ly, we obtain tabulated results for  $g^{(4,4)}(r)$  and  $g^{(4,3)}(r)$ . Based on these results and Eq. (7), Eq. (6) (with the KSA incorporated) can now be solved for a new  $u^{(4,3)}(r)$ , which is then compared with the  $u^{(4,3)}(r)$  of Eq. (8). Table I lists the two sets of values for  $(d/dr)[u^{(4,3)}(r)]$ . Figure 1 is a plot of the same. It is clear that in the important region, 2.8 < r < 4.5 Å, the difference does not exceed a few percent.

By the "important region" we mean where the contribution to the binding energy or the chemical potential  $\epsilon_1$  of the He<sup>3</sup> atom is dominant. Equation (27) of Ref. 2 lists three sources of contribution.  $u^{(4,3)}(r)$  enters through two of them, one of which is six times larger than the other and is the only one suitable for making direct comparison. It appears as

$$\epsilon_{1}^{(1)} = \frac{\hbar^{2} \rho_{4}}{8m_{4}} \frac{7}{3} \int \left( \frac{d}{dr} u^{(4,3)}(r) \right) \left( \frac{d}{dr} g^{(4,3)}(r) \right) d\vec{r} .$$
(9)

A simple numerical integration yields 34.8 °K for Eq. (8) and 35.6 °K for Eq. (6). While a difference of 0.8 °K is merely 2% of  $\epsilon_1^{(1)}$ , it is almost 30% of

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<sup>1</sup>C-W. Woo, H-T. Tan, and W. E. Massey, Phys. Rev. Letters <u>22</u>, 278 (1969); Phys. Rev. <u>185</u>, 287

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## Coherence Transfer and Frequency Shifts in Spin-Exchange Collisions\*

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Bender's theory of frequency shifts in spin exchange is applied to two illustrations of coherence transfer. The effects of coherence transfer include changes in the shift-to-broadening ratio and a frequency shift which does not reverse with polarization.

The theory of frequency shifts by spin-exchange collisions<sup>1,2</sup> has been significant for understanding precise experiments in hydrogen masers<sup>3</sup> and optical pumping, <sup>4</sup> as well as for measurement of spin-exchange cross sections.<sup>5</sup> This theory is commonly applied as if the survival of coherence from one collision to the next (sometimes called "coherence transfer") could be ignored. However multiple collisions are not unlikely when single collisions are significant (the Poisson distribution is not sharply peaked). Unexplained shifts in our

own measurements on pressure shifts of the hydrogen hyperfine splitting<sup>6</sup> have forced us to look into some coherence transfer effects and we feel they deserve wider attention.<sup>7</sup> In this paper we will consider some effects of a second collision within the relevant phase relaxation time  $T_2$  (e.g., collision rates  $1/T_e \leq 1/2T_2$ ). We shall refer to the density matrix elements calculated by Bender.<sup>1</sup>

First consider two hydrogen atoms in the presence of the rf field resonant at the  $(F = 1, m_F = 0) - (F = 0, m_F = 0)$  ground-state hyperfine transition frequency

 $\epsilon_1$  on account of the large cancellation between  $\epsilon_1^{(1)}$ and  $\epsilon_1^{(2)}$ . We note that in earlier work<sup>4</sup> on pure He, the uncertainty in the energy due to the KSA is also of the order of 1 °K. This is discouraging but not unexpected. However, we must emphasize that other quantities calculated by our theory, such as structure functions and the effective mass, do not result from such strong cancellations. They are reliable.

It is well known that the KSA violates the sequential relations connecting three-particle distribution functions to two-particle distribution functions. We have a means here of measuring the degree of this violation. Integrating Eqs. (5) and (6) over the coordinates of particles 1 and N, we find that the sequential relations if obeyed give rise to an equality

$$\int g^{(4,4)}(r) \left(\frac{d}{dr} u^{(4,4)}(r)\right) r^2 dr = \int g^{(4,3)}(r) \\ \times \left(\frac{d}{dr} u^{(4,3)}(r)\right) r^2 dr \quad . \quad (10)$$

Using  $u^{(4,3)}(r)$  of Eq. (6) on the right-hand side, we find the equality satisfied to within 10%.

