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Improvements in the description of the surface spin relaxation of atomic hydrogen

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Some possibilities are explored to explain the large discrepancy between theoretical and experimental spin-relaxation rates for the lowest two hyperfine states of hydrogen atoms adsorbed at a helium surface. A three-dimensional description of the collision process of adsorbed atoms is presented, including the coupling of the motions parallel and perpendicular to the surface by the triplet potential. Also the possibility of surface dimers, i.e., triplet bound states at the surface, is studied. Deviations from the high-temperature limit, used in previous papers, are investigated. Effective-mass and surface-deformation effects, resulting from the participation of helium-film modes in the H-H collision process are studied. It turns out that none of the model improvements considered decreases the discrepancy with experiment significantly, except possibly for the surface-deformation effect.

I. INTRODUCTION

Since the pioneering experiments by Silvera and Walraven,[1] the prospect of achieving Bose-Einstein condensation in a weakly interacting Bose gas has stimulated considerable experimental and theoretical efforts to stabilize samples of atomic hydrogen against recombination into molecules. Under the experimental circumstances, including a strong magnetic field ($\simeq 10$ T) and a low temperature (0.1—0.5 K), the hydrogen atoms are confined to the lowest-two hyperfine states. These behave very differently with respect to recombination. Recombination is almost entirely due to the small ϵ admixture of the *a* state, $|a\rangle = |{\downarrow}⍏\rangle - \epsilon|{\uparrow}⍖\rangle$ (↑ and ⍏ denoting electron and proton spin, respectively), where $\epsilon \simeq 2.5\times 10^{-2}/B$ (B in tesla). Statt and Berlinsky[2] pointed out that an atomic gas of atoms in the *b* state $|b\rangle = |{\downarrow}⍖\rangle$, would be much more stable. As experiments have shown,[3,4] such a gas is formed by preferential recombination of *a*-state atoms at the He-coated surface of the stabilization cell. In agreement with Statt and Berlinsky's predictions, its stabilization time is limited by a relatively slow spin relaxation, induced by $b+b$ collisions. Obviously, the rate $1/T_1$ of this relaxation process is of central importance. It has been the subject of a number of recent theoretical papers. The volume relaxation rate was calculated by Statt and Berlinsky,[2] and by Siggia and Ruckenstein.[5] In a reexamination of this problem Ahn *et al.*[6] shed light on a factor-of-2 discrepancy in previously proposed theoretical expressions for $1/T_1$ and studied the influence of relaxing various approximations in the existing calculations, among which is the high-temperature limit (HTL).

As lower and lower temperatures are being used in experiments, H-H surface collisions become the dominant relaxation mechanism. After a first paper on this subject by Lagendijk,[7] three papers[8–10] presented a more detailed calculation. Their results for $1/T_1$ agree, except for a factor of 2, by which the relaxation rate calculated by Ahn *et al.*[10] is smaller than that in both other papers. This discrepancy has the same origin as that in the volume calculation referred to above and was also resolved by Ahn *et al.* in Ref. 6. They also concluded,[6,10] however, that there exists a large discrepancy by a factor of order 50 between theory and experiment. So far no explanation has been found for this major disagreement, and it is the purpose of this paper to investigate some of the possible ways to account for it.

First we will relax an approximation, made in all papers on surface relaxation so far: the assumption that hydrogen atoms, bound to the surface in the only possible surface state $\phi_0(z)$, will not alter their motion in the z direction perpendicular to the surface while colliding with one another (so-called $2\frac{1}{2}$D model[10]). This is a simplification, because the z motion is coupled to the motion parallel to the surface by the central interatomic triplet potential, representing the main atomic interaction. A more extreme approximation which has also been introduced in some calculations is the two-dimensional (2D) description where the H atoms are confined to a plane. In the following we will show that it is possible to give an accurate description of the three-dimensional (3D) coupled motion of the atoms on the surface, using additional states perpendicular to the surface in the so-called coupled-channels [close-coupling (CC)] formalism. A 3D description will supply increased freedom of motion and in principle even the possibility for the atoms, classically speaking, to jump over one another. Thus one could imagine that at some initial relative velocity the atoms would almost come to a standstill on top of one another thus enabling the magnetic dipole spin-spin interaction to act during a longer time. Such a classical argument led us to expect an increase of the relaxation rate in a 3D description, possibly in the form of a resonance, and this was our main motivation for starting this investigation. The result will appear to be a negative one: The value of $1/T_1$ increases by a factor of roughly 1.5 relative to that of Ref. 10, whereas a factor of about 1.2 is already gained by a more refined description of the state $\phi_0(z)$, rather than by the specific three-dimensional aspects introduced in the theory. The spin-spin interactions responsible for $b \rightarrow a$ transitions will be treated to first order, i.e., we adopt the distorted-wave Born approximation (DWBA). For the volume relaxation problem this has been shown to be a valid approximation.[6] The formalism to be used is treated in Sec. II. In Sec. III the main lines of the coupled-channels calculation are pointed out. Problems arising from using the obvious choice of a basis set for the CC problem are analyzed and solved, leading to a different basis set.

