ATOMIC HYDROGEN ON THE SURFACE OF SUPERFLUID HELIUM: THE STICKING PROBABILITY AND POLARONIC BEHAVIOR.

by

DAN SIMON ZIMMERMAN

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Department of Physics

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date: 12 Sep 82
Abstract

A study is made of the interaction between hydrogen atoms and the surface elementary excitations of superfluid ^4He. Calculations for the sticking probability and for the energy and effective mass of a hydrogen atom bound to the surface are presented.

As a first step in the calculations, we formulate the Hamiltonian describing a hydrogen atom interacting with the surface of ^4He in its ground state together with the interaction coupling to the surface elementary excitations (the ripplons). The derivation is based on the association of the surface ground state with a flat surface and the excited states with a sinusoidally varying height of the surface. The interaction potential is derived by summing a ^4He-H atom-atom pair potential over helium atoms below the surface. The atom-atom pair potential is chosen so that the derived surface potential is a Morse potential with parameters which are fitted to the effective surface potential derived by Mantz and Edwards for a hydrogen atom interacting with N-1 helium atoms.

The energy and angle dependent sticking probability, S(E,θ), and the thermally averaged sticking probability, S(T), are calculated. Results are compared with the experimental value of S(T), S(T)=0.035±0.005, measured for the temperature range 0.18<T<0.27K.

The possibility that a hydrogen atom bound above the surface may exhibit polaronic behaviour is investigated. The energy of the hydrogen surface "polaron" and its effective mass
are calculated using perturbation theory. The hydrogen atom is found to be weakly coupled to the surface elementary excitations, and therefore the polaronic effects are weak. The contribution to these results from virtual transition to free states is emphasized.
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I. INTRODUCTION

Experimental efforts to stabilize high densities of spin polarized atomic hydrogen at temperatures below 1K have led to a great deal of interest in the properties of atomic hydrogen interacting with the free surface of superfluid $^4$He. In the experiments performed the walls of the cell in which the atoms are confined are coated with superfluid $^4$He. The reason is that the walls necessarily attract the hydrogen atom through Van der Waals forces, and therefore some fraction of the atoms are trapped in a bound state above the surface. At a given temperature the density of atoms on the surface is a strongly increasing function of the binding energy and therefore one desires to minimize the surface density by choosing a surface with the smallest possible binding energy. The lowest possible values for the binding energy are achieved by coating the walls of the cell with superfluid $^4$He, with $^3$He or with $^3$He-$^4$He mixtures.

At low densities the atoms in the bound state move as free particles, on the surface, resembling a two dimensional ideal gas. A hydrogen atom, in the bound state, distorts the surface beneath it. While moving parallel to the surface, the atom carries the distortion along with its motion, and thus it acquires an effective mass $m^*$ greater than the hydrogen mass $m$.

A hydrogen atom in the gas, with energy $E$, incident on the surface from an angle $\theta$ to the normal to the surface has a probability $S(E,\theta)$ of sticking to the surface. The thermally averaged sticking probability $S(T)=\langle S(E,\theta) \rangle$ has been measured by
Jochemesen et al.⁵ and a value of \( S = 0.035 \pm 0.005 \) was found in the temperature range \( 0.18 < T < 0.27 \text{K} \).

In Chapter 2 we explain the motivation for performing these experiments and the reasons for using liquid helium surfaces. We describe the experiments performed by the UBC atomic hydrogen group in which the binding energy and the sticking probability were measured.⁴⁻⁵ Then the model which we used to describe the surface is presented and finally the work of Guyer, Miller and Yaple, which suggested that a hydrogen atom becomes "localized" above the surface, is introduced.¹⁴

In Chapter 3 the hydrogen-surface potential is derived along with the coupling to the elementary surface modes. A model Hamiltonian describing the system is introduced, and its properties are described.

In Chapter 4 the sticking probability and the thermally averaged sticking probability are calculated. Theoretical results for the thermally averaged sticking probability are compared with experimental values. The dependence of the results on the coupling function to the ripplons is emphasized.

In Chapter 5, the ground state energy of the system is calculated using perturbation theory and the effective mass, \( m^* \), for an atom moving on the surface is estimated. The importance of polaronic effects for the bound hydrogen atom is explored.
II. ATOMIC HYDROGEN AND THE SURFACE OF $^4$HE

2.1 Spin Polarized Hydrogen

The interaction between two hydrogen atoms depends on the total electronic spin, $S$, of the atoms.\textsuperscript{15}

For $S=0$, the interaction potential has a large well depth, and therefore two hydrogen atoms interacting through this singlet potential form a bound state, i.e., recombine into a hydrogen molecule with a binding energy of 4.5eV (50,000K).

For $S=1$, the potential is mainly repulsive except for a weak Van der Waals attraction whose depth well is 6.5K at a separation of 4.15Å.\textsuperscript{16-18} The triplet potential resembles the $^4$He-$^4$He atom-atom potential which has a deeper well (of about 10K).\textsuperscript{19}

Applying a magnetic field will align the spins and force the atoms to interact through the triplet potential, suggesting that a magnetic field and low temperatures would be enough to prevent recombination of hydrogen atoms into molecules. Unfortunately the nuclear spin perturbs the electronic spin states and therefore one of the two lowest hyperfine energy levels of a hydrogen atom in a large magnetic field contains a small admixture of electronic spin which is not aligned with the magnetic field. Thus a slow recombination rate still remains even after the magnetic field is applied.

Hydrogen atoms, like helium atoms, obey Bose-Einstein statistics. Due to the similarity of the atom-atom interaction potential and the same statistics, the low temperature phase of spin polarized hydrogen atoms is expected to show quantum
properties similar to $^4$He at low temperature.

Calculations for the low temperature phase of a system of hydrogen atoms suggest that, for pressures below 100 bars, the system will remain gaseous even at $T=0K$.\textsuperscript{20-22} At a certain temperature $T_0$, which depends on the density, $n_\text{H}$, the gas is expected to undergo a phase transition into a Bose-Einstein condensed state, i.e. a state where a macroscopic fraction of the hydrogen atoms occupy the zero momentum state. This phase with its exotic quantum properties is the ultimate goal of the experimental efforts.

A still unresolved question is the relation between the superfluid phase transition observed experimentally for $^4$He and Bose-Einstein condensation. A microscopic calculation which shows a phase transition of the Bose-Einstein type has not yet been performed. The difficulty is a consequence of the strong interaction between $^4$He atoms which make it impossible to find a small expansion parameter to solve the system perturbatively. Hydrogen atoms at the densities needed to observe Bose-Einstein condensation are weakly interacting and therefore a perturbative approach is justified. Comparison between theory and experiment may shed a new light on the relation between the superfluid phase transition and Bose-Einstein condensation.

The temperature $T_0$ in which the phase transition is expected to occur is related to the density through the relation:

\begin{equation}
T_0 = 1.6 \times 10^{-14} n_\text{H}^{\frac{3}{2}} \text{ K}
\end{equation}
which means, for example, that at $T=0.1\text{K}$ a density of $1.6 \times 10^{19}$ atoms/cm$^3$ is needed to observe condensation. The highest densities already achieved in laboratories are 2-3 orders of magnitude smaller.

The main difficulty in achieving these densities is recombination of hydrogen atoms into hydrogen molecules. Recombination occurs as a 3 body process in the gas and as a 2 body process on the surface of the container in which the atoms are contained, since the surface acts as the third body needed to conserve energy and momentum.

Assuming that the hydrogen atoms, trapped above the surface, are in thermal equilibrium with hydrogen atoms in the bulk, the density of the atoms on the surface is given in the low density limit by:

$$m_s = m_b \Lambda e^{E_B/kT}$$

(2)

where $n_s$ and $n_b$ are surface and bulk densities, $E_B$ is the binding energy, $\Lambda$ is the thermal de Broglie wavelength and $k$ is Boltzmann constant.