(1969).

<sup>2</sup>W. E. Massey, C-W. Woo, and H-T. Tan, Phys. Rev. A <u>1</u>, 519 (1970).

<sup>3</sup>H-K. Sim and C-W. Woo, Phys. Rev. <u>185</u>, 401 (1969).

<sup>4</sup>See, for example, E. Feenberg, *Theory of Quantum Fluids* (Academic, New York, 1969).

 $\omega_0$ . After the first collision the density matrix has changed as shown in Bender's Table III, where all initial off-diagonal elements are set equal to zero except the one connecting the two m = 0 sublevels (and its conjugate element). This particular transition is a simple case because no new offdiagonal elements are created in the collision. Section 3 of Bender's paper shows that (in the lowdensity limit) the real part of the fractional change in this element is proportional to the linewidth of the transition caused by spin exchange. The imaginary part gives the observed shift in the resonance frequency and their ratio is simply related to the

atomic wave functions.

Extending this calculation beyond such an "instantaneous" collision at time t' we allow the new off-diagonal element to advance in phase by  $\omega_0(t)$ -t') until at t = t'' another atom (No. 3) collides with atom No. 1 which we have been following. Taking atom No. 3 as having the density matrix of the ensemble from which the first atoms were picked, we apply Bender's unitary transformation to the direct product matrix and then trace over coordinates of one atom at a time to get the results of the second collision:

$$(\rho_{\text{atom }3}^{ff})_{42} = \rho_{42}^{i} \left\{ 1 - \frac{1}{4} (1 - \cos\Delta) - \frac{1}{32} (1 - \cos\Delta)^{2} - \frac{1}{16} (\sin^{2}\Delta) (\rho_{22}^{i} - \rho_{44}^{i})^{2} - i \left[ \frac{1}{4} (\sin\Delta) - \frac{1}{32} (\sin\Delta) (1 - \cos\Delta) \right] (\rho_{22}^{i} - \rho_{44}^{i}) \right\},$$
(1)

$$(\rho_{\text{atom 1}}^{ff})_{42} = \rho_{42}^{i} \left\{ 1 - \frac{1}{2} (1 - \cos\Delta) + \frac{3}{32} (1 - \cos\Delta)^{2} - i \left[ \frac{1}{2} (\sin\Delta) - \frac{7}{32} (\sin\Delta) (1 - \cos\Delta) \right] (\rho_{22}^{i} - \rho_{44}^{i}) \right\}.$$
 (2)

The total effect of the second collision is just the average of these:

$$(\rho_{av}^{ff})_{42} = \rho_{42}^{i} \left\{ 1 - \frac{3}{8} (1 - \cos\Delta) + \frac{1}{32} (1 - \cos\Delta)^{2} - \frac{1}{32} (\sin^{2}\Delta) (\rho_{22}^{i} - \rho_{44}^{i})^{2} - i \left[ \frac{3}{8} (\sin\Delta) - \frac{1}{8} (\sin\Delta) (1 - \cos\Delta) \right] (\rho_{22}^{i} - \rho_{44}^{i}) \right\}.$$
(3)

. .

After the second collision, the imaginary part of the fractional change is proportional to the population difference  $(\rho_{22}^i - \rho_{44}^i)$  as before, but two new features appear: First, the ratio of the imaginary to real parts is no longer the same as in the singlecollision model, so that interpreting the observed ratio in terms of atomic structure becomes complicated if spin-exchange processes dominate. Second, the presence of the positive term in the real part suggests that line narrowing could occur through spin-exchange under certain circumstances (such narrowing would be analogous to the optical narrowing by the process of "coherent diffusion"<sup>8</sup>). These results are implicitly contained in Bender's Eq. (25).