An alternate possibility to increase the theoretical value for the relaxation rate would be the possible existence of surface dimers, where hydrogen atoms H↓ would be bound to each other on the surface by the weakly attractive van der Waals part of their mutual triplet interaction. This is investigated in Sec. IV, where we also go into the deviations from the high-temperature limit (HTL), and comment on the effective-mass and surface-deformation effect. Finally, we draw our conclusions in Sec. V, and offer some ideas for future investigations.

II. MAGNETIC SPIN-SPIN INTERACTIONS TREATED IN DWBA

Compared to a previous calculation of Ahn *et al.*[10] the treatment of the weak magnetic spin-spin interactions to first order (DWBA) remains the same. The only difference in the present 3D theory is the description of the spatial motion parallel and perpendicular to the He surface. In this section we will introduce and work out the effective cross length λ_{eff} for the relevant spin transitions, leaving the spatial wave function as yet unspecified. The expressions to be given are also more general in the sense that the HTL is not introduced.

The differential cross length for the relevant processes $\alpha \rightarrow \beta = bb \leftrightarrow ab$ or $aa \leftrightarrow ab$ is given by

$$\lambda_{\alpha\rightarrow\beta}(\vec{\mathrm{k}}_\beta,\vec{\mathrm{k}}_\alpha)=\frac{\mu^2}{2\pi\hbar^4 k_\alpha}\,|\,T_{\alpha\rightarrow\beta}(\vec{\mathrm{k}}_\beta,\vec{\mathrm{k}}_\alpha)\,|^2\;, \tag{1}$$

where μ is the reduced mass $(=\frac{1}{2}m_{\mathrm{H}})$, and $\vec{\mathrm{k}}_\alpha$ and $\vec{\mathrm{k}}_\beta$ are the asymptotic initial and final relative H-H wave vectors, respectively, with directions parallel to the x-y plane, i.e., the surface. In the DWBA the expression for the T matrix is

$$\begin{aligned} T_{\alpha\rightarrow\beta}(\vec{\mathrm{k}}_\beta,\vec{\mathrm{k}}_\alpha) \\ &= \langle \chi^-_{\beta\vec{\mathrm{k}}_\beta}\Psi_\beta\,|\,(V-V_1)(1-P_{12})(1-P_{AB})\,|\,\chi^+_{\alpha\vec{\mathrm{k}}_\alpha}\Psi_\alpha\rangle\;. \end{aligned} \tag{2}$$

In this expression the functions Ψ indicate normalized two-particle spin functions. The factors containing the electron and proton permutation operators P_{12} and P_{AB}, respectively, introduce the correct antisymmetrization. The distorted waves χ^+ and χ^- are solutions of the spatial Schrödinger equation containing the distortion introduced by the triplet potential V_1. At infinity each of them contains a plane wave with amplitude 1 and with the wave vector indicated, in addition to an outgoing (ingoing) wave when the superscript is $+$ $(-)$. They will be treated in detail in Sec. III. The potential V is the total interatomic potential

$$V = P_0 V_0 + P_1 V_1 + H_{SS} + H_{SI}\;, \tag{3}$$

where P_0 (P_1) stands for the projection operator on the electron singlet (triplet) state, with central potential V_0 (V_1).

In terms of Eq. (2) the models for the surface collision considered in Ref. 10 are easily explained. The so-called $2\frac{1}{2}$D model is obtained if the triplet potential V_1, both in the role of distorting potential and of transition operator, is replaced by its value averaged over the z_1 and z_2 dependent bound surface states of each of the atoms, leaving a potential which depends on the interatomic distance ρ parallel to the surface only. The $2\frac{1}{4}$D model, on the other hand, is obtained if in Eq. (2) $V_1(R)$ is in both roles replaced by $V_1(\rho)$, an approximation which, properly speaking, is only valid for larger ρ values. In the 2D model the additional approximation is introduced of neglecting the finite extent of the z probability distribution for each of the atoms. In all of these approximations the ρ dynamics is decoupled from the z dynamics.