Solid surfaces bind atomic hydrogen with large binding energies (the least binding is molecular hydrogen with a binding energy of $38K^2$), implying that at temperatures below $1\text{K}$ essentially all the atoms will stick to the solid surface and recombine. The only alternative is to use liquid helium to coat the walls of the container. For helium surfaces the binding energy was measured by several groups giving the following
results:

a) $^4$He surface: 1.15±0.05K Morrow et al.  
1.01±0.06K Cline et al. 
0.89±0.07K Matthey et al. 

b) $^3$He surface: 0.42±0.05K Jochemsen et al. 

c) $^3$He-$^4$He surface: 0.34±0.03K van Yperen et al. 

In addition to the low binding energy needed to minimize surface densities, thick helium films are also expected to shield atomic hydrogen from paramagnetic impurities on the substrate below the liquid.

2.2 The UBC Experiment

The sticking probability and the binding energy were measured for $^4$He and $^3$He surfaces by the UBC atomic hydrogen group.

A cylindrical pyrex cell of diameter 1cm and length 7cm is filled at room temperature with hydrogen molecules and helium atoms. After the cell is cooled, the hydrogen molecules form a solid and the helium atoms form a liquid on the walls of the cell. An rf discharge pulse is used to cause hydrogen molecules to evaporate from the walls and dissociate into hydrogen atoms. After the termination of the discharge pulses, the remaining hydrogen molecules and helium atoms condense again on the walls while some amount of hydrogen atoms remain trapped inside the cell in a gaseous state. Maximum densities of 0.5x10$^{13}$ atoms/cm$^3$ were obtained in this way.

A pulsed magnetic resonance technique was used to observe
transitions between the atomic hydrogen hyperfine levels $|00\rangle$ and $|10\rangle$. The atoms were observed at temperatures less than 1K, with zero magnetic field, at a density of the order of $10^{10}$ to $10^{11}$ atoms/cm$^3$.

The hyperfine frequency observed is shifted from its value for free hydrogen atoms $f_0 = 1420405751.768(2)$ Hz$^2$, due to the interaction of the atoms with the surface and due to a "pressure shift" proportional to the density of $^4$He atoms in the cell.

The pressure shift is negligible below 1K and therefore most of the contribution to the frequency shift comes from the surface atoms. The frequency shift depends on the surface density and therefore is strongly temperature dependent.

If $\Delta_s$ is the change in the hyperfine frequency for a surface atom, the average phase shift per sticking event is given by $\gamma = 2\pi \tau_s \Delta_s$, where $\tau_s$ is the average time an atom spends on the wall. Assuming a Poisson distribution of times on the surface (with $\tau_s$ as average) and a Poisson distribution of times in the gas, with an average time $\tau_b$, the free induction decay curve is given by:

$$S(t) = S(0) e^{i(\omega_0 - \Delta \omega)t} e^{-t/\tau_2}$$

where:

$$\omega_0 = 2 \pi f_0$$

$$\Delta \omega = \frac{\gamma}{\tau_b (1 + \gamma^2)}$$

$$\frac{1}{\tau_2} = \frac{\gamma^2}{\tau_b (1 + \gamma^2)}$$

$\Delta \omega$ and $1/\tau_2$ were measured at different temperatures and the
values obtained are shown in Table 1. By eliminating \( \gamma \), Equations 5 and 6 are solved for \( \tau_b \) in terms of the measured quantities \( \Delta \omega \) and \( 1/T_a \) giving:

(7) \[
\frac{1}{\tau_b} = \Delta \omega \left( T_a \Delta \omega + \frac{1}{T_a \Delta \omega} \right)
\]

The sticking probability \( S \) is given by \( S = \frac{\tau_c}{\tau_b} \) where \( \tau_c \) is the average time between wall collisions. \( \tau_c \) was estimated using a computer simulation for atoms inside a cell whose dimensions are similar to those of the cell used in the experiment. A value of \( \tau_c = 7.4 \times 10^{-5} T^{-0.5} \text{sec} \) was thereby obtained.

Using Equation 7 and the value of \( \tau_c \), \( S \) was calculated at various temperatures. An experimental error equal to 10% of \( 1/T_a \) was attributed to \( \Delta \omega \) and to \( 1/T_a \). These results are shown in Table 1.

The binding energy was obtained from values of \( \Delta \omega \) in the temperature range where the fraction of the atoms on the walls is small. Then \( \Delta \omega \) is given by:

(9) \[
\Delta \omega = 2\pi A_s \left( \frac{A}{V} \right) e^{E_\lambda/kT}
\]

where \( A \) is the surface area of the cell and \( V \) is the volume.

The binding energy is obtained from the slope of \( \ln (\Delta \omega T^k) \) as a function of \( 1/T \). The value \( E_b = 1.15 \pm 0.05 \text{K} \) was obtained for \(^4\text{He}\) and \( E = 0.42 \pm 0.05 \text{K} \) for \(^3\text{He}\). The value \( S = 0.016 \pm 0.005 \) was obtained for the sticking probability on \(^3\text{He}\).
<table>
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<th>Kelvin</th>
<th>$1/T_\alpha$</th>
<th>$\Delta \omega$</th>
<th>$S$</th>
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<td>26.14</td>
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<td>107.13</td>
<td>0.051±0.007</td>
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<td>77</td>
<td>105.6</td>
<td>0.037±0.005</td>
</tr>
<tr>
<td>0.185</td>
<td>105</td>
<td>104.3</td>
<td>0.036±0.004</td>
</tr>
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<td>152</td>
<td>85.77</td>
<td>0.035±0.005</td>
</tr>
<tr>
<td>0.171</td>
<td>189</td>
<td>50.89</td>
<td>0.036±0.005</td>
</tr>
</tbody>
</table>

*Table I - The measured temperature dependence of the relaxation rate $1/T_\alpha$ and the frequency shift $\Delta \omega$, along with the resulting values of the averaged sticking probability $S$. 
2.3 **Surface Polarons**

Guyer, Miller and Yaple (GMY) suggested the possibility that a hydrogen atom, bound to the surface, would reduce its energy by becoming "localized" i.e. its effective mass would become greatly enhanced. Although a positive kinetic energy is associated with localization, a reduction in the total energy may be obtained because the negative atom-surface interaction potential may increase in magnitude, thus becoming more negative, as the the atom becomes localized. GMY referred to the localized atom as a "surface polaron".

GMY assumed a Gaussian wave packet with half width $\delta$ for the two dimensional (the parallel) wave function of the bound hydrogen. They assumed an ad-hoc $\delta$-function contact potential and obtained matrix elements for the hydrogen-surface coupling which were independent of ripplon wave vectors.

GMY calculated the positive kinetic energy term and the negative interaction term and looked for the conditions which would give a total negative energy. They associated a "localized" hydrogen atom with this negative energy.

The GMY work is not based on a realistic surface-atom potential and therefore should be regarded as being only qualitative. A major shortcoming is that $\delta$, the half width, cannot be estimated from GMY calculations and therefore the polaron size or its energy are not given.
2.4 The Model For The Superfluid Helium Surface

Throughout this work we will use the following model, introduced by Frenkel\textsuperscript{25} and Atkins\textsuperscript{26}, to describe the properties of the surface of $^4\text{He}$.

The helium liquid is treated as an incompressible, non-viscous classical liquid in which the only possible density fluctuations are surface waves restored by the surface tension and by the presence of the earth's gravitational field. Frenkel proposed that the elementary excitations, of the free surface of $^4\text{He}$ are quantized surface waves, called ripplons, and Atkins explained the temperature dependence of the surface tension by assuming a contribution to the surface energy from thermally excited ripplons.