Finally, consider a Zeeman transition in hydrogen atoms in a weak magnetic field (e.g.,  $\sim 0.5$  G) under the influence of spin-exchange collision with atomic tritium. Because of the larger nuclear moment in tritium, the four Zeeman transitions in the two isotopes are all resolved. Then the initial hydrogen matrix has nonzero off-diagonal elements with frequency  $\omega_0$  connecting, for example, the states  $(F=1, m_F=+1)$  and  $(F=1, m_F=0)$ . Let the tritium be completely unpolarized. Again using Bender's transformation matrices, the tritium matrix at the end of the first collision is (ignoring terms which do not survive later time averages)

$$(\rho_T^f)_{11} = \frac{1}{4} - \frac{1}{8}(1 - \cos\Delta)(\rho_{33}^i - \rho_{11}^i)$$
, (4a)

$$(\rho_T^f)_{11} = \frac{1}{4}$$
, (4b)

$$(\rho_T^f)_{33} = \frac{1}{4} + \frac{1}{8}(1 - \cos\Delta)(\rho_{33}^i - \rho_{11}^i) , \qquad (4c)$$

$$(\rho_T^f)_{44} = \frac{1}{4}$$
, (4d)

$$(\rho_T^f)_{21} = \frac{1}{8} (1 - \cos\Delta) (\rho_{21}^i) , \qquad (4e)$$

$$(\rho_T^f)_{32} = \frac{1}{8} (1 - \cos\Delta) (\rho_{21}^i)$$
 (4f)

Again, the tritium atom advances in phase between collisions, until at time t'', the last two elements have become

$$\begin{split} \left[\rho_{T}^{i}(t^{\prime\prime})\right]_{21} &= \frac{1}{8}(1 - \cos\Delta)(\rho_{21}^{i}) e^{-i(\omega_{2}-\omega_{0})(t^{\prime\prime}-t^{\prime\prime})} = e_{T}, \\ (5a) \\ \left[\rho_{T}^{i}(t^{\prime\prime})\right]_{32} &= \frac{1}{8}(1 - \cos\Delta)(\rho_{32}^{i}) e^{-i(\omega_{3}-\omega_{0})(t^{\prime\prime}-t^{\prime\prime})} = g_{T}, \end{split}$$

where  $\omega_2$  and  $\omega_3$  are the frequencies associated with  $(\rho_T^f)_{21}$  and  $(\rho_T^f)_{32}$ , respectively.

Since the collisions are uncorrelated in time, we may weight these elements by the probability of a collision  $(1/T_e)e^{-t/T_e} dt$  and average over the time between collisions:

$$\overline{e}_{T} = \frac{1}{8} (1 - \cos \Delta) (\rho_{21}^{i}) \\ \times [1 - i(\omega_{2} - \omega_{0})T_{e}] / [1 + (\omega_{2} - \omega_{0})^{2}T_{e}^{2}], \quad (6a)$$

$$\overline{g}_{T} = \frac{1}{8} (1 - \cos\Delta) (\rho_{21}^{i}) \\ \times [1 - i(\omega_{3} - \omega_{0})T_{e}] / [1 + (\omega_{3} - \omega_{0})^{2} T_{e}^{2}] .$$
 (6b)

The second collision for this tritium atom involves a second hydrogen atom with the same density matrix as the first. Using Bender's unitary transformation a second time, we find the final

off-diagonal element for the second hydrogen atom, in the limit of small hydrogen polarization (diagonal elements approximately equal):

$$(\rho_{H}^{ff})_{21} = \rho_{21}^{i} - \frac{1}{4}(1 - \cos\Delta)[\frac{3}{2}\rho_{21}^{i} - \frac{1}{2}\operatorname{Re}\{\overline{e}_{T}\} - \frac{1}{2}\operatorname{Re}\{\overline{g}_{T}\}] + \frac{1}{4}i(1 - \cos\Delta)[\frac{1}{2}\operatorname{Im}\{\overline{e}_{T}\} + \frac{1}{2}\operatorname{Im}\{\overline{g}_{T}\}].$$
(7)

The imaginary terms in Eq. (7) represent a frequency shift which does *not* reverse with polarization. They are proportional to  $(1 - \cos \Delta)^2$  and represent spin coordinates which effectively left the first hydrogen atom to ride with the tritium atom until second collision, after which they contribute to the hydrogen resonance. These terms depend on the frequency difference between the

<sup>2</sup>L. C. Balling, R. J. Hanson, and F. M. Pipkin, Phys. Rev. <u>133</u>, A607 (1964).

