modulated strong field is given by the real part of

$$E_c(z, t) = E_0 \exp[i\omega_0 T - i\omega_0 z n_{ac}/c]. \tag{3}$$

The spectral density $S(\omega_0 - \mu\omega_s)$ is evaluated in the usual manner in terms of the Fourier transform of $E_c(z, t)$. The sideband number μ is not restricted to integer values; positive μ corresponds to the Stokes spectrum. It can be shown analytically that, independent of all parameters, (a) the Stokes and anti-Stokes spectra are interchanged if the phase angle Δ changes by π, and (b) the total integrated powers into the Stokes and anti-Stokes spectra are the same. The latter result does not contradict the apparent favoring of one side by the observed spectra away from the laser line, since the intense region near the laser frequency contributes heavily to the powers.

For the case of pulse bandwidth Γ comparable to ω_s, the spectra are quite sensitive to Δ. The filament-to-filament spectrum variation is probably largely due to stochastic variations in this phase. The spectra of Fig. 2, computed using $\Gamma = 1\ \text{cm}^{-1}$, $\beta = 100$, $\tau = 0$, and the CRCT value $\omega_s = 2.5\,\text{cm}^{-1}$, compare favorably with some of Shimizu's CS_2 observations. His other observations can be reproduced for different values of β and Δ. Variation of τ has little effect except through Δ.

The spectrum of Fig. 3 represents the long-pulse limit $\Gamma \gg \omega_s$. In this limit the spectra are independent of Δ, and the sideband width, although small, increases with μ. The peak spectral density decreases monotonically, but it can be shown that the integrated *power* in the kth sideband is proportional to the square of $J_k(\beta)$, as in the CRCT theory. A spectrometer with insufficient resolution will perform the integration and produce a spectrum like that of Fig. 1 rather than that of Fig. 3.

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Vacancies and ^{4}He Impurities in Solid ^{3}He[†]

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Hamiltonians to describe vacancies and ^{4}He impurities in solid ^{3}He derived from a Hubbard-like-model starting point are presented and discussed.

Giffard and Hatton[1] used NMR techniques to measure the exchange-lattice relaxation rate[2] in solid ^{3}He in the temperature range 0.4–0.6 °K in the presence of ^{4}He impurity atoms. They found an extra contribution to the rate that is of the form $\eta(x)\ T^{n(x)}$, where x is the ^{4}He concentration and T is the temperature; $n(x)$ varies from 8.3 ± 2 (for $x < 5\times10^{-7}$) to 8.7 ± 0.1 (for $x \simeq 3\times10^{-4}$). Guyer and Zane[3] argued against the interpretation of this effect as being the result of a two-phonon process, as was initially expected; they suggested that it may be due to tunneling processes in the presence of vacancies and ^{4}He atoms in the lattice. In a recent letter[4] (hereafter GZ) they have used a Hubbard-like model Hamiltonian for solid ^{3}He with a single ^{4}He atom present as an impurity, to construct an effective Hamiltonian which describes the exchange of positions of atoms caused by the tunneling motion of the atoms through the lattice in the absence of vacancies. They have found the concentration dependence and the temperature dependence of the relaxation rate in the above case. In this paper, we develop a unified approach for the study of tunneling processes that occur when vacancies are present in the lattice in addition to the ^{4}He atom.

The model Hamiltonian used in GZ may be written in the form

$$H = H_0 + V, \tag{1}$$

where

$$H_0=\phi\sum_i n_{i\uparrow}n_{i\downarrow}+\phi'\sum_{i,\sigma} n_{i\sigma}\rho_i\,,$$

$$V=\Delta\sum_{i,j,\sigma} t_{ij}\,c^\dagger_{i\sigma}c_{j\sigma}+\Delta'\sum_{i,j} t'_{ij}\,a^\dagger_i a_j\equiv\Delta V^F+\Delta' V^B\,.$$

Here, $c^\dagger_{i\sigma}$ ($a^\dagger_i$) creates a ^{3}He atom with spin σ (a ^{4}He atom) with the appropriate ground-state wave function in the ith cell. $n_{i\sigma}$ and ρ_i are the corresponding number operators for ^{3}He and ^{4}He, respectively. ϕ (ϕ') is the hard-core repulsion energy associated with putting two ^{3}He atoms (a ^{3}He atom and a ^{4}He atom) in the same cell. Δ and Δ' have the dimensions of energy, and t_{ij} and t'_{ij} are dimensionless hopping matrix elements (t_{ii} can be chosen to be zero without any loss of generality). In deriving Eq. (1), it is assumed that only one state is available per cell, which forbids two fermions with like spin projections from occupying the same cell. Also, all intercell interactions between atoms are neglected compared to intracell interactions. ϕ, ϕ' are much larger than Δ, Δ'. V will thus be treated as a perturbation on H_0 in Eq. (1). In GZ, ϕ and ϕ' have been taken to be equal to each other. We shall treat this case first and then discuss the case $\phi\neq\phi'$.