Of the terms in Eq. (3) only the spin-dependent electron-electron (H_{SS}) and electron-proton (H_{SI}) magnetic interactions contribute. Defining δ to be the ratio of proton and electron magnetic moments, $\delta = \mu_p/\mu_e$, we will neglect contributions to the T-matrix elements of higher order than $\epsilon^0\delta^1$ and $\epsilon^1\delta^0$. At the same time we introduce the Shizgal approximation.[2,11] These assumptions are shown to be valid in Ref. 6. As a consequence the magnetic interactions are effectively equivalent to the following expression:

$$\begin{aligned} (H_{SS}+H_{SI})_{\mathrm{eff}} &= \hbar^2\gamma_e^2\gamma_p^2\left(\frac{12\pi}{5}\right)^{1/2} \\ &\quad\times\sum_{M=\pm1}\left[T^M_{ep}-\left(\frac{\gamma_e}{\gamma_p}\right)T^M_{ee}\right]\frac{Y^*_{2M}(\hat{R})}{R^3}\;. \end{aligned} \tag{4}$$

Here we use the notation of Ref. 2, $\vec{\mathrm{R}}$ standing for the three-dimensional relative vector between the two colliding atoms, and M being the angular momentum transfer along the direction of $\vec{\mathrm{B}}$. The final expression for the integrated cross length, averaged over initial direction of relative motion, turns out to be

$$(\lambda_{\alpha\rightarrow\beta})_{\mathrm{eff}} = 9\mu^2\gamma_e^2\gamma_p^2\left(1+\epsilon\frac{\gamma_e}{\gamma_p}\right)^2\frac{\sin^2\theta}{k_\alpha^2 k_\beta}\sum_{\substack{m',m\\ \mathrm{even}}}\left[\delta_{m'm}\,|\,r_{m'm}\,|^2\cos^2\theta+\tfrac{1}{4}(\delta_{m',m+2}+\delta_{m',m-2})\,|\,\bar{r}_{m'm}\,|^2(1+\cos^2\theta)\right]\;. \tag{5}$$

Here m and m' are the projections of the relative orbital angular momenta along the z direction perpendicular to the surface, before and after the collision. They take even values only. Furthermore, the angle θ is the inclination of the magnetic field to the z axis. Finally, in this 3D treatment the radial integrals are defined by

$$r_{m'm}=\int_0^\infty dz_1\int_0^\infty dz_2\int_0^\infty d\rho\, u_{m'}(\rho,z_1,z_2)\times\{3\rho^2R^{-5}-2R^{-3}\}\times u_m(\rho,z_1,z_2) \quad (6a)$$

and

$$\bar{r}_{m'm}=\int_0^\infty dz_1\int_0^\infty dz_2\int_0^\infty d\rho\, u_{m'}(\rho,z_1,z_2)\times\{\rho^2R^{-5}\}u_m(\rho,z_1,z_2)\ . \quad (6b)$$

In these formulas, $\vec{\rho}$ is the projection of $\vec{\mathrm{R}}$ along the He surface. The radial functions u emerge from the expansion of the distorted waves χ in Eq. (2):

$$\chi^{\pm}_{\gamma\vec{\mathrm{k}}_\gamma}(\vec{\rho},z_1,z_2)=\left[\frac{2}{\pi k_\gamma}\right]^{1/2}\sum_m i^m e^{\pm i\eta_m}\frac{u_m(\rho,z_1,z_2)}{\sqrt{\rho}}\times\exp[im(\phi-\phi_{\vec{\mathrm{k}}_\gamma})]\ , \quad (7)$$

where η_m is the phase shift for the partial wave m, ϕ is the polar angle of $\vec{\rho}$, and $\phi_{\vec{\mathrm{k}}}$ that of $\vec{\mathrm{k}}$, while α or β may be substituted for γ. Passing from the microscopic quantity λ_{eff} to the macroscopically measurable relaxation-rate constant $(G_s)_{\alpha\to\beta}$ we have

$$(G_s)_{\alpha\to\beta}=(2\mu)^{-1/2}(k_BT)^{-1}\times\int_0^\infty dE_\alpha\lambda_{\text{eff},\alpha\to\beta}(E_\alpha)E_\alpha^{1/2}\exp(-E_\alpha/k_BT)\ . \quad (8)$$

The lower integration limit should be replaced by the threshold energy when $\alpha\to\beta$ is an endothermal reaction. The expression (8) is equivalent with that of Ahn *et al.*,[6] if one substitutes a Boltzmann distribution for their probability distribution function $P(\vec{\mathrm{v}})$. Note that in the HTL, the G_s values for the relevant processes $bb\leftrightarrow ab$ and $aa\leftrightarrow ab$, are identical. The common value is related to the relaxation time by the well-known formula $1/T_1=2n_sG_s$.

