scattering amplitude is split into two parts corresponding to ionization before and after compound-nucleus formation.

An expression for the ratio of scattered protons with and without simultaneous ionization is obtained by combining Eqs. (2) and (3):

$$\frac{N_1\,|\,2+D^{-1}[\exp-i\theta][\sin\delta(E')\exp i\delta(E')+\sin\delta(E)\exp i\delta(E)]\,|^2}{|\,1+C^{-1}\sin\delta(E)\exp i[\delta(E)-\varphi]\,|^2}\,. \tag{4}$$

The fit of the measured ratio with formula (4) is shown in Fig. 1(b); only D and φ are varied while C and θ are determined from the fit of the singles yield with formula (2). The following values are found: $D=-0.62\pm0.05$ and $\theta=0.20\pm0.06$ rad. The inequality of the parameters D and C and of the parameters θ and φ, respectively, shows that the Coulomb scattering and the nuclear resonant scattering interfere in a different way for the case with and without simultaneous K-shell ionization.

We conclude, therefore, that the phase change observed is due to the influence of dipole and higher-multipole ionization amplitudes, causing angular momentum exchange, on the combined process of inner-shell ionization and the scattering of the ionizing particle from the nucleus. This influence manifests itself through the change of the impact-parameter–dependent ionization probability in the neighborhood of a nuclear scattering resonance; or, formulated in a different way, in the change of the shape of a nuclear s-wave resonance when measured with or without simultaneous K-shell ionization. In the study of time-delay effects in compound-nucleus formation, this effect should be taken into account.

This work was performed as part of the research program of Fundamenteel Onderzoek der Materie with financial support from Nederlandse Organisatie voor Zuiver-Wetenschappelÿk Onderzoek.

[1] J. Benn, E. B. Dally, H. H. Muller, R. E. Pixley, H. H. Staub, and H. Winkler, Phys. Lett. 20, 43 (1966).
[2] J. S. Blair, P. Dyer, K. A. Snover, and T. A. Trainor, Phys. Rev. Lett. 41, 1712 (1978).
[3] G. Ciochetti, A. Molinari, and R. Malvano, Nuovo Cimento 29, 1262 (1963).
[4] G. Ciochetti and A. Molinari, Nuovo Cimento 40, 69 (1965).
[5] W. Henneberg, Z. Phys. 86, 592 (1933).
[6] G. Breit, Phys. Rev. Lett. 1, 200 (1958).
[7] G. Breit, Phys. Rev. Lett. 2, 401 (1959).
[8] M. de Wit, C. R. Fischer, and W. Zwickendraht, Proc. Nat. Acad. Sci. U. S. A. 45, 1047 (1959).
[9] H. L. Jackson and A. Galonsky, Phys. Rev. 89, 370 (1953).
[10] See, for example, A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1961), Vol. I, p. 430.

Theory of Spin Relaxation and Recombination in Spin-Polarized Atomic Hydrogen

B. W. Statt and A. J. Berlinsky
Department of Physics, University of British Columbia, Vancouver, British Columbia V6T 1W5, Canada

(Received 23 September 1980)

A calculation is presented of the relaxation rate T_1^{-1} between the lowest two hyperfine states of a dilute gas of H atoms in high magnetic field at low temperatures. Dipole-dipole interactions dominate T_1^{-1}, leading to long relaxation times at low temperatures ($T_1^{-1}\approx10^{-2}n_{\mathrm{H}}T^{1/2}$ sec^{-1} at $H\approx100$ kG). The recombination rate due to wall collisions is much greater than T_1^{-1} and can lead to a depletion of the lowest hyperfine state from thermal equilibrium and an effective recombination rate equal to T_1^{-1}.

PACS numbers: 34.10.+x

Recently, two groups have stabilized samples of spin-polarized atomic hydrogen ($\mathrm{H}\downarrow$). Silvera and Walraven[1] have obtained densities up to 5×10^{16} cm^{-3} at 0.27 K, and Cline *et al.*[2] report densities up to 10^{17} cm^{-3} at 0.30 K, both in high magnetic fields, with holding times of greater than an hour. These conditions are now close to those necessary for Bose-Einstein condensation. Siggia and Ruckenstein's recent Letter[3] on the properties of Bose-condensed $\mathrm{H}\downarrow$ predicts the formation of a two-component superfluid, with each component consisting of atoms in one of the two lowest hyperfine states of hydrogen. The degeneracy temperature for each component is simply related to the density of atoms in each of the two hyperfine states, and a fundamental assumption of their theory is that the relative populations of the states do not equilibrate, i.e., that T_1 is infinite for these two levels.

