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Calculation of nuclear-spin-relaxation rate for spin-polarized atomic hydrogen

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Approximations introduced in previous calculations of spin relaxation for spin-polarized atomic hydrogen are investigated by carrying out a more exact coupled-channel calculation. With the exception of the high-temperature approximation, the approximations turn out to be justified up to the 10^{-3} level of accuracy. It is shown that at the lowest temperatures for which experimental data are available, the high-temperature limit underestimates relaxation rates by a factor of up to 2. For a comparison with experimental data it is also of interest to pay attention to the expression for the atomic hydrogen relaxation rates in terms of transition amplitudes for two-particle collisions. Discrepancies by a factor of 2 among previous derivations of relaxation rates are pointed out. To shed light on these discrepancies we present two alternative derivations in which special attention is paid to identical-particle aspects. Comparing with experiment, we find our theoretical volume relaxation rate to be in better agreement with measured values than that obtained by other groups. The theoretical surface relaxation rate, however, still shows a discrepancy with experiment by a factor of order 50.

I. INTRODUCTION

In the last few years important progress has been made towards the realization of Bose-Einstein condensation of atomic hydrogen. Since the first experimental successes achieved by Silvera and Walraven,[1] the main ingredients for stabilization of atomic hydrogen against recombination have been the creation of electron-spin-polarized hydrogen in a strong magnetic field at low temperatures and its confinement in a He-coated cell. Under the experimental conditions, however, recombination still takes place to a considerable extent, due to the depolarizing influence of the hyperfine interaction with the nuclear spins: Of the two lowest 1*s* hyperfine states populated, the state $|b\rangle = |\downarrow\Downarrow\rangle$ ($\downarrow$ electron spin, $\Downarrow$ proton spin) is still fully electron polarized, but the state $|a\rangle = |\downarrow\Uparrow\rangle - \epsilon|\uparrow\Downarrow\rangle$ contains the electron spin-up state by an amplitude $\epsilon \simeq 2.5\times10^{-2}/B$ (with B in tesla).

Statt and Berlinsky[2] have pointed out that a gas of pure *b*-state atoms (H), in which also the nuclear spins are polarized, would recombine much more slowly. Such a gas would be obtained automatically by the preferential recombination of the *a* atoms. Recent experiments[3,4] have led to promising results in this direction. As predicted by Statt and Berlinsky, however, the stabilization time of the H gas is still limited by the $b \rightarrow a$ transitions induced by two-particle collisions, both in the bulk and at the surface. Clearly, the corresponding relaxation time T_1 is of great importance in achieving the conditions necessary for Bose-Einstein condensation. Cline *et al.*[3] measured T_1 both for volume relaxation and for relaxation of hydrogen atoms adsorbed on a ^{4}He surface. Sprik *et al.*[4] extended these measurements both by enlarging the temperature range and by considering also surface relaxation on ^{4}He and ^{3}He-^{4}He mixtures.

The measured volume relaxation rates $1/T_1$ were about a factor of 2 smaller[5] than those calculated by Statt and Berlinsky[2] and by Siggia and Ruckenstein.[6] We shall see in the following that the discrepancy by this factor of 2 can be eliminated.

At the time of the measurements of Cline *et al.*[3] a complete calculation of the surface relaxation rates was not yet available. By the time of the completion of the measurements of Sprik *et al.*,[4] four surface relaxation calculations had been carried out. The first of these, by Lagendijk,[7] pointed for the first time to the strong anisotropy expected for the relaxation rate with respect to the direction of the stabilizing field relative to the He surface, but did not take into account the finite spatial extent of the bound-state wave function perpendicular to the surface for an adsorbed hydrogen atom. Three subsequent papers,[8–10] submitted for publication almost simultaneously, did take this effect into account. In addition, Siggia and Ruckenstein[8] studied the virtual atomic hydrogen bulk state mixed into the surface state by the triplet interaction and found a nonvanishing relaxation rate in lowest order in the spin-spin interactions for a perpendicular magnetic field. From angular-momentum conservation along this field obeyed by the two-atom system, it can be seen, however, that this contribution should vanish: The change in spin angular momentum to lowest order in the spin-spin interactions is $\pm\hbar$, while the relative orbital angular momentum of the two atoms, and thus also its change, is an even multiple of $\hbar$, owing to Bose-Einstein statistics.

The other two papers[9,10] contain theoretical results which are to a large extent equivalent, except for a factor-of-2 discrepancy in T_1. Reference 10 contains a comparison with experiment from which it appears (see also Ref. 4) that the theoretical surface relaxation rate is a factor of order 50 smaller than the experimental value, so that some important effect seems to have been overlooked in the theoretical considerations. A discussion of this discrepancy is outside the scope of this paper. Rather, our purpose is to estimate the reliability of some of the approximations introduced in the existing calculations of the volume relaxation by relaxing them in a more exact calculation. This calculation confirms the validity of the approximations up to the 10^{-3} level of accuracy, except for the approximation of neglecting the change in internal energies of the colliding H atoms compared with their collision energy, the so-called high-temperature limit (HTL). Owing to the low-energy cross section going to infinity instead of to a constant, deviations from the HTL turn out to be significant at the lowest temperatures (80–100 mK) for which experimental data are available.