III. A 3D DESCRIPTION OF H-H SURFACE COLLISIONS

A. Mainlines

The functions $u_m(\rho,z_1,z_2)$ satisfy the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial\rho^2}+\frac{\frac{1}{4}-m^2}{\rho^2}\right]+H_s(z_1)+H_s(z_2)+V_1(\rho,z_1,z_2)\right]u_m=Eu_m\ , \quad (9)$$

where $H_s(z)=-(\hbar^2/2m_H)\partial^2/\partial z^2+V_s(z)$ is the one-particle surface Hamiltonian, and $V_s(z)$ is the potential, binding the H atoms to the He surface. Note that E actually depends on the spin state α or β. Clearly, the motions parallel and perpendicular to the surface are not separable; they are coupled by the triplet potential $V_1(\rho,z_1,z_2)$. The equation may be solved by expanding the solutions in a complete set of two-particle surface states, according to

$$u_m(\rho,z_1,z_2)=\sum_k v_{mk}(\rho)\psi_k(z_1,z_2)\ . \quad (10)$$

Substituting (10) in (9) and taking the scalar product with ψ_l we get for a general nonorthogonal set

$$\left\{\underline{N}\left[-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{d\rho^2}+\frac{\frac{1}{4}-m^2}{\rho^2}\right]-E\right]+\underline{M}_s+\underline{M}_1\right\}\underline{v}_m(\rho)=0\ , \quad (11)$$

in which

$$N_{kl}=\langle\psi_k\,|\,\psi_l\rangle\ ,$$

$$M_{s,kl}=\langle\psi_k\,|\,[H_s(z_1)+H_s(z_2)]\,|\,\psi_l\rangle\ ,$$

and

$$M_{1,kl}=\langle\psi_k\,|\,V_1\,|\,\psi_l\rangle\ .$$

It is also convenient to substitute the expansion (10) in Eqs. (6), and to define matrix elements of the magnetic dipole expressions, according to

$$Y_{0,kl}=\langle\psi_k\,|\,(3\rho^2R^{-5}-2R^{-3})\,|\,\psi_l\rangle$$

and (12)

$$Y_{2,kl}=\langle\psi_k\,|\,\rho^2R^{-5}\,|\,\psi_l\rangle\ .$$

Carrying out an $\underline{N}^{-1/2}$ transformation to diagonalize the second-order differential term in Eq. (11), and next an orthogonal transformation $\underline{U}$ which diagonalizes $\underline{M}_s$ and asymptotically decouples the equations (11), we obtain the coupled-channels equations for the radial functions in the form of an equation for the vector $\underline{w}_m(\rho)=\underline{U}^{-1}\underline{N}^{1/2}\underline{v}_m(\rho)$,

$$\left[-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{d\rho^2}+\frac{\frac{1}{4}-m^2}{\rho^2}\right]+\underline{D}+\underline{C}-E\right]\underline{w}_m(\rho)=0\ . \quad (13)$$

In this set of coupled equations the diagonal ($\underline{D}$) and coupling ($\underline{C}$) matrices are given by

$$\underline{D}=\underline{U}^{-1}\underline{N}^{-1/2}\underline{M}_s\underline{N}^{-1/2}\underline{U}$$

and (14)

$$\underline{C}=\underline{U}^{-1}\underline{N}^{-1/2}\underline{M}_1\underline{N}^{-1/2}\underline{U}\ .$$

The matrix $\underline{D}$ thus contains the eigenvalues of the two-particle surface Hamiltonian. These, as well as the $\underline{C}$ matrix elements of the triplet interaction and the elements of the magnetic dipole matrices $\underline{Y}_0$ and $\underline{Y}_2$, transformed like $\underline{D}$ and $\underline{C}$ in Eq. (14), are calculated in advance. The set of coupled equations (13) is then solved numerically using a modified Numerov method,[12] integrating in the direction of increasing ρ, starting at some $\rho_s=0$—1.5 a.u., with a limited number of independent basis solutions, up to a coupling radius $\rho_c = 20-100$ a.u. The tendency to numerical dependence[13] in classically forbidden regions is prevented by linearly combining the solutions to suitable new ones. Between ρ_c and a matching radius $\rho_m = 500-3000$ a.u. the central interaction becomes negligible, so that the equations are decoupled. At ρ_m the solutions are matched to the asymptotic (free) expressions. The radial DWBA integrals (6) are evaluated simultaneously with the CC integrations, using the transformed dipole matrices $\underline{Y}_0$ and $\underline{Y}_2$. Finally, since the $m=0\rightarrow m'=0$ transition is dominant, we restrict ourselves to the r_{00} integral in the following.

Our approach to this problem, merging the DWBA for the weak magnetic interactions with the CC formalism for the strong triplet interaction, is a special case of the CCBA approach described in Austern,[14] where in this case we have only one open channel for the spatial part.