<sup>3</sup>S. B. Crampton, Phys. Rev. <u>158</u>, 57 (1967); D. Kleppner, H. D. Berg, S. B. Crampton, N. F. Ramsey, R. F. C. Vessot, H. E. Peters, and J. Vanier, *ibid*. <u>138</u>, A972 (1965).

<sup>4</sup>For a recent review see F. G. Major, in *Methods of Experimental Physics*, edited by B. Bederson and W. L. Fite (Academic, New York, 1968), Vol. 7, Pt. B. p. 1. <sup>5</sup>L. C. Balling, Phys. Rev. 151, 1 (1966).

<sup>6</sup>E. S. Ensberg and C. L. Morgan, in *Proceedings of* the International Conference on Precision Measurement and Fundamental Constants, edited by D. N. Langenberg

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isotopes and amount to averaging the frequencies of several transitions in the sample.<sup>7(a), 7(b)</sup> Much more complicated situations can arise,

especially when lines in neighboring atoms are not completely resolved. In such a case, accidental coincidences between multiple quantum transitions can also contribute to the spin-exchange shifts. The case of Rb and H isotopes provide a variety of such coincidences. Additional shifts also occur in the case of double resonance.<sup>9</sup>

In conclusion, the predictions of a single-collision model do not include many experimentally realized conditions. One must expect to find frequency shifts which do not reverse with polarization and shift-to-broadening ratios which are not constant.

and B. N. Taylor, NBS Special Publication 343 (U. S. GPO, Washington, D. C., 1971).

<sup>7</sup>Special cases of coherence transfer are discussed in (a) L. D. Schearer, F. D. Colegrove, and G. K. Walters, Rev. Sci. Instr. <u>35</u>, 767 (1964). (b) H. G. Dehmelt, *ibid.* <u>35</u>, 768 (1964). (c) G. A. Ruff and T. R. Carver, Phys. Rev. Letters <u>15</u>, 282 (1965). (d) G. W. Series, Proc. Phys. Soc. (London) <u>90</u>, 1179 (1967).

<sup>8</sup>M. A. Giochon, J. E. Blamont, and J. Brossel, Compt. Rend. <u>243</u>, 1859 (1956). For a recent review see G. zu Putlitz, *Atomic Physics*, edited by B. Bederson, V. W. Cohen, and F. Pichanick (Plenum, New York, 1969), p. 227.

<sup>9</sup>Double resonance is a common technique for measuring the magnetic field in the H maser. See D. Kleppner *et al.*, Ref. 3.

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## Theory of the Liquid-Solid Phase Transition

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We reanalyze in greater generality the recently predicted phenomena associated with the liquid-solid phase transition.

Recently, <sup>1</sup> the density response of a fluid has been investigated with particular emphasis on those fluctuations which may be considered as precursors to freezing. Neglecting the instabilities against nucleation and growth of small crystallites, a definite stability limit has been found at which the supercooled liquid as a whole becomes intrinsically unstable with respect to a density fluctuation of wave number  $Q_0$ .  $Q_0$  is the position of the first maximum in the structure factor S(Q) and corresponds to the lattice vector of the solid into which the liquid freezes.

It is the purpose of this note to show that the

stability limit of the liquid and the associated phenomena may be derived in greater generality, and therefore, that the predictions of Ref. 1 are more general than the approximations suggest.

In doing so we write the free energy F of the fluid in a static applied potential  $V_{ex}(r)$  in the form

$$F[n] = \int V_{ex}(\vec{\mathbf{r}}) n(\vec{\mathbf{r}}) d^3r + F_s[n] + \frac{1}{2} \int \int V(|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|) n(\vec{\mathbf{r}}) n(\vec{\mathbf{r}}') d^3r d^3r' + F_c[n],$$
(1)

 $F_s[n]$  is the free energy of noninteracting particles with density n(r) at pressure p and temperature

<sup>\*</sup>Research sponsored by the U. S. Air Force Office of Scientific Research, Air Force Systems Command, under AFOSR Grant No. 249-67.

<sup>&</sup>lt;sup>1</sup>P. L. Bender, Phys. Rev. <u>132</u>, 2154 (1963).