In addition we shall consider two alternative derivations of the theoretical expression for $1/T_1$ to shed light on the above-mentioned discrepancies of a factor of 2. We shall show that the volume and surface relaxation rates calculated in Refs. 6 and 8 should be divided by a factor of 2. The same applies to the volume relaxation rate as calculated in Ref. 2 and corrected according to Ref. 5, as well as to the surface relaxation rate calculated in Ref. 9.

In Sec. II we present the above-mentioned more exact calculation of the volume relaxation. On the basis of this, we subsequently rely on the usual approximations in the following sections. In Sec. III we give an expression for the volume relaxation rate starting from two-particle scattering of identical bosons, supplemented by some kinetic gas theoretical considerations. In Sec. IV we use a different starting point: the Kubo-Tomita approach[11] to the longitudinal relaxation rate. This derivation has the advantage that identical-particle aspects are handled systematically in second quantization. In a final conclusion, presented in Sec. V, we compare our theoretical relaxation rates with the experimental values of Refs. 3 and 4.

II. STUDY OF APPROXIMATIONS

In the papers on volume and surface relaxation rates discussed in the foregoing, various approximations have been introduced: (1) The distorted-wave (or plane-wave) approximation, i.e., the transition amplitudes are calculated to first order in the noncentral spin-dependent interactions. (2) Exchange is neglected. (3) The Shizgal approximation,[12] i.e., all magnetic-dipole moments participating in the interatomic interaction are assumed to coincide with the center of mass of their respective hydrogen atoms. (4) The coupling matrix elements are only taken into account up to order $\epsilon^1\delta^0$ and $\epsilon^0\delta^1$, where $\delta=\mu_p/\mu_e$, the ratio of proton and electron magnetic moments. Within the framework of the distorted-wave approximation [assumption (1)] this implies that the coupling is restricted to the triplet channels, i.e., singlet parts of the wave function are left out of consideration. (5) The high-temperature limit.

Although each of the approximations (1)–(4) looks reasonable, we considered it worthwhile to investigate their reliability by a more exact coupled-channel calculation for H-H scattering in a strong magnetic field. In particular, the neglect of singlet channels for which the central potential has a repulsive part with a much smaller range might in principle have significant influence due to the closer approach of the H atoms.

The coupled-channel (close-coupling) method is obtained from the time-independent Schrödinger equation for the scattering process by expanding the total scattering wave function in a set of internal states of the scattering partners, which is in principle complete but in practice restricted. The expansion coefficients depend on the relative radius vector $\vec{r}$ of the two nuclei and characterize the probability amplitudes for the atoms to be in the corresponding internal states at this relative position. The internal states may in principle also depend parametrically on r. After substitution of this expansion the inner product of both sides of the Schrödinger equation is taken with each of the internal states. A well-defined coupled-channel problem is obtained if the set of internal states as well as the corresponding matrix elements of the Hamiltonian operator are specified.

For the spin part of the internal states we choose states with quantum numbers (S,M_S,I,M_I) for the total electron spin $\vec{S}$ and total proton spin $\vec{I}$, magnetic quantum numbers referring to the magnetic field direction. For the space part we restrict ourselves to the lowest Σ_g^+ and Σ_u^+ electron states. Since we are interested in the order of magnitude of the effect of the finite extent of the electronic probability distribution around the nuclei, we take simple Heitler-London wave functions. For the spatial electronic contribution to the internal energy we take the triplet and singlet potentials calculated by Kolos and Wolniewicz.[13] The spin contribution consists of the electron and proton Zeeman energies in the external magnetic field. Clearly, the antisymmetry requirement for the electrons thus admits 16 combined space-spin functions. Owing to our restriction to these 16 states, nonadiabatic effects from the nuclear kinetic-energy term survive only in small diagonal terms which do not contribute to the channel coupling and are therefore left out.

The matrix elements of all noncentral spin-spin interactions include four electron-proton Fermi contact terms, as well as one electron-electron and four electron-proton magnetic dipole-dipole interactions. In the calculation of these matrix elements none of the electrons is assigned preferentially to one of the nuclei, contrary to the distorted-wave method, where the coupling interaction is only interatomic. All of the matrix elements are calculated either analytically or reduced to Kolos-Wolniewicz–type integrals for which numerical algorithms exist.[13,14] We use a modified Numerov method[15] to solve the coupled equations. Three complications to be dealt with in the calculation are worth mentioning.

The first is the problem of numerical instability associated with the tendency to numerical linear dependence, due to channel coupling in classically strongly forbidden radial regions.[16] We make use of a well-known recipe to circumvent this problem: choosing new linear combinations of the solutions at some radii within the region of the channel coupling.