B. CC scheme with eigenstates of the surface Hamiltonian

An obvious choice for the ψ_k, which we have tried to use in the first instance, are the symmetrized products of one-particle eigenstates of the surface Hamiltonian $H_s(z)$. An advantage of using this set is that the transformation (14) is not necessary, M_s being already decoupled for large ρ. At large distances only $\psi_0(z_1,z_2)=\phi_0(z_1)\phi_0(z_2)$ survives, where $\phi_0(z)$ is the only existing one-particle bound state. In the $2\frac{1}{2}$D approximation the expansion (10) is essentially restricted to ψ_0 for all distances. However, in this 3D description, at smaller distances unbound continuum states will be mixed in by the interatomic interaction. Since these are difficult to handle, we put a second hard wall parallel to the surface at a large distance, for which we take 100 a.u. This is based on the assumption that in a time-dependent description particle-wave packets do not come close to it. As a consequence, the boundary condition $u_m=0$ at 100 a.u. may also be imposed in the stationary description. The discrete orthogonal set $\phi_i(z)(i=0,1,2,\ldots)$ thus obtained has been calculated accurately with numerical integration, with the use of a potential as introduced by Stwalley[15]: $V_s(z)=-c_3/(z+z_0)^3$ with a hard wall at $z=0$. Taking c_3 to be the long-range van der Waals constant for a He surface[15] ($\simeq 219.7$ K Å^3) we found a value of 2.43 a.u. for z_0 in order to obtain a binding of 0.91 K, contrary to Stwalley, who found $z_0=3.85$ a.u. on the basis of a semiclassical approximation. We believe that our final results are not very sensitive to the specific choice for the surface potential, if it (a) tends to a van der Waals potential with the correct strength for large z, (b) has a strongly repulsive part near the He surface, and (c) has the correct binding energy. For instance, replacing the Stwalley-type potential by $-c_3/z^3+c_5/z^5$, satisfying the same conditions, turned out to have a negligible effect.

After evaluation of r_{00} in the 3D model, restricting ourselves to one channel, we find the result to be larger than the value obtained in the $2\frac{1}{2}$D model by about 10%. This must be due to the averaging procedure applied to the triplet potential and to the dipole-dipole interactions. Indeed, in Ref. 10 a Gaussian function $F(z)$ ($z=z_1-z_2$) was used with $F(0)=0.0503$ a.u.$^{-1}$ from Edwards and Mantz.[16] If we replace this parameter in the $2\frac{1}{2}$D approach by $F(0)=0.0568$ a.u.$^{-1}$, a value more consistent with the behavior of the function $\phi_0(z)$, we find the $2\frac{1}{2}$D and 3D model (one channel) results to be approximately equivalent, as indicated in Table I. Apparently, the Gaussian function corresponding to the latter $F(0)$ resembles the exact weighing function, based on $\psi_0(z_1,z_2)$, more closely.

The accuracy of the present CC calculation is only limited by the number N of $\phi_i(z)$ states included, and in connection with the increase of computation time with N^6 only N values up to 10 turned out to be feasible in our case. From our calculations we conclude that values of r_{00} for this range of N do not converge sufficiently. There is no indication that the presence of the second hard wall contributes to the bad convergence. An "adiabatic" calculation of the dynamics of the H atoms in the z_1-z_2 plane for fixed ρ, including the triplet interaction, indicates that the slow convergence is due to the unadapted behavior of the surface eigenstates $\psi_k(z_1,z_2)$ for small z_1-z_2 and for large z_1 and z_2. At small ρ values the strongly repulsive inner part of the triplet potential will force the wave function $u_m(\rho,z_1,z_2)$ to be very small near the line $z_1=z_2$ in the z_1-z_2 plane. This behavior can only be obtained by superposing many surface states. For large z_1 and z_2, on the other hand, one expects an exponential decay of the wave function as it describes a state of two particles bound to the surface. Also from this point of view one should expect to need many ψ_k functions, each of the continuum one-particle states $\phi(z)$ having a sinelike behavior for large z.

TABLE I. Radial integrals r_{00} (10^{-3} a.u.$^{-2}$) in Eq. (6a) as a function of incident collision energy E (K), in the high-temperature limit, for the $2\frac{1}{2}$D and 3D models. The $2\frac{1}{2}$D results are given for a Gaussian weighing function $F(z)$ with $F(0)=0.0503$ a.u.$^{-1}$ (Edwards and Mantz, Ref. 16) and 0.0568 a.u.$^{-1}$, respectively, and with an exact averaging, based on $\phi_0(z)$. For the 3D model convergence of r_{00} is shown, as a function of the maximum value M of the parameters m and n, and of the corresponding number N_ψ of ψ_{mn} and ψ^a_{mn} functions included in the coupled-channels calculation.

Option	N_ψ	0.1 K	0.2 K	0.3 K	0.4 K
$2\frac{1}{2}$D, 0.0503	1	0.80	1.08	1.27	1.41
$2\frac{1}{2}$D, 0.0568	1	0.86	1.18	1.39	1.55
$2\frac{1}{2}$D, $\phi_0(z)$	1	0.86	1.18	1.40	1.56
3D, $M=1$	2	0.95	1.31	1.55	1.72
3D, $M=2$	6	0.96	1.31	1.54	1.71
3D, $M=3$	12	1.03	1.38	1.61	1.76
3D, $M=4$	20	1.03	1.38	1.61	1.76
3D, $M=5$	30	1.04	1.39	1.61	1.77