Eigenstates of H_0 of the form

$$|n,\alpha_j\rangle=c^\dagger_{1\sigma_1}\cdots a^\dagger_m\cdots c^\dagger_{N\sigma_N}|\Psi_0\rangle \tag{2}$$

can be found, where N is the total number of atoms, $|\Psi_0\rangle$ is the vacuum state, and there is one ^{4}He atom in the lattice. The eigenvalues of H_0 are $E_n=n\phi$, $n=0,1,2,\ldots$. The nth energy level is J_n-fold degenerate, and α_j ($j=1,2,\ldots,J_n$) is the degeneracy index.

When there are no vacancies in the lattice[5] and only the lowest energy level E_0 is considered, an effective Hamiltonian[4] (correct to second order in Δ and Δ'), that gives the second-order splitting of the unperturbed energy level E_0, is found quite easily using degenerate perturbation theory. This is because in this case (i) there is no first-order splitting of the level, and (ii) the perturbation connects the level E_0 only to the level E_1. However, this method cannot be generalized directly either to the level E_0 when there are vacancies, or to higher levels E_1, E_2, etc. To include such cases, we make use of a canonical transformation first introduced by Kohn,[6] and subsequently used by Harris and Lange[7] on the Hubbard-model Hamiltonian for electrons in narrow energy bands in a crystal. Our Hamiltonian is somewhat more complicated than this last, owing to the presence of bosons. When applied to Eq. (1), the canonical transformation leads to an effective "master" Hamiltonian (correct to second order in Δ and Δ') from which all second-order processes can be studied, in particular those which occur when there are vacancies in the lattice along with the ^{4}He atom.

We work in a representation with the vectors in Eq. (2) as the basis. When the perturbation V is switched on, $H=H_0+V$ does not have a reducible representation. We carry out a canonical transformation on H to obtain an effective Hamiltonian $\tilde{H}$ that does not connect subspaces corresponding to different values of n (i.e., $\tilde{H}$ has a reducible representation). Thus, we want to find a unitary transformation

$$U=\exp\{-S(\Delta,\Delta')\}\,,\quad S^\dagger=-S$$

such that

$$\tilde{H}=e^S He^{-S}\,, \tag{3}$$

with

$$\langle m,\alpha_j|\tilde{H}|n,\alpha_j\rangle=0\,,\quad \forall n\neq m\,. \tag{4}$$

In Eq. (3), only terms up to second order in Δ and Δ' are to be retained. S is expanded in a double series in Δ and Δ' of the form

$$S=(\Delta/\phi)S_1+(\Delta'/\phi)S'_1+(\Delta/\phi)^2S_2+(\Delta'/\phi)^2S'_2+(\Delta\Delta'/\phi^2)S''_2+\cdots\,. \tag{5}$$

Using Eq. (5) in Eq. (3), we find

$$\begin{aligned}\tilde{H}&=H+[\Delta S_1+\Delta' S'_1,H_0]/\phi\\&\quad+[\Delta^2S_2+\Delta'^2S'_2+\Delta\Delta'S''_2,H_0]/\phi^2\\&\quad+[\Delta S_1+\Delta'S'_1,[\Delta S_1,H_0]+[\Delta'S'_1,H_0]+2\phi V]/2\phi^2,\end{aligned} \tag{6}$$

where S_1 through S''_2 must be chosen so as to satisfy Eq. (4). We proceed as follows: Equation (4) is a rather weak condition, since it says nothing regarding the matrix elements of $\tilde{H}$ when $n=m$, i.e., within a given subspace. We determine the full *operator* form of the first-order terms ΔS_1 and $\Delta' S'_1$ by imposing instead of Eq. (4) the stronger (sufficiency) conditions

$$\begin{aligned}&\Big[H_0,V^F+(1/\phi)[S_1,H_0]\Big]=0,\\&\Big[H_0,V^B+(1/\phi)[S'_1,H_0]\Big]=0\,.\end{aligned} \tag{7}$$