A second complication is that for our choice of internal states certain coupling terms among channels persist into the asymptotic radial region: the Fermi contact interaction of each electron with "its" nucleus. It would have been possible to avoid this by selecting different basis functions from the beginning, i.e., the 16 symmetrized and antisymmetrized products of four $1s$ hyperfine states of the two separate H atoms in an exterior magnetic field. We did not follow this procedure, however, since this would require an orthogonal transformation for each step in the radial integration process to transform the triplet and singlet potentials. Instead, we carry out an orthogonal transformation to asymptotically decoupled channels at an r value equal to r_c which is chosen somewhere between $15a_0$ and $50a_0$. Beyond r_c we found all approximations (1)–(4) to be applicable. We simplified the calculation correspondingly.

A third complication is the implementation of one of the approximations to be studied, the HTL approximation, within the coupled-channels framework. The asymptotic internal energies of the *bb*, *ab*, and *aa* channels are not put in explicitly, but result automatically from the coupling matrix at large distances. As a consequence, they are nondegenerate due to the inclusion of the full Fermi-contact interaction and the spin-Zeeman terms in the coupled-channel problem. We solved this problem by adding in the exterior region a constant diagonal matrix to the coupling matrix making the asymptotic open-channel wave numbers equal. Within r_c this additional contribution is transformed orthogonally to the (S,M_S,I,M_I) representation.

We now come to the results for approximations (1)–(4). We studied them successively within the framework of the high-temperature limit. Subsequently, the reliability of the latter is discussed. The distorted-wave approximation may be investigated by varying the strength of the noncentral spin-spin interactions. It turns out that the S-matrix elements for $a \rightarrow b$ and $b \rightarrow a$ transitions are proportional to this strength up to corrections at the 10^{-3} level. The same conclusion applies to the exchange effects and to the Shizgal approximation. Exchange enters the coupled-channel problem both via the difference between the triplet and singlet potentials and in exchange contributions to the noncentral spin-spin interactions. The latter clearly disappear automatically with the introduction of the Shizgal approximation, so that we carry out a combined test. The importance of the difference among triplet and singlet central potentials follows from a calculation in which the singlet potential is replaced by the triplet potential.

Let us now consider the restriction to order $\epsilon^1\delta^0$ and $\epsilon^0\delta^1$. Within the framework of the distorted-wave approximation, higher orders would show up in deviations of the field dependence of the amplitudes from the factor $1+\epsilon/\delta$. A calculation for $B=10$ and 15 tesla shows the amplitudes to be proportional to the aforementioned factor but for corrections on the 10^{-3} level.

Deviations from the HTL are of much more importance. Without the HTL approximation the effective cross sections for the $bb \leftrightarrow ab$ and $ab \leftrightarrow aa$ transitions are no longer equal. Since the nuclear polarization in the stabilization experiment reaches almost 100%, however, we are only interested in the relaxation constant $G_{bb \rightarrow ab}$. Translational energies at the temperature considered are to be referred to the *bb* internal energy level. As a consequence, relaxation rates are considerably higher without the

HTL at the lower temperatures, due to the facilitated penetration of the centrifugal barrier in the *ab* channel. While at a collision energy corresponding to 0.2 K the effective cross section rises from 4.57×10^{-25} to 5.75×10^{-25} cm^2, the increase at 0.05 K is from 4.59×10^{-25} to 10.88×10^{-25} cm^2. Instead of tending to a constant, the low-energy $bb\rightarrow ab$ effective cross section goes to infinity as $1/\sqrt{E}$. In Sec. V we pay attention to the comparison with experiment, after having discussed the factor-of-2 discrepancies in the theoretical relaxation formulas in the next section.

III. RELAXATION RATES FROM TWO-PARTICLE DISTORTED-WAVE AMPLITUDES

To resolve the factor-of-2 discrepancies between existing derivations of the relaxation rate, it is of importance to define as explicitly as possible the quantities occurring in the derivation, with special emphasis on identical-particle aspects, the treatment of which is probably responsible for the discrepancies. We start with a derivation on the basis of the T-matrix elements for two-particle collisions in the H gas.

For the differential cross section of H-H scattering, our starting point is the expression

$$\sigma_{s's}(\vec{k}_{s'},\vec{k}_s)=\left[\frac{\mu_m}{2\pi\hbar^2}\right]^2\frac{k_{s'}}{k_s}\,|\,T_{s's}\,(\vec{k}_{s'},\,\vec{k}_s)\,|^2\ , \tag{1}$$

associated with the transition from relative wave vector $\vec{k}_s$ and two-electron—two-proton spin state s (for instance $s=bb$) to a final combination $\vec{k}_{s'}$ and s' (for instance, ab, the order of a and b being meaningful in relation to the direction of the wave vector). The reduced mass is denoted by $\mu_m=\frac{1}{2}m_{\mathrm{H}}$. In the distorted-wave approximation, upon which we now base our derivation, the T-matrix element is given by

$$T_{s's}(\vec{k}_{s'},\vec{k}_s)=\langle\chi_{s'}^{(-)}(\vec{r},\vec{k}_{s'})\psi_{s'}\,|\,W\,|\,(1-P_{12})(1-P_{AB})\chi_s^{(+)}(\vec{r},\vec{k}_s)\psi_s\rangle\ \ . \tag{2}$$

