification of the matrix elements of powers of V, alluded to earlier. Consider, for example, the quantity $\langle\theta|V^2|\theta\rangle$. From the single-flip terms, Eq. (12), one obtains

$$\sum_j |\langle\theta|V|j\theta\rangle|^2 = \sum_j\sum_{k(\neq j)} |g(\theta; j,k)|^2$$
$$+\sum_j\sum_{k(j\neq)}\sum_{m(\neq j,k)} g^*(\theta; jk)g(\theta; j,m),$$

and from the double-flip terms, Eq. (13), one obtains

$$\sum_{j<k} |\langle\theta|V|jk\theta\rangle|^2 = \sum_{j<k} |f(\theta; j,k)|^2.$$

There are thus N^2 positive definite terms coming from both the single-flip and double-flip terms, and N^3 single-flip terms arising from products referring to different pairs of particles. The latter may be positive or negative, and for "typical" states $|\theta\rangle$ one can expect a very large degree of cancellation of terms. If $|\theta\rangle$ is such that these cross-product terms have about an equal chance of being positive or negative, one would expect that their sum would be of order $N^{3/2}$ rather than N^3. This type of argument is equivalent to the random phasing discussed and criticized by Philippot.[7]

It is important to recognize the distinction between this type of randomness assumption and that of the preceding section. There, the different members of the ensemble of systems are assumed to have different distributions of impurities. Here the members of the ensemble are identical. The sign of a term referring to a given pair of particles and a given spin state is the same for all members of the ensemble, and has no randomness attached to it. The argument is that the signs (phases) are "effectively random" for most states because of the very many degrees of freedom involved. Obviously, the argument cannot be defended very strongly.

Nevertheless, for the purpose of determining the results of the argument, we shall now proceed as if the signs of the terms in the perturbation matrix elements were strictly random. Clearly, there will then be some states $|\theta\rangle$ for which the deduced motion of $\langle\theta|\rho(t)|\theta\rangle$ and $\langle\theta|\rho(t)|j\theta\rangle$ will be far from the actual motion. However,

when one determines ensemble averages of the spin operators, thereby summing over all states, those relatively few states for which the matrix elements of $\rho(t)$ do not have "typical" behavior, could be expected to be unimportant.

The diagonal singularity condition still holds under the assumption of random signs. One finds that $\langle\theta| V^2 |\theta\rangle$, $\langle\theta| V^2 | j\theta\rangle$, $\langle\theta| V^2 | jk\theta\rangle$, $\langle\theta| V^2 | jkm\theta\rangle$, and $\langle\theta| V^2 | jkmn\theta\rangle$ are of order N^2, N, N, $N^{1/2}$, and 1, respectively. In order that the $\lambda^2 t$ contributions not be made negligible as $N \to \infty$, it must also be true that $\langle\theta| V^2 |\theta\rangle$ is of the same order as $\sum_{\theta'} \langle\theta| V^2 |\theta'\rangle$. That this is true is readily verified.

With these results, the rate equations may be obtained in a manner similar to that in the preceding section, and we need not repeat the details. One obtains precisely the same equations for $\langle\theta| \rho(t) |\theta\rangle$ and $\langle\theta| \rho(t) | j\theta\rangle$ as by the earlier considerations of this section involving use of the partial random phase assumption on the initial density matrix elements.

IV. DISCUSSION

For each of the perturbations considered in this paper, we have obtained in the weak-coupling, long-time approximation, Pauli equations for the diagonal density matrix elements, and equations of the type (9) for the off-diagonal elements. For the random perturbation of Sec. II, no initial random phase assumption was needed in the derivation of these equations. A partial random phase assumption, in the case of spin-spin interactions, was shown to be a sufficient condition for obtaining these equations. Alternately, it was shown, for spin-spin interactions, that no initial statements need be made about the density matrix elements, if one accepts the assumption that the phases in the perturbation matrix elements can be treated as random.

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Effect of Elastic Strain on Interband Tunneling in Sb-Doped Germanium*

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The effects of uniaxial compression and of hydrostatic pressure on the direct and indirect tunneling processes in germanium tunnel diodes have been studied experimentally under forward and reverse bias at 4.2°K and compared with Kane's theory. The diodes were formed by alloying indium doped with $\frac{3}{8}\%$ gallium on (100) and (110) faces of germanium bars containing an antimony concentration of $5.5 \times 10^{18}/cm^3$. The first order change of the tunneling current with stress was measured at fixed bias voltages. For biases smaller than 8 mV the current is direct and not affected by the relative shifts of the (111) conduction band valleys. In the bias range of indirect tunneling the anisotropic tunneling from the (111) valleys was observed in agreement with theory. In the range of direct tunneling to the (000) conduction band the current change is correlated with the stress induced change of the direct band gap and of the energy separation between the (111) and (000) conduction bands. This separation was found to be 0.160 ± 0.005 eV at zero stress in agreement with optical measurements on degenerate germanium. Some details of the bias dependence of the pressure effect including some fine structure at small biases remain unexplained.

I. INTRODUCTION

AS a result of extensive experimental and theoretical efforts, the main features of the tunneling process in Esaki tunnel diodes[1] have been clearly established. However, since it is difficult to assess the validity of some of the simplifying assumptions and approxima-

tions which underlie our present theoretical understanding of this process, it is not clear to what extent the existing theories[2,3] should explain the finer details of the experimental observations. This problem is particularly difficult to resolve because tunnel diodes can only be made in highly impure materials. This fact

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