Equation (7) is satisfied by the choice

$$\begin{aligned}S_1=\sum_{i,j,\sigma}t_{ij}[&(n_{i\sigma}-n_{j\sigma})+(\rho_i-\rho_j)-\tfrac{3}{4}(n_{i\sigma}-n_{j\sigma})\\&\times(\rho_i-\rho_j)^2-\tfrac{3}{4}(n_{i\sigma}-n_{j\sigma})^2(\rho_i-\rho_j)]\,c^\dagger_{i,-\sigma}c_{j,-\sigma}\,,\end{aligned} \tag{8}$$

$$\begin{aligned}S'_1=\sum_{i,j,\sigma}t'_{ij}[&(n_{i\sigma}-n_{j\sigma})-\tfrac{3}{4}(n_{i\sigma}-n_{j\sigma})\\&\times(n_{i,-\sigma}-n_{j,-\sigma})^2]\,a^\dagger_i a_j\,.\end{aligned}$$

(We have used the fact that $\rho_i^2=\rho_i$, since there is only one ^{4}He atom present, or effectively, the ^{4}He density is very low.)

Next, Eq. (4) is imposed successively on the coefficients of Δ^2, Δ'^2, and $\Delta\Delta'$ in the expression on the right of Eq. (6), giving the matrix elements of S_2, S_2', and S_2'' when $n\neq m$; those when $n=m$ may be chosen to be zero.[6] Then, $\tilde{H}$ has a reducible representation (each subspace decoupled from all the others); its matrix elements within a submatrix are simply the corresponding ones of the sum of the first, second, and fourth terms on the right of Eq. (6). We can write[8] a rather complicated operator expression based on the above arguments, whose matrix elements in each subspace are identical with those of $\tilde{H}$.

We now discuss explicitly the subspace corresponding to $n=0$, i.e., when there is no more than one atom per site. We call this the "physical subspace" since, at temperature T, the probability factor $\exp(-E_n/kt)$ is overwhelmingly the largest for states in this subspace for reasonable parameter values. The operator expression for $\tilde{H}$ is considerably simplified in this case because "mixed" operators such as

$$\sum_{i,j,\sigma} t_{ij}(n_{i\sigma}-n_{j\sigma})^2(\rho_i-\rho_j)c_{i,-\sigma}^\dagger c_{j,-\sigma},$$

$$\sum_{i,j,\sigma} t_{ij}'(n_{i\sigma}-n_{j\sigma})^2(n_{i,-\sigma}-n_{j,-\sigma})^2 a_i^\dagger a_j$$

[see Eq. (8)] that would occur in the terms involving $[H_0, S_1]$, $[H_0, S_1']$, etc., in Eq. (6) do not contribute to the matrix elements of $\tilde{H}$ in this subspace.

We discuss two cases:

(*a*) *No vacancies in the lattice*. We find that first-order terms in Δ, Δ' do not occur in this case, case, and $\tilde{H}$ may be written in the form

$$\tilde{H}=\tfrac{1}{2}\sum_{i,j} J_{ij}\vec{\mathrm{I}}_i\cdot\vec{\mathrm{I}}_j+\sum_{i,j,\sigma} J_{ij}' n_{i\sigma}\rho_j + \tfrac{1}{2}\sum_{i,j,\sigma} J_{ij}'' c_{i\sigma}^\dagger a_i a_j^\dagger c_{j\sigma}, \qquad (9)$$

where the operator $\vec{\mathrm{I}}_i$ is given by

$$I_i^+=c_{i\uparrow}^\dagger c_{i\downarrow}, \quad I_i^-=c_{i\downarrow}^\dagger c_{i\uparrow}, \quad I_i^z=\tfrac{1}{2}(n_{i\uparrow}-n_{i\downarrow}).$$