A quantum hydrodynamic formulation of the problem gives the following quantization for the modes:\textsuperscript{27}

\[ h(\vec{r}) = \frac{1}{\alpha} \sum_{\vec{q}} h_{\vec{q}} e^{i \vec{q} \cdot \vec{r}} \]

\[ \Pi_{\vec{q}} = \frac{\sigma_0}{\alpha} h_{\vec{q}} \quad [h_{\vec{q}}, \Pi_{\vec{q}'}] = i \hbar \delta_{\vec{q} \vec{q}'} \]

\[ \Pi_{\vec{q}} = i \left( \frac{\hbar \omega_{\vec{q} \omega_{\vec{q}}}}{2} \right)^{\frac{1}{2}} (\Gamma_{\vec{q}}^+ - \Gamma_{\vec{q}}^-) \]

\[ h_{\vec{q}} = \left( \frac{-\hbar q}{2 \omega_{\vec{q}}} \right)^{\frac{1}{2}} \Gamma_{\vec{q}}^+ + \Gamma_{\vec{q}}^- \]

\[ \omega_{\vec{q}} = \left( \frac{\varrho q^2 + \frac{\sigma_0}{\omega_{\vec{q}}^2} q^2}{\varrho} \right)^{\frac{1}{2}} \]

\[ H = \sum_{\vec{q}} \hbar \omega_{\vec{q}} (\Gamma_{\vec{q}}^+ \Gamma_{\vec{q}}^- + \frac{1}{2}) \]

where $h(\vec{r})$ is the displacement of the surface, at position $\vec{r}$, from its equilibrium height at $z=0$, $\sigma_0 = 0.378$ erg/cm\textsuperscript{2} is the surface tension at $T=0K$, $\varrho = 0.145$ g/cm\textsuperscript{3} is the density at zero
pressure, $g$ is the earth's gravitational acceleration and $r_q^+$ is a creation operator for a surface elementary excitation (a ripplon) with momentum $q$ and energy $\omega_q$.

This model does not take into account the compressibility of the liquid, which gives rise to other modes (phonons, rotons...). Also being an hydrodynamic treatment, it becomes inaccurate for ripplons with wave vectors comparable in magnitude to the inverse interatomic distance.

For thin helium films the Van der Waals attraction between the substrate and the liquid becomes important and the constant $g$ in Equation 10 has an added term equal to the force per unit mass at the free surface due to the substrate. Also the dispersion relation and $h(r^*)$ are modified to allow for the finite thickness of the film:

$$h_q = \left( \frac{4 \pi g \tanh q^2}{2 \pi \omega_q} \right)^{1/2} \left( r_q^+ + r_q^- \right)$$

(11)

$$\omega_q = \left( \frac{g + \frac{\omega_0}{\omega_q} q^2 \tanh q d}{3} \right)^{1/2}$$

where $d$ is the thickness of the film. For values of $q > 10^{-2} \text{Å}^{-1}$ the gravitational term is negligible compared to the surface tension term and can be ignored.

A quantity which will become important in what follows, is the thermally averaged mean square displacement of the surface $\langle h^2 \rangle$. Widom noticed, that with $g=0$, $\langle h^2 \rangle$ is divergent due to the long wavelength ripplons. Cole observed that the divergence is removed for non-zero values of $g$. Cole found
that \( \langle h^2 \rangle \) can be written as a sum of a temperature dependent term and a temperature independent term:

\[
\langle h^2 \rangle = \delta_1^2 + \delta_2^2
\]

\[
\delta_1^2 = \frac{k_t}{6\pi (s_0 \sigma_0)^{1/2}} q_m^{3/2}
\]

\[
\delta_2^2 = \frac{kT}{l_2 \pi \sigma_0} \ln \left[ \left( \frac{s_0}{s_0 \sigma_0} \right) \left( \frac{kT}{\hbar} \right)^4 \right]
\]

The first term, which does not depend on \( g \) or on the temperature \( T \) of the surface, corresponds to the contribution from the zero point motion of the ripplons. It depends on the ripplon cut-off \( q_m \) as \( q_m^{1.5} \) which makes the value of this term rather uncertain. The value \( q_m = 1.0 \text{Å}^{-1} \) was obtained by requiring that the total number of surface modes be equal to the number of atoms in a monolayer at the surface.\(^2\,^5\)

The second term, which is temperature dependent, diverges logarithmically as \( g \) vanishes. Most of the contributions to the second term result from long wavelength fluctuations.
III. THE HAMILTONIAN

3.1 The Atom Surface Coupling

The interaction between a hydrogen atom and the surface of $^4$He results from the interaction between $^4$He and hydrogen atoms. The $^4$He-H atom-atom potential is attractive for large enough values of interatomic separation and repulsive for smaller distances. Therefore the surface-atom potential also has an attractive and a repulsive part. A hydrogen atom approaching the surface will first be attracted and then, for smaller distances, it will be repelled.

The $^4$He-H atom-atom pair potential can be parametrized by assuming a functional form for the different parts of the potential with parameters which are fitted to experimental data and theoretical predictions. The attractive part, which results from Van der Waals forces, is a sum of inverse powers with a leading term proportional to $X^{-6}$, where $X$ is the interatomic distance. When integrated over helium atoms below the surface this term give rise to a term proportional to $Z^{-3}$ in the surface-hydrogen potential, where $Z$ is the distance of the hydrogen atom from the surface. The repulsive part can be modeled by an exponential or by a power law.

The atom-surface potential can be generated by summing the atom-atom potential over the liquid. This procedure usually does not generate an accurate surface potential. One of the reasons is that short range correlations between the gas and the surface atoms are not properly taken into account. An exact approach would be to try to solve the N-body Schrodinger
equation for N-1 helium atoms and one hydrogen atom. Clearly this is not an exactly soluble problem.

Mantz and Edwards\textsuperscript{32} used a variational procedure based on the Feynman-Lekner\textsuperscript{33-34} variational method to relate the N-body problem to a one body problem for a hydrogen atom in an effective surface potential $U_0(Z)$. (The reason for the subscript zero will become apparent in the following.) The derivation takes into account the liquid surface density profile and includes the effects of $^4\text{He}-^4\text{He}$ and $^4\text{He}-\text{H}$ correlations. Solving the one dimensional Schrödinger equation for the ME effective potential, a binding energy $E_B=0.63K$ is obtained. This value is smaller by 0.3K to 0.5K than the experimentally measured binding energy. The reason for the discrepancy is the variational nature of the calculation and the uncertainty in the $^4\text{He}-\text{H}$ atom-atom potential. ME emphasized that the approximations used tended to underestimate the magnitude of the binding energy.

ME assumed that the liquid is in its ground state, i.e. not distorted by elementary excitations, and therefore the ME effective potential corresponds to the coupling between a hydrogen atom and the liquid surface in the ground state. To obtain the coupling to the surface elementary excitations it would be necessary to perform a calculation in the same spirit as the ME calculation, assuming that the surface is in its excited states.

We adopt a simpler procedure which is based on the association of the ground state with a flat surface and the
excited states with a sinusoidally varying height of the surface. We first construct an effective $^4$He-H atom-atom potential which, when summed over $^4$He below a flat surface (and therefore a surface in the ground state) yields the ME potential. Then we sum that effective $^4$He-H potential over $^4$He atoms below a sinusoidally varying surface to obtain the coupling to the ripplons.

We treat the $^4$He liquid as an incompressible classical fluid with a sharp density profile $\Sigma(\vec{r},z) = \Sigma_0 \Theta(\frac{\zeta}{2} + h(\vec{r}))$, where $\Sigma_0 = 0.145$g/cm$^3$ is the $^4$He bulk density, $\vec{r}$ is a two dimensional vector on the surface, and $\Theta(x)$ is a unit step function which is zero for $x>0$.