Here, P_{12} is a permutation operator of electrons 1 and 2, while P_{AB} permutes protons A and B. Before explaining further the notation of Eq. (2), it is useful to point to some aspects of its derivation from a wave-packet description as given, for instance, by Austern.[17] In this derivation one takes into account an ensemble of normalized relative motion precollision wave packets, each of which consists of four parts in the two-electron—two-proton configuration space, nonoverlapping for $t\rightarrow-\infty$ and mutually related by particle permutation. Each of these four gives rise to a scattered wave. Each scattered wave contributes four incoherent terms to the signal in an H detector, which is insensitive to the particle labels of the H-atom constituents. The factor of 4 arising from the corresponding incoherent summation over particle compositions is compensated by the normalization factor of the initial antisymmetrized wave function in Eq. (2). Each of the spin states s and s', together with the corresponding momenta, can be combined with four possible particle compositions of the colliding H atoms. In the product $\chi_s\psi_s$ such a particle labeling is arbitrarily selected. The same particle labeling is then chosen for the bra state. Even if s (or s')$=bb$, the particle composition $1A+2B$ is not identical to $2B+1A$, once the direction of the wave vector is specified (cf. the aforementioned corresponding remark for the spin states). The functions ψ stand for spin states, while the functions χ are distorted waves containing asymptotically plane waves $\exp(i\vec{k}\cdot\vec{r})$ in addition to outgoing (ingoing) waves if the superscript is $+$ $(-)$. Finally, W is the total interatomic spin-spin interaction for the primary particle composition selected, in addition to $P_0V_0(r)+(P_1-1)V_1(r)$. Here, P_0 (P_1) is a projection operator upon singlet (triplet) spin states, while V_0 (V_1) is the singlet (triplet) potential.

On the basis of the results of the preceding section with respect to exchange, we need to take into account only the $P_{12}P_{AB}$ permutation term. For the spin transitions of interest, it is easily seen that only the even-l part of the distorted waves contributes in Eq. (2). Furthermore, the part $P_0V_0+(P_1-1)V_1$ contributes in order ϵ^2 or higher order only and is therefore neglected. For the spin-spin interactions we introduce the Shizgal approximation. Their matrix elements are approximated to order $\epsilon^1\delta^0$ and $\epsilon^0\delta^1$, implying that the selection rule $\Delta(M_S+M_I)=\pm1$ is valid for the total spin projection along the magnetic field.

To avoid confusion about factors of 2 we give the final result for the T-matrix element:

$$\begin{aligned}T_{s's}(\vec{k}_{s'},\vec{k}_s)=\pm\frac{4\pi}{k_s'}\frac{4\pi}{k_s}\sum_{\substack{l',l\\ \text{even}}}\sum_{m',m}i^{l-l'}Y_{l'm'}(\hat{k}_{s'})Y_{lm}^{*}(\hat{k}_s)e^{i\eta_{l'}}e^{i\eta_l}r_{l'l}(-1)^m(2l'+1)^{1/2}(2l+1)^{1/2}\\ \times\begin{bmatrix}l' & 2 & l\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}l' & 2 & l\\ m' & \pm1 & m\end{bmatrix}2\sqrt{6}\frac{\mu_0}{4\pi}\mu_e\mu_p(1+\epsilon/\delta)\end{aligned} \tag{3}$$

in conventional notation, η_l and $\eta_{l'}$ being triplet phase shifts for initial and final channels and $r_{l'l}$ being the radial integral

$$r_{l'l}=\int_0^\infty u_{l'}(k_{s'},r)r^{-3}u_l(k_s,r)dr \ , \tag{4}$$

in which the partial distorted waves u are normalized at infinity as sine functions. Equation (3) is valid for all relevant combinations $s's$, the upper signs being valid when s' contains one b state less than s and the lower signs when s' contains one b state more. In the HTL we have $k_{s'}\simeq k_s=k$.

Before substituting Eq. (3) in Eq. (1), let us first consider the relaxation process in a volume V of dilute H$\downarrow$ gas. The change in the number N_b of b atoms in a time interval dt due to the $bb\rightarrow ab$ transition with all possible final relative velocity directions (so that ba should not be considered in addition to ab) is given by

$$(dN_b)_{bb\rightarrow ab}=-\tfrac{1}{2}\,dt\int vN_b^2/V^{-1}P(\vec{v})\sigma^{\mathrm{tot}}_{ab,bb}(\vec{v})d\vec{v} \ , \tag{5}$$

where the integration runs over all initial relative velocities $\vec{v}$ and σ^{tot} is the 4π-integrated cross section for a single $\vec{v}$:

$$\sigma^{\mathrm{tot}}_{ab,bb}(\vec{v})=\int d\hat{k}_{s'}\sigma_{ab,bb}(\hat{k}_{s'},\vec{k}_s) \ . \tag{6}$$

The factor of $\frac{1}{2}$ is included in Eq. (5) to avoid double-counting of the bb pairs and $P(\vec{v})d\vec{v}$ is the probability that an arbitrarily selected atomic pair has relative velocity in the volume element $d\vec{v}$ near $\vec{v}$.