The coefficients J_{ij}, J_{ij}', and J_{ij}'' are defined as

$$J_{ij}=(4\Delta^2/\phi)t_{ij},$$

$$J_{ij}'=-(\Delta^2/2\phi)t_{ij}^2-(\Delta'^2/\phi)t_{ij}'^2,$$

$$J_{ij}''=-(4\Delta\Delta'/\phi)t_{ij}t_{ij}'.$$

Equation (9) is equivalent to Eq. (6) in GZ, although it is in a different form. $\sum_i a_i^\dagger c_{i\sigma}\exp(i\vec{\mathrm{k}}\cdot\vec{\mathrm{x}}_i)$ creates a mass-fluctuation wave[4] in the lattice. The processes described by Eq. (9) have been discussed in GZ. Using Eq. (9) as the exchange Hamiltonian for impure solid ^{3}He, we have found[8] the ^{4}He-concentration dependence of the Zeeman-exchange relaxation time,[2] the transverse relaxation time, and the exchange specific heat. The results of these calculations will be published elsewhere.[9] A calculation of the magnetic susceptibility is underway.

(*b*) *Vacancies present in the lattice*. In this case we find that $\tilde{H}$ does have first-order terms in Δ and Δ'. These terms are

$$\sum_{i,j,\sigma}[\Delta t_{ij}(1-n_{i,-\sigma}-\rho_i)c_{i\sigma}^\dagger c_{j\sigma}+\Delta' t_{ij}'(1-n_{i\sigma})a_i^\dagger a_j]. \qquad (10)$$

The two terms in the expression (10) represent, respectively, the hopping of a ^{3}He atom and a ^{4}He atom into an empty lattice site.[10] In the absence of a ^{4}He atom, the expression in (10) can be written as

$$-\Delta\sum_{i,j,\sigma} t_{ij}A_{i\sigma}^\dagger A_{j\sigma}, \qquad (11)$$

where $A_{i\sigma}^\dagger=(1-n_{i,-\sigma})c_{i\sigma}$. From the equation of motion for $A_{k\sigma}^\dagger=\sum_i A_{i\sigma}^\dagger\exp(i\vec{\mathrm{k}}\cdot\vec{\mathrm{x}}_i)$, using the expression (11) and nearest-neighbor hopping, we find that $A_{k\sigma}^\dagger$ creates a wave (with wave vector $\vec{\mathrm{k}}$) propagating through the lattice,[11] describing the motion of a vacancy in the crystal, when the second-order effects are negligible. The energy-dispersion relation for these waves is $\epsilon(\vec{\mathrm{k}})=-\Delta t\sum_{\vec{a}}\exp(i\vec{\mathrm{k}}\cdot\vec{\mathrm{a}})$, where $\vec{\mathrm{a}}$ represents a nearest-neighbor lattice vector.

The second-order correction to the expression in (10) has also been found:

$$\begin{aligned}
&-(\Delta^2/\phi)\sum_{i,j,k,\sigma} t_{ki}t_{ij}n_{i,-\sigma}(1-n_{k,-\sigma}-\rho_k)c_{k\sigma}^\dagger c_{j\sigma}\\
&-(\Delta^2/\phi)\sum_{i,j,k,\sigma} t_{ki}t_{ij}(1-n_{k,-\sigma}-\rho_k)c_{k\sigma}^\dagger c_{i\sigma}c_{i,-\sigma}^\dagger c_{j,-\sigma}\\
&-(\Delta^2/\phi)\sum_{i,j,k,\sigma} t_{ki}t_{ij}\rho_i(1-n_{k,-\sigma}-\rho_k)c_{k\sigma}^\dagger c_{j\sigma}\\
&-(\Delta'^2/\phi)\sum_{i,j,k,\sigma} t_{ij}'t_{ik}'n_{i\sigma}(1-n_{k\sigma})a_k^\dagger a_j\\
&-(\Delta\Delta'/\phi)\sum_{i,j,k,\sigma} t_{ik}t_{ij}'(1-n_{k,-\sigma}-\rho_k)c_{k\sigma}^\dagger c_{i\sigma}a_i^\dagger a_j\\
&-(\Delta\Delta'/\phi)\sum_{i,j,k,\sigma} t_{ik}'t_{ij}(1-n_{k,-\sigma})a_k^\dagger a_i c_{i\sigma}^\dagger c_{j\sigma}. \qquad (12)
\end{aligned}$$

The sum over lattice sites in the terms of the above expression consists of two parts: $j=k$ and $j\neq k$. The former gives only the exchange terms on the right of Eq. (9), and the latter describes second-order hopping processes in the presence of vacancies.