For a hydrogen atom located at $(R,Z)$ the effective surface-atom interaction is given by:

$$U(R, Z) = n_{\text{He}} \int d^2 \vec{r} \int d\zeta \sqrt{\left[(1-R^2) + (z-\zeta)^2\right]} \Theta\left(\frac{\zeta}{2} - h(\vec{r})\right)$$

$n_{\text{He}}$ is the $^4$He number density and $\nu$ is the effective atom-atom potential.

Expanding $U(R, Z)$ in powers of $h(\vec{r})$, using the normal mode decomposition of $h(\vec{r})$ and keeping only the linear and the quadratic terms in the expansion in powers of $h(\vec{r})$ we obtain:
The first term is the static potential which couples hydrogen atoms to a flat surface. The second term, which is linear in the ripplon variables, will be referred to as the linear coupling term. The third term is the quadratic coupling to the ripplons.

3.2 The System Hamiltonian

The total Hamiltonian of the system is written as a sum of three terms:

\begin{equation}
H = H_V + H_H + H_I
\end{equation}

where \(H_V\) describes the surface of \(^{3}\text{He}\) through its elementary excitations, \(H_H\) describes the free hydrogen atoms in the gas and the atoms bound to the surface, and \(H_I\) describes the interaction between the atom and the surface.

The system is assumed to be confined within a box with volume \(V = A \times L\), where \(A\) is the surface area and \(L\) is the length.
of the box in the direction normal to the surface.

The free ripplon part of the Hamiltonian is given by:

\begin{equation}
H_r = \sum \frac{1}{i} \omega_{\mathbf{q}} V_{\mathbf{q}}^+ V_{\mathbf{q}}
\end{equation}

The free hydrogen part of the Hamiltonian is given by:

\begin{equation}
H_h = \sum \left( \frac{k^2}{2m} + E(\sigma) \right) a_{\mathbf{k},\sigma}^+ a_{\mathbf{k},\sigma}
\end{equation}

where \( a_{\mathbf{k},\sigma}^+ \) is a creation operator for a hydrogen atom in the state \( | \mathbf{k} \rangle | \sigma \rangle \)

\begin{equation}
\Psi_{\mathbf{k},\sigma}(\mathbf{r},z) = \frac{1}{\sqrt{A}} \exp \left( i \mathbf{q} \cdot \mathbf{r} \right) \phi_{\sigma}(z)
\end{equation}

\( \mathbf{q} \) is a two dimensional wave vector corresponding to a plane wave on the surface, and \( \phi_{\sigma}(z) \) is the solution of the Schrödinger equation, labeled by the quantum number \( \sigma \), for the surface potential \( U_\sigma(z) \) and with energy \( E(\sigma) \).

The potential \( U_\sigma(z) \) has only one bound state. For this state we assign to \( \sigma \) the symbol \( B \) and \( E(B) = -E_B \). Solutions with positives energies are associated with free atoms in the gas. These solutions become plane waves far above the surface and \( \sigma \) can be identified with \( k_z \), the wave vector for vertical motion.

The interaction term is the sum of the linear coupling and the quadratic coupling terms. The linear term is given by:
and the quadratic term is given by:

\[ \frac{1}{2A} \sum_{\sigma, \sigma'} \left\langle \sigma \left| \frac{\partial^2 \mathcal{H}_{G}(Z)}{\partial Z^2} \right| \sigma' \right\rangle q_{\sigma} q_{\sigma'}^+ \]

A similar coupling terms were used by Cole\[27\] to calculate escape rates for electrons trapped above the surface of "He.

3.3 The Morse Potential

A significant amount of numerical calculations can be avoided by using a Morse potential to model \( U_0(Z) \).

\[ U_0(Z) = \mathcal{E} \left[ e^{-a \beta (Z - z_0)} - 2 e^{-\beta (Z - z_0)} \right] \]

For a Morse potential the ground state wave function, the free states \( |\sigma\rangle \) and the matrix elements \( \langle \phi \left| \frac{\partial u_0(Z)}{\partial Z} \right| \sigma \rangle \) can be calculated analytically.

The effective pair potential which gives a Morse potential for \( U_0(Z) \) is given by:\[35\]

\[ V(x) = \frac{\mathcal{E} \beta^2}{\pi m_{\text{He}} x} \left[ e^{-a \beta (x - z_0)} - 2 e^{-\beta (x - z_0)} \right] \]

The coupling function is given by:

\[ \frac{\partial u_0(Z)}{\partial Z} = 2 \mathcal{E} \left[ \frac{e^{2 \beta z_0} e^{-a \beta \frac{x^2}{1 + \frac{x^2}{\beta^2}}} \frac{1}{\beta^2}}{(1 + \frac{x^2}{\beta^2})^{\frac{1}{2}}} - \frac{e^{\beta z_0} e^{-\beta \frac{x^2}{1 + \frac{x^2}{\beta^2}}} \frac{1}{\beta^2}}{(1 + \frac{x^2}{\beta^2})^{\frac{1}{2}}} \right] \]
The ground state wave function and the binding energy are given by:

\[ \phi_b(z) = \left[ \frac{p}{\mathbf{r}(z)} \right]^{\frac{1}{2}} e^{-\frac{1}{2} \xi^2} \]

\[ E_b = \mathcal{E} \left[ 1 - \frac{1}{\mathcal{E}} \left( \frac{\mathbf{r}^2}{a \mathcal{E}} \right)^{\frac{1}{2}} \right] \]

(25)

where

\[ \xi = 2 \left( \frac{a \mathcal{E}}{k^2 \mathcal{E}} \right)^{\frac{1}{2}} e^{-\beta |z-z_0|} \]

\[ \mathcal{S} = \left( \frac{a m E_b}{k} \right)^{\frac{1}{2}} / h \beta \]

The normalized free solution with energy \( U \) is given by:

\[ \phi(z) = \sqrt{\frac{2}{L}} \frac{|n(0.5-L-i\gamma)|}{2 \Gamma(2i\gamma)} \xi^{-\frac{1}{4}} \mathcal{W}_{d,i\delta}(\xi) \]

(26)

where

\[ d = \left( \frac{2m \mathcal{E}}{k^2 \mathcal{E}} \right)^{\frac{1}{2}} \]

\[ \delta = \left( \frac{a m \mathcal{E}}{k^2 \mathcal{E}} \right)^{\frac{1}{2}} \]

and \( \mathcal{W}_{d,i\delta}(\xi) \) is Whittaker’s function. The normalization of the free waves is a box normalization, and therefore the asymptotic behavior of the perpendicular part of the free wave function is \( \sim \sqrt{\frac{2}{L}} \sin(\pi z - \delta) \).

The matrix element \( \langle B \frac{\partial u_b(z)}{\partial \xi} | B \rangle \) is given by:

\[ -2 \beta \mathcal{E} \left\{ \frac{e^{2\beta \mathcal{E}} \left[ \left( \frac{4 \beta}{\sqrt{8m \mathcal{E}}} e^{-\beta^2} \right) \right]}{(1 + q^2 + p^2)^{\frac{1}{2}}} \Gamma(2s + 2s + 2s + 2s + 2s) \right\} \]

(27)

The matrix element \( \langle B \frac{\partial u_b(z)}{\partial x} | B \rangle \) is given by:
The parameters \( p \), \( \varepsilon \) and \( Z_0 \) are obtained by fitting the position of the minimum, the well depth and the zero crossing of the ME potential to \( p \), \( \varepsilon \) and \( Z_0 \) respectively. The values obtained are \( \varepsilon = 4.48K \), \( p = 0.52\text{\textdegree}^{-1} \) and \( Z_0 = 4.2\text{\AA} \). The solid line in Figure 1 shows the Morse potential with these parameters. The circles show the value of the ME potential.