Equation (5) also follows more formally from the Wang-Chang-Uhlenbeck quantum-mechanical Boltzmann equation[18] for the one-particle distribution function,

$$\frac{\partial}{\partial t}f_\mu(\vec{p},t)=\sum_{\mu_1}\sum_{\mu'}\sum_{\mu_1'}\int\int\int d\vec{p}_1 d\vec{p}\,' d\vec{p}\,'_1[f_{\mu'}(\vec{p}\,',t)f_{\mu_1'}(\vec{p}\,'_1,t)-f_\mu(\vec{p},t)f_{\mu_1}(\vec{p}_1,t)]\frac{k'}{\mu_m k}$$
$$\times\tfrac{1}{2}\sigma_{\mu\mu_1,\mu'\mu_1'}(\vec{k},\vec{k}\,')\delta\left[\frac{\hbar^2k^2}{2\mu_m}-\frac{\hbar^2k'^2}{2\mu_m}\right]\delta(\vec{p}+\vec{p}_1-\vec{p}\,'-\vec{p}\,'_1) \ , \tag{7}$$

by integrating over $\vec{p}$ and substituting a Maxwell-Boltzmann distribution for each of the f functions in the collision term. Here the normalization of the differential cross section is as defined in Eqs. (1) and (2). Subscripts μ in Eq. (7) stand for a or b. One should take care of the different conventions[19] for σ, which differ by a factor of 2. In the terminology of de Groot *et al.*[19] the Wang-Chang-Uhlenbeck equation is conventionally formulated[20] with a "classical" differential cross section, giving this equation the same appearance as the classical Boltzmann equation. The latter differential cross section is equal to half the differential cross section as defined by Austern.[17]

From Eq. (5) we find the following for the rate of change of the b atom density:

$$\left[\frac{dn_b}{dt}\right]_{bb\rightarrow ab}=-G_v n_b^2 \ , \tag{8}$$

with the volume relaxation rate constant G_v being given by

$$G_v=\tfrac{1}{2}\int vP(\vec{v})\sigma^{\mathrm{eff}}d\vec{v} \ , \tag{9}$$

the effective cross section σ^{eff} being defined as the total cross section (6) averaged over all directions of $\vec{v}$. Subscripts of σ^{eff} can be omitted in the HTL, effective cross sections for all relevant spin transitions being equal:

$$\sigma^{\mathrm{eff}}(v)=(384\pi/5)\left[\frac{\mu_0}{4\pi}\mu_e\mu_p\right]^2\hbar^{-4}k^{-4}\mu_m^2$$
$$\times\sum_{\substack{l',l\\ \mathrm{even}}}|r_{l'l}|^2(2l+1)(2l'+1)$$
$$\times\begin{bmatrix}l' & 2 & l\\ 0 & 0 & 0\end{bmatrix}^2(1+\epsilon/\delta)^2 \ . \tag{10}$$

Note that this value for σ^{eff} is a factor of 2 smaller than that given by Eq. (9) in Ref. 2.

With all other relevant spin transitions added to Eq. (8) we have the usual equations

$$\frac{dn_a}{dt}=G_v(n_b+n_a)(n_b-n_a) \ ,$$
$$\frac{dn_b}{dt}=-G_v(n_b+n_a)(n_b-n_a) \ . \tag{11}$$

Subtracting these equations we find the relaxation rate

$$1/T_1=2nG_v, \quad n=n_a+n_b \tag{12}$$

which after substitution of Eqs. (9) and (10) turns out to be a factor of 2 smaller than the value of Ref. 2 after correction[5] by the authors. It shows the same discrepancy with the plane-wave Born approximation (PWBA) value of Ref. 6.

IV. SECOND-QUANTIZATION DERIVATION

As a further support for the foregoing result, we use a starting point based on Kubo and Tomita's approach[11] to spin relaxation. It was also briefly mentioned in Ref. 8. For convenience we consider a gas of a and b atoms, interacting only through the weak spin-spin noncentral interactions. Omitting the central interactions will not have consequences for our discussion of factor-of-2 discrepancies. As we shall see, we are led to the same equations (12) and (9), with σ^{eff} replaced by the plane-wave Born value.