Experimental work in our own laboratory has focused on magnetic resonance studies of atomic-hydrogen gas at low temperature,[4] and thus it is important for us to understand how the H-atom spins come to thermal equilibrium. We have also suspected for some time that the recombination rate of H atoms into H_2 molecules is sensitive to the relative populations of the hyperfine states, and hence that the recombination rate might depend on T_1. A theory of this dependence is given below. The main result of this Letter, however, is the T_1 calculation which gives the temperature, field, and density dependence of the relaxation rate of the two lowest hyperfine levels of H↓.

At low enough temperatures, in a high magnetic field, only the lowest two hyperfine states are appreciably populated. The lowest state, $|a\rangle = |$↓⤈$\rangle - \epsilon|$↑⤈$\rangle$ (↓ electron and ⤈ proton spin) contains a small admixture ϵ of spin-up electron, whereas the other state $|b$↓⤈$\rangle$ is a pure Zeeman state. In high field, the admixture constant ϵ is approximately given by $\epsilon \approx a/(2\mu_e H_0)$ where a is the zero-field hyperfine splitting. Also at high fields, spin exchange does not equilibrate the proton spins because the electron and proton systems are effectively decoupled. This leaves the dipole-dipole interaction as the only other feasible mechanism for relaxation.

By assuming a two-level system we relate the relaxation rate, T_1^{-1}, to the transition rates for the various two-body elastic collisions, ω_i. Considering the rate of change of the population difference in the high-temperature limit, we find

$$T_1^{-1} = 4(\omega_1 + \omega_2), \tag{1}$$

where $\omega_1 = \omega(a,b;a,a) = \omega(a,b;b,b)$, as we will show later, and $\omega_2 = \omega(a,a;b,b)$. Here $\omega(\sigma_1,\sigma_2;\sigma_1'\sigma_2')$ is the rate of transitions for two atoms initially in hyperfine states σ_1 and σ_2 into hyperfine states σ_1' and σ_2'. By using the distorted-wave Born approximation, we have

$$\omega_k(\sigma_1,\sigma_2;\sigma_1',\sigma_2') = N(2\pi/\hbar)(1/4\pi)\int d\Omega_k d\Omega_{k'} |\langle \vec{k}';\sigma_1'\sigma_2'|P_s^\dagger H_{dd} P_s|\vec{k};\sigma_1,\sigma_2\rangle|^2 \rho_f(k), \tag{2}$$

where H_{dd} is the dipole-dipole Hamiltonian, $\rho_f(k)$ the final density of states, and P_s the operator which projects out the properly symmetrized two-atom states. These states will have total nuclear spin I, total electron spin S, and angular momentum l. The Pauli principle for protons and electrons is satisfied if $I+S+l$ is even.

Before evaluating the spin matrix elements, consider which dipole-dipole interactions are important. The strongest interaction which flips the proton is the electron-proton interaction, $H_{dd}^{ep} \propto +\gamma_e\gamma_p$. For the electron it is the electron-electron interaction, $H_{dd}^{ee} \propto -\gamma_e^2$. Therefore, the total interaction Hamiltonian is

$$H_{dd} = \hbar^2 \gamma_e \gamma_p (12\pi/5)^{1/2} \sum_{m=\pm 1} [T_{ep}^m - (\gamma_e/\gamma_p) T_{ee}^m] Y_2^{m*}(\Omega_{12})/R_{12}^3, \tag{3}$$

where

$$T_{ep}^m = S^0(1) I^m(2) + S^0(2) I^m(1); \quad T_{ee}^m = S^0(1) S^m(2) + S^m(1) S^0(2).$$

$Y_l^m(\Omega)$ is a spherical harmonic and R_{12} the distance between the two colliding atoms, 1 and 2.