Solving the Schrodinger equation, for the Morse potential with these parameters, we get \( E_B = 0.70K \) compared with the value \( E_B = 0.63K \) obtained by using the exact ME potential. Both of these values are significantly smaller than the experimental values and therefore in some of the calculations we will compare the results obtained with the above parameters with results obtained with parameters adjusted to give the experimental values for the binding energy. By making the depth of the well \( \varepsilon \) deeper, higher binding energies are obtained. For example the parameters \( p = 0.52\text{\textdegree}^{-1} \), \( \varepsilon = 5.52K \) and \( Z_0 = 4.2\text{\AA} \) give the experimental value of the binding energy \( E_B = 1.15K \) as measured by the UBC group.
Figure 1 - The Morse surface potential (the solid line) compared to the ME potential (the circles).
3.4 Properties Of The Matrix Elements

We describe the $q \to 0$ and the $\sigma \to 0$ limits of the matrix elements. The following properties hold regardless of the potential $\partial u_q(z)$ used.

First we notice that the bound state expectation value of $\frac{\partial u_0(z)}{\partial z}$ is zero, which is a general property of any potential and its bound states. For the $q \to 0$ limit the matrix element $\langle B | \frac{\partial u_q(z)}{\partial z} | B \rangle$ vanishes as $q^2$, and the matrix element squared, a quantity which appears often in perturbative calculations, vanishes as $q^8$. This power law behavior is large enough to eliminate infrared divergences in all the calculations which we performed.

The expectation value of $\frac{\partial u_q(z)}{\partial z}$ between the ground state and the free states does not vanish as $q$ vanishes and therefore infrared singularities are more likely to occur in calculations involving $\langle \sigma | \frac{\partial u_q(z)}{\partial z} | B \rangle$.

The small energy limit of $\langle \sigma | \frac{\partial u_q(z)}{\partial z} | B \rangle$ is linear in $\sigma$, which is a consequence of the box normalization of the free waves, and therefore the matrix element squared is proportional to the perpendicular energy.
IV. THE STICKING PROBABILITY

4.1 Theory

We calculate the probability per collision $S(E, \Theta)$ for a free hydrogen atom, incident on the surface from an angle $\Theta$ and with energy $E$, to scatter into the bound state. The calculation is performed using first order time dependent perturbation theory, where the unperturbed Hamiltonian is $H_0 + H_\text{p}$ and the perturbation is the linear term in $H_\text{p}$. This approximation corresponds to sticking processes in which the number of ripplons on the surface is changed by one. Two channels are available: a ripplon can either be created or be destroyed while a hydrogen atom sticks to the surface. The most probable event is sticking while creating a ripplon.

The unperturbed states, corresponding to the unperturbed Hamiltonian, are two-dimensional plane waves multiplied by solutions to the surface potential $U_0(z)$ for the hydrogen wave function and ripplon states in the number occupation representation for the surface states.

During a sticking event with creation of a ripplon on the surface, the state of the system changes from its initial state $|\tau> |\mathbf{k}^\tau> |m_\mathbf{k}^\tau>$ to a final state $|\mathbf{k}^\tau> e^{-i \mathbf{k}^\tau \cdot \mathbf{r}} |m_\mathbf{k}^\tau + 1>$, where $\mathbf{k}^\tau$ is a two dimensional wave vector for the hydrogen on the surface. The initial and final energies are given by:
The rate of transition is given by:

\begin{equation}
\begin{split}
R(E_j, \Theta) &= \frac{4\pi}{k} \sum_{Q_k} \frac{k Q_k}{2} \left\langle E \left| \frac{\partial u_{\Theta}(Q_k)}{\partial Q} \right| \sigma \right\rangle^2 \left( 1 + m(Q_k) \right) \left( 1 + N(Q_k) \right) \delta(E_i - E_j) \\
\end{split}
\end{equation}

where \( m(Q_k) = (e^{\frac{\hbar \omega_k}{kT}} - 1)^{-1} \) and \( N(Q_k) \) is the analogous function for hydrogen atoms.

The sticking probability \( S(E, \Theta) \) is given by normalizing the rate of transition to a unit incident flux.

\begin{equation}
S(E, \Theta) = \frac{L R(E_j, \Theta)}{E/(2m)} \frac{1}{cos \Theta}
\end{equation}

The thermally averaged sticking probability is obtained by averaging \( S(E, \Theta) \) over a distribution \( P(E, \Theta) \) of incident particles.

\begin{equation}
S(T) = \frac{\int_{0}^{\infty} dE \int_{0}^{\pi/2} d\Theta \ P(E_j, \Theta) S(E_j, \Theta)}{\int_{0}^{\infty} dE \int_{0}^{\pi/2} d\Theta \ P(E_j, \Theta)}
\end{equation}

We used \( P(E_j, \Theta) \sim e^{-E_j/kT} \sin \theta \cos \theta \) which is the distribution of incident particles for a Boltzman gas at temperature \( T \).

The angular integration in Equation 33 can be performed analytically giving the following result:
where \( X = \left( \frac{\hbar^2 q}{2m} \right)^2 - C^2 \)
and \( C = \frac{\hbar}{\Omega q} + \frac{\hbar^2 q^2}{2m} - E_B - \frac{\hbar^2 \sigma^2}{2m} \)

\( \Theta(X) \) restrict the q integration interval to be from the minimum to the maximum ripplon wave vector allowed by conservation of energy and conservation of surface momentum. The integrand diverges as \((q-q_i)^{-0.5}\) at the limits \( q_i \) i=1,2 of the integration.

Appendix A explains the numerical methods used to perform the numerical integration.

4.2 The Low Temperature Approximation

We calculate the low temperature dependence \((kT \ll E_B)\) of the sticking probability. At low temperatures the incident particles have very little energy and therefore the incident free waves have small values of \( \sigma \). In the low energy limit the matrix element \( \langle \sigma | \frac{\partial u_q(z)}{\partial z} | \sigma \rangle \) is proportional to \( E^{0.5} \) and therefore we define \( M(q) \) through the equation:

\[
(35) \quad \langle \sigma | \frac{\partial u_q(z)}{\partial z} | \sigma \rangle = \frac{1}{V^3} \quad M(q) \quad E^{1/2} \quad \cos \Theta
\]

Assuming that the bound state is nearly empty, \( N(q-k)=0 \), using Equation 31 and ignoring terms containing \( E \) in \( \sigma(E_i-E_f) \) we obtain:
\[
S(E, \theta) = S_0 \frac{1}{E} \cos \theta
\]

where:

\[
S_0 = \left( \frac{m q_0}{2 \pi \hbar \sigma_0} \right)^{\frac{1}{2}} \frac{|M(q_0)|^2}{\left[ \frac{\hbar}{2} \left( \frac{\sigma_0 q_0}{\tilde{q}_0} \right)^{\frac{1}{2}} + \frac{\hbar^2}{m q_0} \right]^{\frac{1}{2}}}
\]

and \( q_0 \) satisfies the relation:

\[
E_0 = \hbar \left( \frac{q_0^2}{\sigma_0} \right)^{\frac{1}{2}} + \frac{\hbar^2 q_0^2}{2m}
\]

\( q_0 \) is the wave vector of the ripplon created when a hydrogen atom with negligible kinetic energy is trapped by the surface potential. The ripplon created and the bound hydrogen atom have the same wave vector magnitude \( q_0 \) with opposite directions.

For the thermally averaged sticking probability we obtain:

\[
S(T) = \frac{\pi^{\frac{1}{4}}}{\tilde{q}} S_0 T^{\frac{1}{2}}
\]

which shows that in the low temperature limit the sticking probability is proportional to \( T^{0.5} \).