A derivation along these lines has the advantage that it is based on the second-quantization formalism so that identical-particle aspects are dealt with in a more straightforward way. We discuss the surface relaxation ($d=2$) along with the three-dimensional case ($d=3$). We consider a system of N atoms in a "volume" L^d with corresponding periodic boundary conditions for the single-particle wave functions $\phi_\mu L^{-d/2}\exp(i\vec{k}\cdot\vec{r})$, ϕ_μ being a one-atom internal wave function ($\mu=a$ or b), and leaving out a wave function for the motion perpendicular to the surface for the case of adsorbed atoms. The Hamiltonian of the system consists in the first place of an unperturbed part H_0, which is a sum of a (free) translational part H_0^{tr} with single-particle eigenvalues e_α, and an internal part H_0^{int} with single-particle eigenvalues ϵ_α. In second-quantized form

$$\begin{aligned} &H_0=H_0^{\text{tr}}+H_0^{\text{int}}=\sum_\alpha(e_\alpha+\epsilon_\alpha)c_\alpha^\dagger c_\alpha \ , \\ &e_\alpha=\hbar^2k_\alpha^2/2m_H,\ \ \epsilon_\alpha=\epsilon_a \ \text{ or } \epsilon_b \ . \end{aligned} \tag{13}$$

The perturbing spin-spin part is correspondingly

$$H_1=\tfrac{1}{2}\sum_{\kappa,\lambda,\mu,\nu}(h_1)_{\kappa\lambda,\mu\nu}c_\kappa^\dagger c_\lambda^\dagger c_\mu c_\nu \ , \tag{14}$$

h_1 standing for the interaction among a pair of atoms. Formally, a system with this Hamiltonian is known to be equivalent to a fictitious spin-$\frac{1}{2}$ gas (obeying Bose statistics) in an external homogeneous magnetic field. In the following we shall use terms like spin temperature, etc., on the basis of this analogy.

The eigenstates of the unperturbed Hamiltonian are $|N_1,N_2,N_3,\ldots\rangle$, N_α being the number of atoms in state α ($=\vec{k}_\alpha\mu_\alpha$). We now describe the translational subsystem by a canonical ensemble with a certain temperature ($\beta=1/k_BT$) and the spin subsystem by one with a spin temperature ($\beta_s=1/k_BT_s$). The density operator is thus in conventional notation given by

$$\rho(t)=Z^{-1}\exp\{-[\beta H_0^{\text{tr}}+\beta_s(t)H_0^{\text{int}}]\} \ . \tag{15}$$

In the spirit of the high-temperature limit we neglect the heat capacity of the spin system relative to that of the translational system and consider the relaxation of β_s to β, taking the latter to be constant. The spin temperature corresponds directly to the a and b occupations; thus we are able to derive a relaxation time.

According to first-order time-dependent perturbation theory, the change in the average total spin energy in a time interval τ large compared to a typical collision time but small relative to the time between collisions is

$$\begin{aligned} \Delta\langle\mathscr{E}\rangle=\frac{1}{\hbar^2}\sum_{N'}\sum_N(\mathscr{E}_{N'}-\mathscr{E}_N) \\ \times|\langle N'|H_1|N\rangle|^2 f(\tau,\omega_{N'N}) \\ \times Z^{-1}\exp\{-[\beta E_N+\beta_s(t)\mathscr{E}_N]\} \ . \end{aligned} \tag{16}$$

A short-hand notation N is used for a sequence $\{N_\alpha\}$ of occupation numbers, $E_N=\sum N_\alpha e_\alpha$ and $\mathscr{E}_N=\sum N_\alpha\epsilon_\alpha$, while

$$\begin{aligned} &f(\tau,\omega)=\sin^2(\tfrac{1}{2}\omega\tau)/(\tfrac{1}{2}\omega)^2 \ , \\ &\hbar\omega_{N'N}=(E_{N'}+\mathscr{E}_{N'})-(E_N+\mathscr{E}_N) \ . \end{aligned} \tag{17}$$

We now approximate $\Delta\langle\mathscr{E}\rangle$ to first order in $\beta_s-\beta$ assuming the deviation from equilibrium to be small. The zero-order term vanishes for large τ, owing to the symmetry of the H_1 factor in N' and N and the δ-function character of f. We thus have

$$\frac{d\langle\mathscr{E}\rangle}{dt}\simeq\frac{\Delta\langle\mathscr{E}\rangle}{\tau}=\frac{1}{T_1}(\langle\mathscr{E}\rangle_t-\langle\mathscr{E}\rangle_\infty) \ , \tag{18}$$

in which

$$\begin{aligned} \frac{1}{T_1}=\frac{2}{N\hbar^2}\sum_{(\alpha\beta)(\gamma\delta)}\sum_N[1/Z(\beta_s=\beta)]\exp[-\beta(E_N+\mathscr{E}_N)]\tau^{-1}f(\tau,\omega_{N'N})\,|(h_1)_{\alpha\beta,\gamma\delta}+(h_1)_{\alpha\beta,\delta\gamma}|^2 \\ \times N_\gamma N_\delta(N_\alpha+1)(N_\beta+1) \ . \end{aligned} \tag{19}$$