We are going to keep the leading terms of order $\gamma_e\gamma_p$ and $\epsilon\gamma_e^2$ but discard terms of higher order in ϵ and γ_p/γ_e. The only nonzero matrix element involving the singlet interaction ($S=0$) occurs in $\omega(a,a;b,b)$, is of order $\epsilon\gamma_e\gamma_p$, and will therefore be ignored. This term corresponds to a simultaneous proton-electron spin-flip (${}_e\langle 0,0| \otimes {}_p\langle 0,0| H_{dd} |1,-1\rangle_e \otimes |1,-1\rangle_p$) and also involves a change from the triplet to singlet potential during the collision. All the other terms of interest have $I=S=1$. Therefore, the atoms interact via the triplet potential and l must be even.

The spin matrix elements are

$$\langle a,a|[T_{ep}^1 - (\gamma_e/\gamma_p) T_{ee}^1]|a,b\rangle = (1/\sqrt{8})[1 + \epsilon\gamma_e/\gamma_p], \tag{4a}$$

$$\langle b,b|[T_{ep}^{-1} - (\gamma_e/\gamma_p) T_{ee}^{-1}]|a,b\rangle = -(1/\sqrt{8})[1 + \epsilon\gamma_e/\gamma_p]. \tag{4b}$$

Also, $\omega_2 \simeq 0$ since it contains only terms of higher order. Now we must evaluate the square of the spatial matrix element

$$M(K)=\int d\Omega_k d\Omega_{k'}\left|\langle\vec{k}'|Y_2{}^1(\Omega_{12})R_{12}{}^{-3}|\vec{k}\rangle\right|^2. \tag{5}$$

Following the procedure outlined by Shizgal,[5] we evaluate $M(k)$ after solving for the spatial wave function by using standard partial wave analysis. The triplet potential used here is a fit to the Kolos and Wolniewicz potential.[6]

The radial wave equation is solved numerically for given k and l and the resulting wave function, $u_l(k,R_{12})$, is used to evaluate

$$M(k)=\frac{64\pi^3}{5V^2}\sum_{l,l'\,\text{even}}(2l+1)(2l'+1)C^2(ll'2;00)r_{l,l'}{}^2k^{-4}, \tag{6}$$

where

$$r_{l,l'}=\int_0^\infty dR_{12}u_l(k,R_{12})u_{l'}(k,R_{12})R_{12}{}^{-3}. \tag{7}$$

The only two terms which feel the potential at the low energies of concern here, <0.6 meV, are the r_{02} and r_{22} terms. These values are obtained numerically and the asymptotic form[5] is used for the rest of the $r_{l,l'}$ terms.

Once this is done, the relaxation rate can be written in the form

$$T_1{}^{-1}=n_{\mathrm{H}}\bar{v}_{\mathrm{rel}}\tfrac{1}{2}\beta^2\int_0^\infty e^{-\beta E}\sigma_{\mathrm{eff}}(E)E\,dE, \tag{8}$$

where n_{H} is the atom density, $\bar{v}_{\mathrm{rel}}$ the average relative thermal velocity, $\beta=(kT)^{-1}$, and

$$\sigma_{\mathrm{eff}}=(48\pi/25)\mu^2\gamma_e{}^2\gamma_p{}^2[1+\epsilon\gamma_e/\gamma_p]^2\sum_{l,l'\,\text{even}}(2l+1)(2l'+1)C^2(ll'2;00)r_{ll'}{}^2k^{-4}, \tag{9}$$

where μ is the reduced mass. In order to perform the thermal average, we evaluated $\sigma_{\mathrm{eff}}(E)$ for $0.001\ \mathrm{meV}<E<0.6$ meV. This results in σ_{eff} of the form $\sigma_{\mathrm{eff}}(E)=a+bE$. After performing the thermal average, we obtain

$$T_1{}^{-1}=0.956\times10^{-4}T^{1/2}-0.105\times10^{-4}T^{3/2}\ \mathrm{sec}^{-1} \tag{10}$$

for $H_0=100$ kG and $n_{\mathrm{H}}=10^{16}\ \mathrm{cm}^{-3}$. This expression is valid up to the point where σ_{eff} becomes nonlinear ($\gtrsim 2$ K) and down to ~ 50 mK where the collisions become inelastic. For other values of field $T_1{}^{-1}$ scales with $[1+\epsilon\gamma_e/\gamma_p]^2$.