4.3 RESULTS

4.3.1 \( S(E, \theta) \)

For a given incident energy \( E \) and angle \( \theta \) the sticking probability is a function of the temperature \( T \) of the helium film through the thermally averaged occupation number for the
ripplons $1 + n(q)$ in Equation 31. We calculate $S(E, \Theta)$ at zero temperature assuming that the bound state is empty and using the parameters $E = 4.48K$, $\beta = 0.52 Å^{-1}$ and $Z_0 = 4.2 Å$ which give a binding energy of $0.70K$. We find that, for the values $0 < E < 1K$ and $0 < \Theta < 85°$, $S(E, \Theta)$ can be fitted with an accuracy better than 7% to

$$S(E, \Theta) \equiv 0.055(1 + 1.25E) E^{\frac{1}{2}} \cos \Theta$$

We note that $S(E, \Theta)/(E^{\frac{1}{2}} \cos \Theta)$ is very weakly dependent on $\Theta$ and therefore Equation 40, where $S(E, \Theta)/(E^{\frac{1}{2}} \cos \Theta)$ is independent of $\Theta$, is a good approximation. Figure 2 shows $S(E, \Theta)/(E^{\frac{1}{2}} \cos \Theta)$ as a function of $E$, at $\Theta = 45°$ for various film temperatures. There is a large deviation from the low energy limit $S(E, \Theta) \sim E^{\frac{1}{2}} \cos \Theta$, for $0 < E < 1K$, implying large deviations from the low temperature limit for the temperature range in which the experiment was performed. At higher temperatures $S(E, \Theta)$ increases due to the higher number of thermally excited ripplons on the surface. At these temperatures $S(E, \Theta)/(E^{\frac{1}{2}} \cos \Theta)$ continues to be mainly dependent on the energy with only a small angular dependence.
Figure 2 - The sticking probability at $\theta = 45^\circ$ as a function of the atom energy for various values of the film temperature $T$. 

\[ s(E, \theta = 45^\circ) / \sqrt{E \cos \theta} \times 10^{-2}K^{-1/2} \]
4.3.2 \( S(T) \)

The thermally averaged sticking probability \( S(T) \) was calculated for different values of common surface and gas temperature \( T \) by performing the double integration (see Appendix A) in Equation 33 and using \( S(E,\Theta) \) obtained with the parameters specified in the previous section. The solid line in Figure 3 shows the results obtained for \( S(T) \). The experimental bars in Figure 3 correspond to the values of the sticking probability measured at UBC (see Table 1). For the temperature range in which the experiment was performed there is good agreement between our results and the data.

Unfortunately, the experimental data are not sufficiently accurate over a wide enough range of temperature to reveal the temperature dependence of the sticking probability, and therefore we cannot test this feature of our results.

The parameters used to calculate the previous results give a binding energy of 0.70K which is smaller than the measured binding energy. We have also calculated \( S(T) \) using the same values of \( \beta \) and \( Z_0 \) but changing \( \varepsilon \) to get higher binding energies. Increasing \( \varepsilon \) will make the well depth larger and the binding energy will increase. The sticking probability also increases with the deepening of the well.

We varied \( \varepsilon \) to get the different values for the binding energy measured by the different groups. The symbols in Figure 3, at \( T=0.2K \), correspond to the values of \( S(T) \) for the different values of \( E_B \). These results are noticeably higher than the experimental values of \( S(T) \). Variation of the other
parameters shows that the sticking probability is mainly dependent on the value of the binding energy.

Thus we are left with a factor of between 1.5 and 2 discrepancy between the size of the measured sticking probability and the value which we calculated for \( S(T) \), when the parameters are fitted to the measured binding energies.

The discrepancy most likely is due to an inaccuracy in the function which we use to model the atom-ripplon coupling.

We have also calculated \( S(T) \) with a matrix element which corresponds to a coupling independent of \( q \) and equal to \( \frac{\partial \nu_0(q)}{\partial \xi} \). This coupling can be derived assuming that the hydrogen atom interacts only with an element of liquid just below the position of the atom. The dashed line in Figure 3, calculated with parameters which yield \( E_g = 1.15K \), shows a much lower \( S(T) \), in better agreement with the experimental data. This shows that the form of the \( q \)-dependent coupling can have a marked effect on the sticking probability even for coupling functions which have the same \( q=0 \) limit. We believe that a the correct \( q \) dependence lies somewhere in between the two forms considered above.
Figure 3 - The thermally averaged sticking probability $S(T)$ versus the common temperature $T$ of the film and the gas. The solid line represents $S(T)$ for $E_B=0.70\,\text{K}$. The vertical bars represent the experimental data shown in Table I while the symbols O, □ and + correspond to the theoretical results for $E_B=0.89\,\text{K}$, $E_B=1.01\,\text{K}$ and $E_B=1.15\,\text{K}$ respectively. The dashed line corresponds to a different ripplon atom coupling and $E_B=1.15\,\text{K}$ as explained in the text.
V. THE HYDROGEN SURFACE POLARON

5.1 Introduction

In this chapter we will explore the possibility that a hydrogen atom bound to the helium surface may exhibit significant polaronic behaviour.

The concept of a polaron was introduced to describe a conduction electron moving in an ionic crystal. The electron polarizes the lattice in its vicinity, and while moving in the crystal it carries with it the polarization. The electron is said to be moving with an accompanying "phonon cloud". Such a system is referred as a polaron.

A Hamiltonian containing a free phonon part, a Bloch electron term, and an electron-phonon interaction term was introduced by Frohlich to describe this problem. A straightforward perturbative calculation, in which the interaction term perturbs the free phonons and Bloch electron states, is not adequate for certain crystals, the reason being that the coupling constant multiplying the interaction term is large. Therefore different methods were introduced to calculate the polaron energy and its mass for weak, intermediate and strong coupling.

An ingenious method, which can be used for all values of the coupling constant, was introduced by Feynman. The method consists of eliminating the phonon coordinates exactly from the Hamiltonian, thus obtaining an effective but exact formulation of the problem containing only the electron variables. Next the problem is treated variationally with results which are lower in
energy, and therefore more accurate, than results obtained by any other method.

A similar problem is an electron bound above the surface of \(^4\text{He}\) interacting with the ripplons in the presence of an external electric field. Jackson and Platzmann, (JP), suggested that the bound electron will show polaronic properties.\(^{38-39}\) They proposed that the strength of the coupling between the electron and the surface could be changed continuously from the weak to the strong limit by varying the strength of the electric field or the thickness of the film or by choosing different substrates on which the liquid film resides. JP used Feynman's approach to calculate the electron effective mass as a function of the coupling.

In both problems, discussed above, some degrees of freedom are not taken into account. For the electron-phonon problem, the electron is assumed to be in a certain band, and therefore no inter-band virtual transitions are considered. For the electron-ripplon problem the electron is assumed to be in the ground state of the surface potential, and thus excited perpendicular states are not considered.

In our case a hydrogen atom in the bound state above the surface interacts with the surface and distorts it. While moving parallel to the surface the atom drags with it the distortion of the surface thus acquiring an effective mass \(m^*\), different from its free mass \(m\). In this Chapter we calculate the energy of the hydrogen-ripplon system, the effective mass \(m^*\) and the number of ripplons in the "ripplon cloud" moving with
the atom. We consider the effect of the free surface states on these results. We also look at the localization proposed by GMY using our coupling function.