C. New analytic basis of surface states

What we need to circumvent the problems, stated in Sec. III B, is a new set of ψ_k, including functions with the property of being effectively zero near the line $z=z_1-z_2=0$, and showing an exponential decay for large z_1 and z_2. We define functions ψ_k according to

$$\psi_{mn}(z_1,z_2)=(z_1^m z_2^n+z_1^n z_2^m)\exp[-\lambda(z_1+z_2)]\ , \tag{15a}$$

and

$$\psi_{mn}^a(z_1,z_2)=\begin{cases}\psi_{mn}(z_1,z_2)(\,|z\,|-a)^2, & |\,z\,|\geq a\\ 0, \quad |\,z\,|<a\ .\end{cases} \tag{15b}$$

The parameters m and n are positive integers. The values $m,n=0$ are excluded to fulfill the boundary condition at $z_1=0$ and $z_2=0$. The ψ_{mn} subset defines functions especially suited for large ρ, the ψ_{mn}^a subset for small ρ. For continuity reasons, with respect to first derivative, the factor $(\,|z\,|-a)$ is squared.

Let us now turn to the values to be chosen for a and λ. The value for a should not be chosen too small (i.e., $a\geq 2$ a.u.) in order to give the H atoms the opportunity to avoid the strongly repulsive part of the triplet potential. On the other hand, it should be small enough ($a\leq 6$ a.u.) to allow the H atoms to profit from their mutual van der Waals well and to penetrate the repulsive potential to some distance. In view of this a reasonable choice for a is the *two*-dimensional H-H scattering length ($\simeq$2.47 a.u.). The value of λ was optimized by minimizing the expectation value of the surface Hamiltonian in the state $\psi_{00}(z_1,z_2)$. The function ψ_{00} thus obtained, for $\lambda=0.199$ a.u.$^{-1}$, turns out to resemble closely the "exact" surface state $\phi_0(z_1)\phi_0(z_2)$. Note that in the definition of the functions in Eqs. (15) a second wall, at large z, does not come into play.

Again, before tackling the CC problem, the matrix elements of $\underline{D}$, $\underline{C}$, $\underline{Y}_0$, and $\underline{Y}_2$ are calculated in advance. For all of these, introducing center-of-mass and relative coordinates (Z and z, respectively), the Z integration can be carried out first, yielding the functions

$$\begin{aligned}F_{mn}(z,\alpha)&=\int_{z/2}^{\infty}dZ\,(Z+z/2)^m(Z-z/2)^n e^{-\alpha Z}\\ &=\frac{e^{-\alpha z/2}}{\alpha^{n+m+1}}\sum_{t=0}^{m}\binom{m}{t}(n+m-t)!(\alpha z)^t\ .\end{aligned} \tag{16}$$

As a further advantage of the present analytical basis set, the matrix elements of $\underline{N}$ and the operator $\partial^2/\partial z_1^2+\partial^2/\partial z_2^2$ can subsequently be worked out analytically, using the binomial formula, whereas the matrix elements of $\underline{C}$, $\underline{Y}_0$, and $\underline{Y}_2$ have to be integrated numerically in z. For the surface interaction we have again employed a Stwalley type potential. For this the Z integrals can be expressed in the exponential integral[17] $E_1(x)$ by recursion, and the z integration has to be carried out numerically.

After integration of the CC equations (13) and simultaneous evaluation of Eqs. (6), the radial integrals can be found, see Table I. In this case they appear to converge for increasing maximum M of m and n values included in the basis set. Owing to the growing numerical linear dependence of the basis functions in Eq. (15) for increasing M, the value $M=5$ is the limit for this choice of functions. The resulting factor of about 1.25 in the radial integrals contributing quadratically to the relaxation rate, we conclude that a proper treatment of the three-dimensional aspects of the surface collision reduces the so-called "factor-of-50" discrepancy to a factor of 35. Clearly, there still remains a major discrepancy.

IV. OTHER MODEL IMPROVEMENTS

In some papers[4,18] it is suggested that the interaction of the hydrogen atoms with the dynamical modes of the helium film may have a great influence on the collisions of the H atoms sticking to the surface. In practical calculations this interaction may be translated into two distinct effects[18]: the effective-mass and the surface-deformation effect. A hydrogen atom moving parallel to the surface causes a deformation of the helium film, which has to be dragged along, leading to an increased effective mass. On the other hand, since it is favorable for H atoms to have as great an overlap of their helium film deformations as possible, an extra attractive surface-deformation H-H potential has to be included when solving the scattering problem. The effective mass μ_{eff} has been estimated[18,19] to be about 1.1 times the bare mass. With the use of μ_{eff} instead of μ we find for a typical collision energy an increase of only 4—6 % in the radial integrals r_{00}.