Now that the relaxation rate has been determined, let us consider the recombination processes. At 1.0 K, where there is a substantial ^{4}He density (if we assume the sample container walls are coated with a ^{4}He film), the dominant process involves bulk collisions where

$$\mathrm{H}+\mathrm{H}+{}^4\mathrm{He}\rightarrow\mathrm{H}_2+{}^4\mathrm{He}. \tag{11}$$

The rate constant for this process has been measured by Hardy *et al.*[4] Below 1 K other processes dominate the recombination rate. One must consider three-body bulk collisions where

$$\mathrm{H}+\mathrm{H}+\mathrm{H}\rightarrow\mathrm{H}_2+\mathrm{H}, \tag{12}$$

and wall processes where

$$\mathrm{H}+\mathrm{H}+\mathrm{wall}\rightarrow\mathrm{H}_2+\mathrm{wall}. \tag{13}$$

The rate constants for these processes are not known but one can extract an estimate from the bulk-^{4}He value.

This is done by assuming an effective kinetic cross section whereby recombination always occurs when the necessary atoms are within a certain volume. We obtain a cross section of ~ 34 Å^2 from the bulk-^{4}He rate constant and will now assume that this value applies to the other recombination processes as well as assuming it to be temperature independent.

Recombination of two H atoms requires that they interact via the singlet potential since only the singlet potential supports bound states. For H↓ the population of the upper two hyperfine states is low enough to be insignificant. However, the admixture in $|a\rangle$ is large enough for reasonable values of H_0 that it becomes the dominant source of recombination. We will use this assumption in determining the various rate constants for recombination in a high magnetic field.

In order to determine the rate constant for the wall processes, the surface density must be calculated. For low enough surface density this can be done by assuming the simple model given by Edwards and Mantz.[7] The surface density is given by

$$\sigma_{\mathrm{H}}=n_{\mathrm{H}}\Lambda\exp(E_B/kT),$$

where $\Lambda = \hbar/(2\pi mkT)^{1/2}$ and E_B is the binding energy of H on a ^{4}He surface. This expression will be valid until the interatomic interactions limit the surface density,[7] at about 10^{14} cm^{-2}.

Two values for E_B are used here. Mantz and Edwards[8] give a lower limit of $E_B = 0.6$ K whereas Guyer and Miller[9] calculate $E_B = 0.1$ K. By using the above information, we find that the dominant recombination mechanism involves collisions between two atoms on the surface. The initial rate constant for this process, $\tau^{-1} = Kn_H(t=0)$, is given by

$$\tau^{-1} = 4.54\times 10^{-17} T^{-1/2}(A/V)[\tfrac{3}{8}\epsilon^2 + \exp(-\gamma_e H_0/kT)]\exp(2E_B/kT)n_H(0). \tag{14}$$

τ^{-1} is plotted versus temperature in Fig. 1 for both values of E_B, along with the relaxation rate T_1^{-1}.

Finally, let us consider the population dynamics of the quasi-two-level system of H$\downarrow$ under the influence of both recombination and relaxation. Considering wall recombination only, the rate equations for the two populations are[10]

$$dn_a/dt = -K_{\rm rec}n_a(2n_a + n_b) - K_{\rm rel}(n_a - n_b)(n_a + n_b), \tag{15a}$$

$$dn_b/dt = -K_{\rm rec}n_a n_b + K_{\rm rel}(n_a - n_b)(n_a + n_b). \tag{15b}$$

We will now discuss two limiting cases, the first where $K_{\rm rec} \ll K_{\rm rel}$. In order for two atoms to recombine, one must be in a state $|a\rangle$. This favors a heavier depletion of $|a\rangle$ than of $|b\rangle$ but since relaxation rate is fast, the two states remain equally populated. Therefore, the two populations follow the rate equation $dn/dt = -Kn^2$, with a rate constant $K_{\rm rec}$.