5.2 The Hydrogen-Ripplon Interaction Energy

5.2.1 Theory

For the purpose of this chapter we will write the total Hamiltonian in the following one particle notation:

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U_0(z) - \frac{\hbar^2}{2m} \nabla_z^2 + \sum_{\vec{q}_g} \hbar \omega_{\vec{q}_g} V_{\vec{q}_g}^+ V_{\vec{q}_g}^\dagger \]

\[ - \frac{1}{\sqrt{A}} \sum_{\vec{q}_g} \left( \frac{\hbar q_r}{2s_0 \omega_{\vec{q}_g}} \right)^{1/2} \left( V_{\vec{q}_g}^+ + V_{\vec{q}_g}^\dagger \right) \frac{\partial \psi_{\vec{q}_g}(z)}{\partial z} \cdot \vec{p} \cdot \vec{r} \]

\[ + \frac{1}{\sqrt{A}} \sum_{\vec{q}_g, \vec{q}_g'} \left( \frac{\hbar q_r}{2s_0 \omega_{\vec{q}_g}} \right)^{1/2} \left( V_{\vec{q}_g}^+ + V_{\vec{q}_g}^\dagger \right) \frac{\partial^2 \psi_{\vec{q}_g, \vec{q}_g'}(z)}{\partial z^2} \cdot \vec{p} \cdot \vec{r} \]

The energy of the hydrogen polaron is obtained by calculating the ground state energy of the above Hamiltonian. The calculation is based on perturbation theory where the unperturbed Hamiltonian is given by:

\[ H_0 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U_0(z) - \frac{\hbar^2}{2m} \nabla_z^2 + \sum_{\vec{q}_g} \hbar \omega_{\vec{q}_g} V_{\vec{q}_g}^+ V_{\vec{q}_g}^\dagger \]

and the perturbation terms are the coupling to the ripplons terms. The unperturbed Hamiltonian is separable. Its eigenfunctions are ripplon states in the occupation number representation multiplied by hydrogen atom surface states. The hydrogen state is a 2-D free wave multiplied by a solution of
$U_0(z)$. The energy is the sum of the perpendicular energy ($-E_g$ for the bound state or $\frac{\hbar^2\sigma^2}{2m}$ for the state $|\sigma\rangle$), the parallel free particle kinetic energy and ripplon energies. The perturbative part of the Hamiltonian consists of a term which is linear in the ripplon variables and a second term which is quadratic. The effect of these terms is to mix the parallel, the perpendicular, and the ripplons states.

In order to take into account all the contributions to the energy, to second order in the ripplon variables, we must calculate the contribution from the linear coupling term in second order perturbation theory and the contribution from the quadratic term in first order perturbation theory.

The hydrogen-ripplon interaction energy $\Delta E(k)$ is defined as the correction to the unperturbed energy, of a hydrogen atom with surface wave vector of magnitude $k$, due to the coupling terms. The total energy of such an atom will be given by:

$$E(k) = -E_g + \frac{\hbar^2 k^2}{2m} + \Delta E(k)$$

(43)

We define $\Delta E(k) = \Delta E^1 + \Delta E^2(k)$, where $\Delta E^1$ is the contribution to $\Delta E(k)$ from first order perturbation theory and $\Delta E^2(k)$ is the contribution from second order perturbation theory.

The results from the perturbative calculations are:
\[ (44) \quad \Delta E' = \frac{1}{2n} \sum_{q} \frac{h q}{2 s_0 \omega_q} \left[ 1 + m(q) \right] \langle \phi | \frac{\partial^2 u_s(x)}{\partial x^2} | \phi \rangle = \frac{1}{2} \langle \phi | \frac{\partial^2 u_s(x)}{\partial x^2} | \phi \rangle \langle x^2 \rangle \]

where \( \langle h^2 \rangle \) is the thermally averaged mean square displacement from equilibrium of the surface.

\[ \Delta E^2(k) = -\frac{1}{A} \sum_{q} \sum_{\sigma} \frac{h q \left( 1 + m(q) \right) \langle \sigma | \frac{\partial u_s(x)}{\partial x} | \phi \rangle \langle x \rangle^2}{2 s_0 \omega_q \left( \frac{h^2 \sigma^2}{2m} + \frac{h^2 q^2}{2m} + E_B + \frac{\omega}{m} \right) - \frac{h^2 q^2}{2m} \langle \sigma \rangle^2} \]

The sum over \( \sigma \) includes a term corresponding to the single bound state and a sum over a continuum of free states:

\[ \sum_{\sigma} f(\sigma) \rightarrow \frac{1}{\pi} \int_{0}^{\infty} f(\sigma) d\sigma' + f(0) \]

where \( f(\sigma) \) is an arbitrary function of \( \sigma \). Therefore we will define:

\[ \Delta E^2(k) = \Delta E^2_c(k) + \Delta E^2_b(k) \]

where \( \Delta E^2_c(k) \) and \( \Delta E^2_b(k) \) are the contributions to \( \Delta E(k) \) from the free states and the bound states respectively. Thus \( \Delta E(k) \) is given as a sum of three terms.

\[ \Delta E(k) = \Delta E^2_c(k) + \Delta E^2_b(k) + \Delta E' \]

These results differ from the usual results obtained in polaronic calculations for the electron-phonon or the electron-
rippon system, by the inclusion of the terms $\Delta E'$ and $\Delta E^2(k)$. For those problems only the linear coupling term was considered and non-adiabatic corrections were neglected. In our case $\Delta E_c^2(0)$ is calculated and its magnitude shows that it cannot be neglected. Also $\Delta E'$ is included to avoid a non physical result for $T>0$ as will be explained in the following subchapter.

We notice that $\Delta E'$ and $\Delta E^2(k)$ have opposite signs, i.e $\Delta E'$ is positive and $\Delta E^2(k)$ is negative.

5.2.2 The Long Wavelength Limit

The term which is quadratic in the ripplons variables gives a contribution to $\Delta E'$ which is proportional to $\langle h^2 \rangle$. The temperature dependent term diverges logarithmically as $g$, the coupling to the gravitational and/or substrate potential, vanishes. For non-zero $g$ most of the contribution to $\langle h^2 \rangle$, and therefore to $\Delta E'$, come from the long wavelength ripplons. This is clearly an unphysical result because the long wavelength ripplons only shift the position of the surface and therefore cannot significantly change the binding energy. This unphysical result does not occur when both terms are taken into account as mentioned above. Using the sum rule:

$$\frac{1}{\alpha} \langle B | \frac{\partial^2 u_0(z)}{\partial z^2} | B \rangle = \sum_{\sigma} \frac{|\langle \sigma | e u_0(z) / \partial z | \sigma \rangle|^2}{\hbar^2 \sigma^2 / 2m + E_\sigma}$$

and looking at the $q \to 0$ contribution to $\Delta E'$ we notice that the zero $q$ limits of the contribution to $\Delta E^2(0)$ and the same limit for $\Delta E'$ exactly cancel each other. This means that, taking
into account both terms, there is no significant contribution to the binding energy from the long wavelength ripplons.

5.2.3 $T=0$ $k=0$

For the film temperature $T=0$ and approximating a slow hydrogen atom by taking $k=0$, we obtain:

\[ \Delta E' = \frac{1}{2} \left\langle B \left| \frac{\partial^2 u(x)}{\partial z^2} \right| B \right\rangle \delta_{\alpha}^{2} \]

where $\delta_{\alpha}^{2}$ is defined in Equation 12. From Equations 45 and 47 we obtain:

\[ \Delta E_{\alpha}^2(\alpha) = -\frac{1}{A} \sum_{\beta} \frac{\hbar q_{\beta}}{2s_{\omega_{\beta}}} \frac{\left| \left\langle B \left| \frac{\partial u_{\alpha}(z)}{\partial \omega} \right| B \right\rangle \right|^2}{(\hbar \omega_{\beta} + \frac{\hbar^2 q_{\beta}^2}{2m})} \]

\[ \Delta E_{\epsilon}^2(\alpha) = -\frac{1}{A} \sum_{\beta} \frac{\hbar q_{\beta}}{2s_{\omega_{\beta}}} \frac{1}{\pi} \int_{0}^{\infty} d\sigma \frac{\left| \left\langle B \left| \frac{\partial u_{\alpha}(z)}{\partial z} \right| \sigma \right\rangle \right|^2}{E_{\beta} + \frac{\hbar^2 \sigma^2}{2m} + \hbar \omega_{\beta} + \frac{\hbar^2 q_{\beta}^2}{2m}} \]

Ignoring the gravitational term in the ripplon spectrum we obtain for $<h^2>$:

\[ <h^2> = \delta_{\alpha}^{2} = 2.39 \alpha \frac{\hbar^2}{m} \tilde{A}^2 \]

and using a cut off $q = 1\tilde{A}^{-1}$ we obtain: $<h^2> = 2.39 \tilde{A}^2$.