The complicated H—He-film interaction is not yet completely understood, leaving the surface-deformation potential unspecified. In a preliminary calculation, however, we approached the problem from another starting point: We tried to find out how strong an additional surface-deformation potential would have to be to explain the order of magnitude of the remaining discrepancy with experiment. Both in the $2\frac{1}{2}$D and 3D models we introduced a Gaussian surface-deformation potential (FWHM = 10 a.u.), centered at $\rho=0$. Trying out several depths V_M we found an optimum depth at about 3 K, where a low-energy resonance occurs. At $V_M=3$ K the gain factor in r_{00}, compared to the $\mu_{\text{eff}}=\mu$, $V_M=0$ case, varies with the incident energy E: 2.8, 2.2, 1.8, 1.5, and 1.3 at $E=0.05$, 0.1, 0.2, 0.3, and 0.5 K, respectively. This leads to an increase in $G_{s,0}$ (the G_s part corresponding to total angular momentum transfer $\Delta M=0$, see Ref. 10) of a factor 10, 7, and 5 depending on temperature $T=0.1$, 0.2, and 0.4 K, respectively, which is a very promising result indeed. However, it is still not enough to account for the large discrepancy of a factor 35 in G_s, whereas a well of 3 K already seems rather deep, considering that Guyer *et al.*[18] estimated the "parallel binding energy" ($\sim V_M$) to be smaller than, but probably comparable to the perpendicular binding energy ($\simeq$0.9 K) of H at the He film. Note furthermore, that a well of 3 K is almost as deep as the mutual H-H van der Waals well, averaged over $\phi_0(z_1)\phi_0(z_2)$, i.e., about 3.47 K. On the other hand, a well with depth $V_M=1$ K would increase r_{00} only by a factor of 1.2—1.4.

Another possibility, which is likely to have great influence on the relaxation rate, would be the existence of surface dimers. In the gas the van der Waals well of the H-H triplet state is known to be too shallow to contain a bound state. At the surface an extra $-1/4\rho^2$ term in the centrifugal potential appears in the radial equation (9). With our CC method we can integrate the radial functions also for negative energies, and calculate the "mismatch" at the coupling radius ρ_c, which is proportional to the strength of an additional δ-shaped well in the potential, needed to introduce a bound state. In Fig. 1 the mismatch M for the $2\frac{1}{2}$D model is plotted against the magnitude k of the incident wave vector, for $\rho_c=30$ a.u. Obviously, there is no dimer state, althought the mismatch for surface dimers is considerably smaller than that for volume dimers. Extrapolating the surface curve to find the position of a possible positive resonance energy above the threshold is not feasible, because of logarithmic effects near the threshold, due to the $-1/4\rho^2$ term, mentioned before. Investigating the behavior of the radial function and radial integrals for positive energy, no such low-energy resonance appears to exist, indicating there is no nearly bound state either. Finally, including more ψ_k states, in the CCBA approach of Sec. III C, has only a marginal effect on the mismatch M: a decrease of about 3%.

Also for the existence of dimers the magnitude of the effective-mass and surface-deformation effect is of great importance. Therefore the mismatch as a function of the wave number k is also shown in Fig. 1, using a surface-deformation potential $V_M=3.5$ K. In this case a bound state is realized at an energy E very close to threshold. A further analysis indicates that at about $V_M=3$ K the bound dimer is just realized. Note that this is precisely the surface-deformation well depth at which the low-energy resonance occurs, mentioned before, offering an explanation for that effect.

The last possible explanation we investigated in the framework of this paper are deviations from the high-temperature limit. We stress here that the previous calculations of the radial integrals in the CCBA approach still use the HTL, although Eq. (5) for the effective cross length is a general expression. Dropping the HTL for relaxation in the gas phase[6] led to a substantial increase of the relaxation-rate constant G_v at temperatures below 0.1 K. To test the influence of the HTL for surface collisions, the framework of the $2\frac{1}{2}$D approach is sufficient. Carrying out this test leads to a slight increase of the radial integrals. However, the net effect on the surface relaxation rate constant G_s is negative, and amounts to a decrease of about 7.7%. See Fig. 2 for curves of $G_{s,0}$ and $G_{s,2}$ ($\Delta M=\pm 2$ part of G_s) as functions of T with and without HTL.

Returning to the subject of the beginning of this section, we note that the results for an additional surface-deformation potential reported there, which were based on the HTL, change very little if deviations from the HTL (using $B=8T$) are taken into account, so that the conclusions remain valid.