(*c*) *Case* $\phi\neq\phi'$: We now discuss the case $\phi\neq\phi'$ in brief. We may now work in a basis labeled by two integers n, p (corresponding to the eigenvalue $n\phi+p\phi'$ of H_0), where $n=0, 1, 2, \ldots$, and $p=0$ or 1 when only one ^{4}He atom is present. However, expanding $\tilde{H}$ as in Eq. (6) and imposing the condition of Eq. (4) on a matrix element such as

$$\langle m, p=1;\ \alpha_j|\tilde{H}|m+1,\ p=0;\ \alpha_k\rangle \tag{13}$$

leads to the "singular" denominator $(\phi-\phi')$ in the expression for S_1 (and thus for S_2, etc.). We expect from the definitions of ϕ and ϕ' as hard-core repulsion energies that the difference $(\phi-\phi')$ may be quite small. This would invalidate a perturbation expansion of the type used in Eq. (6). We may avoid this difficulty by working in a different basis. However, if we merely want to decouple the physical subspace, corresponding to $n=0$, $p=0$, the above problem does not arise [see Eq. (13)]. In fact our previous experience in the case $\phi=\phi'$ tells us that the choices

$$S_1=\sum_{i,j,\sigma} t_{ij}[(n_{i\sigma}-n_{j\sigma})+(\phi/\phi')(\rho_i-\rho_j)]\,c^\dagger_{i,-\sigma}c_{j,-\sigma}\,,$$

$$S_1'=\sum_{i,j,\sigma} t'_{ij}(\phi/\phi')(n_{i\sigma}-n_{j\sigma})\,a^\dagger_i a_j \tag{14}$$

would be suitable for this purpose. Proceeding as before, we obtain the effective Hamiltonian in the physical subspace, in the two cases (a) and (b). In (a), $\tilde{H}$ is given once again by Eq. (9), with the new definitions

$$J'_{ij}=-(\Delta^2/\phi')t^2_{ij}-(\Delta'^2/\phi')t'^2_{ij}+(\Delta^2/2\phi)t^2_{ij}\,,$$

$$J''_{ij}=-(4\Delta\Delta'/\phi')t_{ij}t'_{ij}\,.$$

In (b) the first-order terms remain unchanged and can be interpreted as before. The operator expressions in the second-order terms are also not affected except for the replacement of ϕ by ϕ' in the last four terms in the expression (12).

We summarize our conclusions as follows: Classically, one regards vacancies in a lattice as localized entities that can occasionally move from site to site, the motion being an increasing function of the temperature. However, in crystals such as solid ^{3}He, the quantum-mechanical zero-point motion of the atoms (which persists even at very low temperatures) is very large.[12] This effect becomes important in studying the dynamics of vacancies at low temperatures, and we have found that the canonical transformation method used here greatly facilitates the analysis. It is seen that the vacancies give rise to waves[11,13] that can propagate through the crystal [see Eq. (11) *et seq.*]. One can therefore think of the lattice energy in solid ^{3}He with vacancies as the sum of the phonon energy and the energy associated with the vacancy waves. One purpose of our work is to help set the problem of diffusion in solid ^{3}He, which has so far been treated phenomenologically,[14] on a more quantitative basis.

When a ^{4}He impurity atom is present, ignoring the presence of vacancies, one finds that mass-fluctuation waves exist. When both an impurity atom *and* vacancies are present, the canonical transformation method continues to remain useful and gives an effective Hamiltonian $\tilde{H}$ capable of describing both vacancy waves, mass-fluctuation waves, and their mutual interaction. Of course, at low ^{4}He and vacancy concentrations, their interaction will be effectively weak.[15] In addition, both wave types can interact with the phonons. In exchange-lattice relaxation, therefore, the exchange energy can be converted into vacancy waves, mass-fluctuation waves, as well as phonons. We have provided a unified method of finding the energy-dispersion relations for the first two of the above. This is necessary in order to develop a quantitative theory of exchange-lattice relaxation in solid ^{3}He when both ^{4}He impurity atoms and vacancies are present.

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Giffard and Hatton is 5×10^{-7}. Although concentration of vacancies is three orders of magnitude smaller than that of impurities, the contribution of the vacancies to the relaxation process may be considerable, since it is much easier for a ^{3}He atom to exchange places with a vacancy rather than with a ^{4}He atom.