This equation is derived by (i) expressing $\beta_s-\beta$ in terms of $\langle\mathscr{E}\rangle-\langle\mathscr{E}\rangle_\infty$ to lowest order in $\epsilon_b-\epsilon_a$, (ii) noting that at most four N' numbers can differ from the corresponding N values for a nonvanishing contribution, and calling their subscripts $\alpha\beta\gamma\delta$; for fixed $\{N\}$ a sequence $\{N'\}$ is defined by giving the two pairs $(\alpha\beta)$ and $(\gamma\delta)$; equalities among these labels lead to negligible contributions for low densities, and (iii) noting that for fixed $\{N\}$ and $(\alpha\beta)(\gamma\delta)$ only four $\kappa\lambda\mu\nu$ combinations in the expression (14) for H_1 contribute.

The coefficient in Eq. (18) may be interpreted as the longitudinal spin-relaxation time T_1, because $\langle \mathscr{E} \rangle$ depends linearly on the total spin projection along the external magnetic field. We now consider the summations over occupation numbers in Eq. (19) to be uncorrelated. This enables us to factorize the numerator and the denominator, and to leave out all factors which do not correspond to the labels α, β, γ or δ.

The subsequent steps are (1) letting α and β, as well as γ and δ, run independently over single-particle states and adding a factor of $\frac{1}{4}$ for compensation, (2) writing out the sum over two-particle matrix elements by introducing relative and center-of-mass coordinates, thus obtaining

$$(h_1)_{\alpha\beta,\gamma\delta}+(h_1)_{\alpha\beta,\delta\gamma}=L^{-d}\delta_{\vec{K}',\vec{K}}T_{\mu_\alpha\mu_\beta,\mu_\gamma\mu_\delta}(\vec{k}',\vec{k}) \ , \tag{20}$$

where $\vec{K}$ and $\vec{K}'$ are the initial and final center-of-mass wave vectors, respectively, $\vec{k}$ and $\vec{k}'$ are the corresponding relative wave vectors, and T stands for the T-matrix element in the plane-wave Born approximation if L is sufficiently large:

$$T_{\mu_\alpha\mu_\beta,\mu_\gamma\mu_\delta}(\vec{k}',\vec{k})=\langle \exp(i\vec{k}'\cdot\vec{r}_{12})\phi_{\mu_\alpha}(1)\phi_{\mu_\beta}(2)\,|\,h_1(12)(1+P_{12})\,|\,\exp(i\vec{k}\cdot\vec{r}_{12})\phi_{\mu_\gamma}(1)\phi_{\mu_\delta}(2)\rangle \ , \tag{21}$$

1 and 2 now standing for a pair of H atoms, (3) approximating $\langle N_\alpha+1\rangle$ and $\langle N_\beta+1\rangle$ for low densities by 1, while

$$\tau^{-1}f(\tau,\omega_{N'N})\simeq 2\pi\hbar\delta\left[\frac{\hbar^2k'^2}{2\mu_m}-\frac{\hbar^2k^2}{2\mu_m}\right] \tag{22}$$

in the high-temperature limit, (4) replacing summations over wave vectors by integrations and noting that for $\vec{K}'=\vec{K}$

$$d\vec{k}_\beta d\vec{k}_\gamma d\vec{k}_\delta=d\vec{K}\,d\vec{k}\,d\vec{k}' \ . \tag{23}$$

The result is

$$\frac{1}{T_1}=\frac{n}{8\hbar^2}\left[\frac{\mu_m}{2\pi\hbar}\right]^{d-1}\sum_{\mu_\alpha,\mu_\beta,\mu_\gamma,\mu_\delta}\int\int d\hat{v}'\,d\vec{v}\,v^{d-2}P(\vec{v})\,|\,T_{\mu_\alpha\mu_\beta,\mu_\gamma\mu_\delta}(\vec{k}',\vec{k})\,|^2 \ . \tag{24}$$

Taking into account that the absolute values of the eight T-matrix elements for $aa\rightarrow ab$, $aa\rightarrow ba$, $ab\rightarrow aa$, $ba\rightarrow aa$, $bb\rightarrow ab$, $bb\rightarrow ba$, $ab\rightarrow bb$, and $ba\rightarrow bb$ are equal, we finally find, for $d=3$,

$$G_v=\tfrac{1}{2}\int d\vec{v}\,vP(\vec{v})\sigma^{\text{eff}} \ , \tag{25}$$

in accordance with the result of the preceding section, and for $d=2$

$$G_s=\tfrac{1}{2}\int d\vec{v}\,vP(\vec{v})\lambda^{\text{eff}} \ , \tag{26}$$

in accordance with Eq. (9) of our previous paper,[10] λ^{eff} standing for the effective "cross length" in two dimensions and $P(\vec{v})$ for a two-dimensional probability.