V. CONCLUSIONS

Summarizing, we note that we have reported on four attempts to account for the large discrepancy of a factor of 50 in the surface-relaxation rate constant G_s. Firstly, including in the model the correlation between the motion of the H atoms parallel and perpendicular to the surface has very little effect. The expected "jump-over" and metastable state in the z direction with two H atoms on top of each other are apparently not confirmed. We have some indications from the above-mentioned calculation

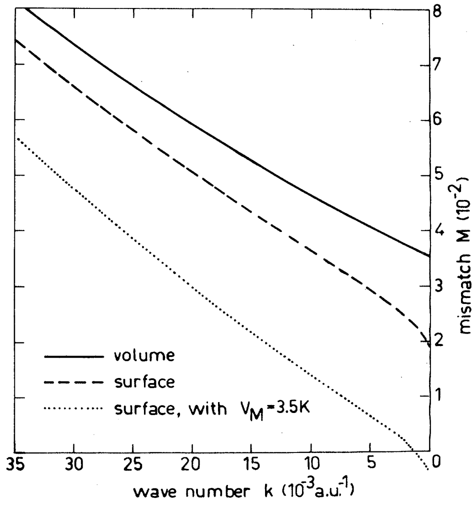

FIG. 1. Mismatch in radial wave function for $m=0$, indicating the depth of an additional δ-shaped well needed to realize a bound state, as a function of distance to threshold, expressed in wave-number units $k=(-2\mu E/\hbar^2)^{1/2}$. Curves are shown for the three-dimensional case (volume), for hydrogen atoms adsorbed at the surface, with and without a surface-deformation potential.

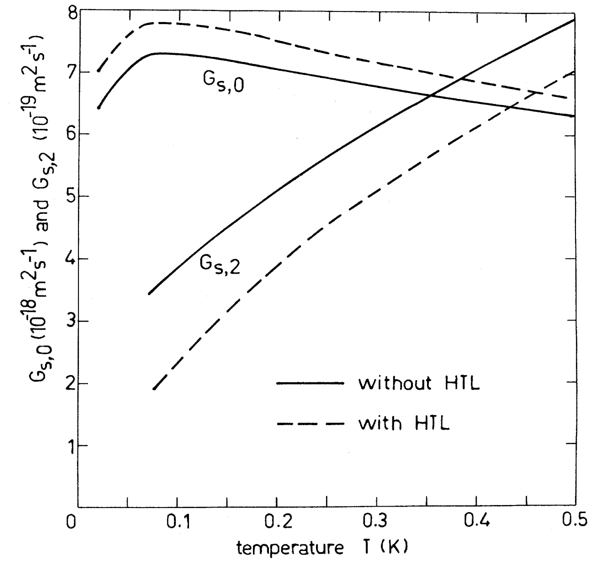

FIG. 2. Surface relaxation-rate constants for $\Delta M=0$ and $\Delta M=\pm 2$ as a function of temperature, with and without high-temperature limit, all in the $2\frac{1}{2}$D approach.

that the metastable state might show up in the behavior of r_{00} at a higher energy, of the order of 1 K.

Secondly, dropping the high-temperature limit turns out to have an insignificant effect altogether. Thirdly, no surface dimers exist, bound by the $-1/4\rho^2$ term in addition to the mutual attractive H-H van der Waals interaction. Finally, concerning the effective mass and surface-deformation effect, we conclude that the former has very little influence on the results. Studies[18,20] of the role of the helium-film modes have as yet not led to reliable estimates of an additional "polaron" contribution to the effective H-H interaction potential. A preliminary calculation shows, however, that an additional surface deformation potential, with a range of the order of 10 a.u., might contribute to the solution of the problem if it has a depth of about 3 K. The gain factor in the surface-relaxation rate constant G_s being of the order 5–10 within the restrictions of our model, this seems the most promising effect to be studied in a more detailed way. This great sensitivity of the relative H-H motion to an additional short-range potential is explained by the absence of a centrifugal barrier in the dominating $m=0 \rightarrow m=0$ transition in two dimensions, contrary to the bulk scattering case, so that the atoms approach one another more closely. For this reason the plane-wave approximation or a simple cutoff of plane-wave radial integrals at some radius is a much less reliable approximation in two than in three dimensions.

Since a large discrepancy is only observed at the surface, not in the gas, it will only be resolved by an effect in which the surface plays a dominant role. Investigations should be directed to the deformation of the electron 1*s* wave functions of the hydrogen atoms at the surface, making $\vec{L}\cdot\vec{S}$ coupling possible and partial depolarization of electron spins. This may lead to an increase in the relaxation rate, but also in direct $b+b$ recombination, the surface acting as a third body. We stress here, that in the published experiments recombination directly from the *bb* state would be difficult to distinguish from an increase of the $bb \rightarrow ab$ relaxation. It is noteworthy that a relatively small admixed $S=0$ amplitude of order 1×10^{-4} in the *bb* state during a H-H surface collision would be sufficient to achieve the K_{bb}/K_{ab} ratio of about 0.3×10^{-2} needed to explain the discrepancy.

Finally, we point to attempts to resolve the existing discrepancy by taking into account the scattering of hydrogen atoms from ripplons.[21] For an adequate description of this effect a proper treatment of the three-dimensional aspects of the H-H surface collisions is probably also essential, the hydrogen-ripplon interactions depending strongly on the *z* coordinates of the atoms. We believe that the (z_1,z_2) basis set, introduced in Sec. III C of this paper may be used successfully in this case also.

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