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Nuclear-Spin Effects Are Important in Analyzing Spin-Exchange Experiments

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Lambert's proof that the inclusion of nuclear spin does not alter the equation of motion for the electronic polarization is shown to be valid only when the hyperfine interaction is negligible. Usually the hyperfine frequency is much greater than the frequency of spin-exchange collisions; then the effect of the hyperfine interaction *between* collisions invalidates Lambert's proof. In general, spin exchange with a second depolarized species relaxes the electronic polarization as the sum of two exponentials, as shown by Gibbs and Grossetête.

Lambert[1] has recently presented a proof that equations describing the effect of spin-exchange collisions on the electronic polarization of systems without nuclear spin also hold for systems with nuclear spin. The range of validity of his proof is discussed in this note.

In 1962 and 1963 Grossetête[2] and Gibbs[3] showed independently that, in general, the electronic polarization relaxes as the sum of two exponentials as a result of spin exchange with a second disoriented species. Experimental evidence of this double-exponential prediction was also presented.[4,5] On the other hand, Balling, Hanson, and Pipkin (BHP) claimed that their analysis without nuclear spin was valid with its inclusion.[6] But in a subsequent erratum they admitted that the replacement of Rb^{87} by a system without nuclear spin was not rigorously justified, yet expressed their feeling that such a replacement was a good approximation.[7] Gibbs pointed out that their Table IV (or VIII) leads to a double-exponential solution, i. e., that Rb^{87} is represented very poorly by a zero-nuclear-spin alkali, in general.[3] Bouchiat has treated the relaxation of the electronic polarization by wall and buffer-gas collisions and shown that, in general, nuclear spin leads to a double-exponential decay.[8] Electron randomization (without affecting the nuclear spin) is equivalent to spin exchange with a disoriented second species in its effect on the electronic polarization.[3] In the absence of alkali–rare-gas molecular formation,[9] the electronic polarization is expected to relax by electron randomization in buffer-gas collisions, and evidence for this and the associated double-exponential decay has been presented.[9–11] Therefore, the importance of including the nuclear-spin effects in analyzing the relaxation of the electronic polarization would seem to be well established even though many experiments measuring spin-exchange and buffer-gas cross sections and diffusion coefficients were performed before this importance was appreciated. For example, it is likely that nuclear-spin-produced nonexponential decays have been attributed to higher diffusion modes.

Lambert's proof[1] begins with Eq. (27) of BHP,[6]

$$\frac{d\rho(1)}{dt}=\frac{1}{4T_1}\,\mathrm{tr}_2[-3\rho(1,2)+(1+2i\kappa)\vec{\sigma}_1\cdot\vec{\sigma}_2\,\rho(1,2)+(1-2i\kappa)\rho(1,2)\,\vec{\sigma}_1\circ\vec{\sigma}_2+\vec{\sigma}_1\cdot\vec{\sigma}_2\,\rho(1,2)\,\vec{\sigma}_1\circ\vec{\sigma}_2]\ . \tag{1}$$

It is useful to sketch Grossetête's careful density-matrix derivation[2] to point out how it differs from Lambert's. She divides the density matrix $\rho(1)$ into two parts, $\rho(1)=\bar{\rho}(1)+\bar{\bar{\rho}}(1)$, where $\bar{\rho}(1)$ describes those atoms which undergo no collisions during the time dt and $\bar{\bar{\rho}}(t)$ describes those which undergo at least one collision in dt. Equation (1) above can be written as [with $\sigma_n(2)\sigma_s(2)=\delta_{ns}+i\epsilon_{nst}\sigma_t(2)$]

$$\frac{d\bar{\bar{\rho}}_1}{dt}=\frac{1}{4T_1}\{-3\rho(1)+\sigma_n(1)\rho(1)\sigma_n(1)+[(1+2i\kappa)\sigma_n(1)\rho(1)+(1-2i\kappa)\rho(1)\sigma_n(1)]P_n(2)+i\epsilon_{snt}\sigma_n(1)\rho(1)\sigma_s(1)P_t(2)\}\ , \tag{2}$$

where summation over repeated indices is understood and where

$$P_k(2)=\mathrm{tr}\,\sigma_k(2)\rho(1,2)=\mathrm{tr}_2\,\sigma_k(2)\rho(2).$$

Equation (2) agrees with (I-5a) and (II-1) of Grossetête's article which describe the dominant variation of $\rho(1)$ *during* a spin-exchange collision. *Between* collisions, which is most of the time in a typical alkali experiment, the variation is dominated by the static Hamiltonian $\mathcal{H}_1$, including the Zeeman and hyperfine interactions,