V. CONCLUSION

From the coupled-channel work described in Sec. II, we conclude that a number of approximations usually introduced for calculating atomic-hydrogen relaxation rates are sufficiently reliable. From the results of Secs. III and IV we conclude that our calculated volume rate is a factor of 2 smaller than the results obtained by other groups. Our value is in better agreement with experiment. This is illustrated in Fig. 1, where we compare with the experimental data of Sprik *et al.*[4] for ^{3}He at $B=8$ T, assuming that no surface relaxation contributes in this case. Note that, contrary to the HTL curve which is proportional to $\sqrt{T}$ at low temperatures, the G_v value without HTL goes to a nonvanishing constant, leading to some improvement of the agreement with the lowest temperature data points. Figure 1 also shows the best fit from Ref. 4 based on the $\sqrt{T}$ behavior. Clearly, the difference between the theoretical results with and without HTL is significant, suggesting that a fit to experimental data should preferably take into account deviations from the $\sqrt{T}$ behavior at low temperatures.

In Fig. 2 we present a comparison with the experimental data of Cline *et al.*[3] We left out data points at 0.24 and 0.22 K, which the analysis of Ref. 4

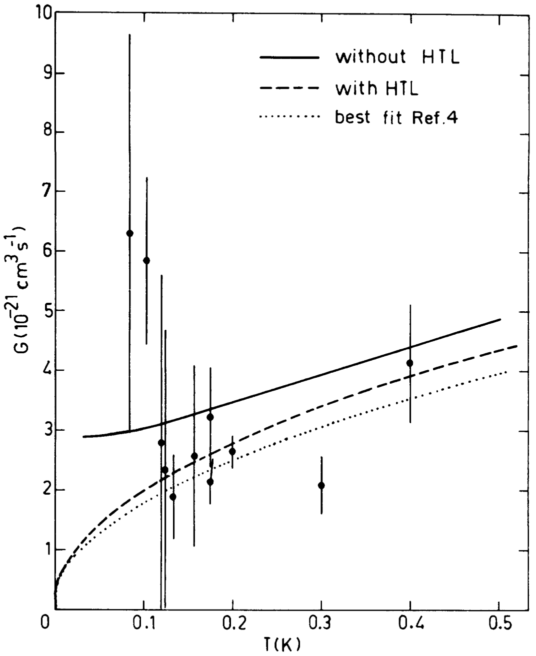

FIG. 1. Comparison with the experimental data of Sprik *et al.* (Ref. 4) for a ^{3}He-coated cell. Theoretical curves include results with and without high-temperature limit. The dotted curve is the Amsterdam best fit based on the $\sqrt{T}$ behavior.

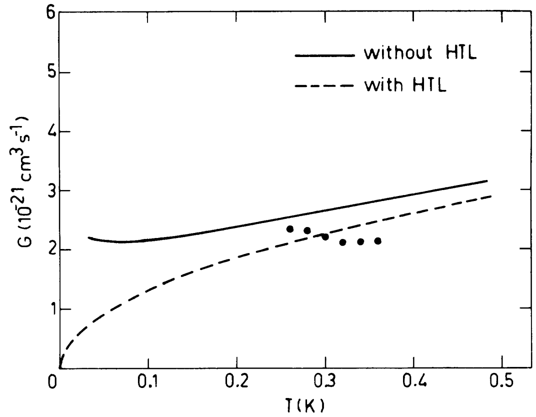

FIG. 2. Comparison with the experimental data of Cline *et al.* (Ref. 3) for a ^{4}He-coated cell. Theoretical curves are based on the calculations of the present paper with and without high-temperature limit.

shows to contain a contribution from surface relaxation. Again we conclude that an increase of the theoretical values by a factor of 2 would deteriorate the agreement with the experiments.[3,4] We point, however, to a recent unpublished result by Yurke *et al.*,[21] which yields a bulk relaxation rate about 4 times our theoretical one. We note that without the HTL the field dependence of G_v differs slightly from that obtained in the HTL, due to the influence of B on $\epsilon_b-\epsilon_a$. At $E/k_B=0.08$ K, for instance, changing the field from 8 to 11 T leads to a deviation of G_v from the $(1+\epsilon/\delta)^2$ field dependence by about 7%.

Also, for the surface relaxation our $1/T_1$ expression is a factor of 2 smaller than that found by other groups. In this case this enlarges the disagreement with experiment[10,4]: For the surface relaxation a major discrepancy with experiment exists, the experimental relaxation being faster than predicted by a factor of order 50. Some of this discrepancy (say, up to a factor of 2) could arise from uncertainties in the analysis of the experimental data. However, a satisfactory explanation for the large remaining discrepancy has not yet been presented. A discussion of this is outside the scope of this paper. In a planned publication[22] we shall give an extensive treatment of the surface relaxation problem, introducing various improvements of our previous calculation,[10] such as dropping the high-temperature limit and including a truly three-dimensional approach to the H-H surface collision.

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This should read $1/T_1 = 2nG_v$.

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