The other limit, $K_{\rm rec} \gg K_{\rm rel}$, appears to be the case at low temperatures. Here the atoms in state $|a\rangle$ recombine faster than the relaxation mechanism can equilibrate the two populations. Therefore, state $|a\rangle$ is almost depleted and recombination occurs only as fast as relaxation can transfer atoms from $|b\rangle$ to $|a\rangle$. The asymptotic behavior of $n_a(t)$ and $n_b(t)$ is given by

$$n_a(t) = (K_{\rm rel}/K_{\rm rec})n_b(t) \tag{16a}$$

$$n_b(t) = n_{b0}\tau/t + \tau, \tag{16b}$$

where $(\tau n_{b0})^{-1} = 2K_{\rm rel}$, n_{b0} being the population of $|b\rangle$ at which the actual solution approaches the asymptotic solution. In this case $n_b(t)$ follows the rate equation for wall recombination but with the rate constant $= T_1^{-1}$.

In light of these results Bose condensation should occur first for atoms in state $|b\rangle$ and perhaps not at all for atoms in state $|a\rangle$. With regard to the discussion of Bose-condensed H$\downarrow$ by Siggia and Ruckenstein,[3] it appears as if the two-component superfluid will not be formed.

This work was supported in part by the National

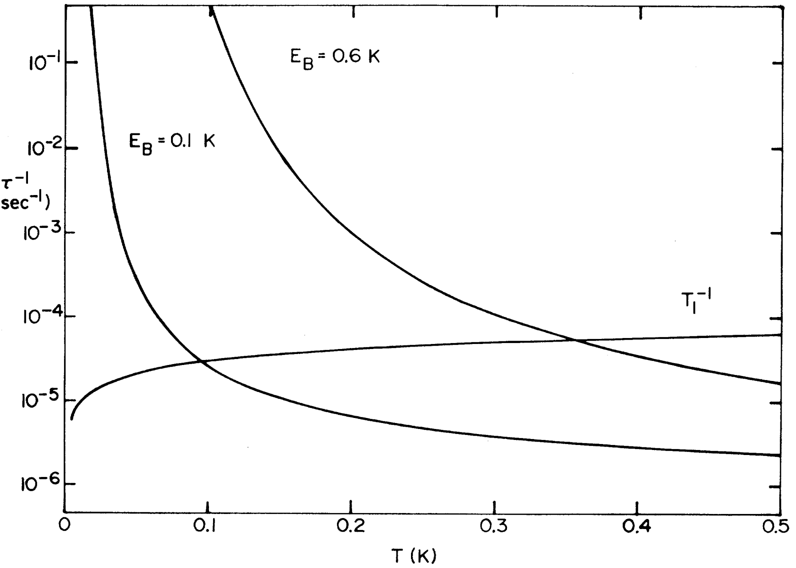

FIG. 1. Recombination rate for two values of binding energy, $n_H(0) = 10^{16}$ cm^{-3}, and $H_0 = 100$ kG. The relaxation rate is also given.

Research Council of Canada. One of us (A.J.B.) would like to acknowledge the support of the Alfred P. Sloan Foundation. We thank W. N. Hardy for suggesting the T_1 calculation. We also thank B. Shizgal for providing some of the computer programs.

---

[1] J. T. M. Walraven, I. F. Silvera, and A. P. M. Matthey, Phys. Rev. Lett. 45, 449 (1980).

[2] R. W. Cline, T. J. Greytak, D. Kleppner, and D. A. Smith, J. Phys. C 7, 151 (1980).

[3] E. D. Siggia and A. E. Ruckenstein, Phys. Rev. Lett. 44, 1423 (1980).

[4] W. N. Hardy, M. Morrow, R. Jochemsen, B. W. Statt, P. R. Kubik, R. M. Marsolais, and A. J. Berlinsky, Phys. Rev. Lett. 45, 453 (1980).

[5] B. Shizgal, J. Chem. Phys. 58, 3424 (1973).

[6] W. Kolos and L. Wolniewicz, Chem. Phys. Lett. 24, 457 (1974).

[7] D. O. Edwards and I. B. Mantz, J. Phys. C 7, 257 (1980).

[8] I. B. Mantz and D. O. Edwards, Phys. Rev. B 20, 4518 (1979).

[9] R. A. Guyer and M. D. Miller, Phys. Rev. Lett. 42, 1754 (1979).

[10] Here we assume that the cross section for two a atoms to recombine is equal to that for one a and one b atom. In fact, these rates may be different because there are different cross sections for forming para-H_2 and ortho-H_2. However, this difference is unlikely to affect the important qualitative features of Fig. 1.