Next we calculate $\left\langle B \left| \frac{\partial^2 u(x)}{\partial z^2} \right| B \right\rangle$. For a Morse potential:
\[ \frac{\partial^2 u_0(x)}{\partial x^2} = 2\beta^2 \epsilon \left[ 2 e^{-2\beta(x-x_0)} - e^{-\beta(x-x_0)} \right] \]

and using:

\[ \langle B | e^{-\gamma(x-x_0)} | B \rangle = \frac{(\hbar \beta)^\gamma}{(8\pi m \epsilon)^{3/2}} \frac{\eta(2\alpha+\gamma)}{\eta(\alpha)} \]

we obtain:

\[ \frac{1}{2} \langle B | \frac{\partial^2 u_0(x)}{\partial x^2} | B \rangle = \beta^2 \epsilon \left[ 2 \frac{(\hbar \beta)^2}{8m \epsilon} \frac{\eta(2\alpha+2)}{\eta(\alpha)} - \frac{\hbar \beta}{(8m \epsilon)^{3/2}} \frac{\eta(2\alpha+1)}{\eta(\alpha)} \right] \]

Using the parameters \( \beta = 0.52 \, \text{Å}^{-1} \), \( \epsilon = 4.48 \, \text{K} \) and \( z_0 = 4.2 \, \text{Å} \) we obtain from Equation 56:

\[ \frac{1}{2} \langle B | \frac{\partial^2 u_0(x)}{\partial x^2} | B \rangle = 0.48 \, \text{K} \, \text{Å}^{-2} \]

and therefore from Equation 53 and 57 we obtain:

\[ \Delta E^1 = 1.15 \, \text{K} \]

We note that this result is sensitive to the wave vector cut-off used as \( q_{\text{m}$^{1.5}$.}

\( \Delta E^2(0) \) is calculated numerically using two-dimensional and one-dimensional Gaussian numerical integration for \( \Delta E_c^2(0) \) and \( \Delta E_b^2(0) \) respectively (see Appendix A). We obtain \( \Delta E_c^2(0) = -0.45 \, \text{K} \) and \( \Delta E_b^2(0) = -0.94 \, \text{K} \) giving \( \Delta E(0) = 0.66 \, \text{K} \)

This result is almost equal in its absolute magnitude to the binding energy \( E_b = 0.70 \, \text{K} \) obtained for the surface potential with
the above parameters. Thus the total energy for a hydrogen atom bound to the surface would be \(-0.70K+0.66K=-0.04K\), in complete disagreement with the measured value of the binding energy.

A possible explanation is the large contribution to \(\Delta E^{1}\) from ripplon wave vectors \(0.5<q<1\text{Å}^{-1}\), which is the part of the spectrum which is not given accurately by the model we used for the surface. The large contribution to the energy from this part of the ripplon spectrum is manifested by the sensitivity of the results to the value of \(q_{m}\). A different model for the surface elementary excitation, which takes into account the compressibility of the liquid may give a different result, less sensitive to the arbitrary cut-off used.

The sensitivity of these results to the ripplon spectrum cut-off can be demonstrated by choosing an ad-hoc cut-off value. For example choosing \(q_{m}=0.75\text{Å}^{-1}\) gives:

\[
\Delta E^{1} = 0.75K \\
\Delta E^{3}_c(0) = -0.40K \\
\Delta E^{3}_g(0) = -0.04K
\]

and therefore \(\Delta E(0)=0.30K\).

Another possible explanation is a breakdown of perturbation theory. A non-perturbative approach to the perpendicular problem may be needed. Due to the fact that the contribution from the free states is the dominant contribution to the change in the energy, an application of Feynman's method would require taking these variables into account. An exact elimination of
the ripplon variables can be done easily but the lack of a suitable and easy-to-use variational method for the rest of the problem is the main obstacle which prevents the calculation from being done.

We have used the Feynman method to calculate $\Delta E^2_{E}(o)$. The difference between results obtained in this way and the previous values for $\Delta E^2_{E}(o)$ obtained from perturbation theory is negligible. This is as expected, since the small size of $\Delta E^2_{E}(o)$ indicates that the coupling between surface atoms and the ripplons is small. In the weak coupling limit, perturbation theory is perfectly adequate, giving the same results as Feynman's method.

5.3 Hydrogen Polaron?

The possible breakdown of perturbation theory does not necessarily imply polaronic behavior, it only shows that the perpendicular problem and the parallel problem are strongly coupled and cannot be separated. Polaronic behavior would emerge for strong coupling between the hydrogen and the ripplons. In this subchapter we will investigate the parallel coupling.

In the following section, we check whether the localization predicted by GMY occurs. We calculate the effective mass on the surface and the number of ripplons moving along with the atom in the bound state.
5.3.1 GMY Localization

We repeat the calculation of GMY which suggested that, in the ground state of the hydrogen-ripplon system, the hydrogen parallel wave packet may be significantly localized. The crucial difference between the following calculations and the one performed by GMY is the coupling to the surface used. GMY assumed a form function coupling between an element of liquid and the atom and obtained matrix elements independent of the ripplon wave vector \( q \). We will use the coupling derived in Chapter 2.

Adopting the approach of GMY, we get for the parallel energy:

\[
E(\gamma) = \frac{\hbar^2 \gamma}{2m} - \int_0^q d\gamma \frac{h^2}{4\pi \rho} \left[ \frac{q^2}{2\hbar} \frac{\langle \psi | \frac{\partial u_q(q)}{\partial \gamma} | \psi \rangle^2}{\hbar^2 (\gamma^2 + \frac{\gamma^2}{\rho^2} \gamma^4)} \right]
\]

The first term is the kinetic energy term corresponding to a two dimensional Gaussian wave packet with half width \( \gamma \), while the second term is the negative potential energy resulting from the linear coupling to the ripplons.

In GMY, the matrix elements were independent of \( q \) and therefore could be taken out of the integrand. Then most of the contribution to the integral is proportional to \( 1/\gamma^2 \) and comes from the long wavelength ripplons. Thus GMY obtained a result which could be made as negative as one wishes by making \( \gamma \) as small as needed, for example, by making the film very thick. In our calculation we do not obtain any contribution from the long wavelength limit because the matrix element \( \langle \psi | \frac{\partial u_q(q)}{\partial \gamma} | \psi \rangle \) vanishes as \( q^2 \) for small \( q \).
Using the parameters \( E = 4.48K, \beta = 0.52A^{-1} \) and \( Z_0 = 4.2A \) we find that for all \( \gamma E(\gamma) > 0 \) implying that the localization effect suggested by GMY is an artifact of the model they used to describe the coupling. The kinetic energy term is also always larger than the potential energy term, giving a positive energy, when the parameters which yield a binding energy of 1.15K are used.

5.3.2 The Effective Mass At T=0K

Next we calculate the effective mass \( m^* \) for a bound hydrogen atom moving above the surface.

We define \( R_B \) and \( R_C \) through the following equations, which are obtained by expanding \( \Delta E_B^2(k) \) and \( \Delta E_C^2(k) \) in powers of \( k^2 \).

\[
\Delta E_C^2(k) = \Delta E_C^2(0) + R_C \frac{\hbar^2}{2m} k^2
\]

\[
\Delta E_B^2(k) = \Delta E_B^2(0) + R_B \frac{\hbar^2}{2m} k^2
\]

For small enough values of \( k \) we can ignore all powers of \( k \) except the quadratic term. Then we get for the total parallel energy of a slow hydrogen atom moving above the surface:
where \( m^* \) is the renormalized hydrogen mass. Using:

\[
\Delta E_{C}^{2}(k) = \frac{1}{\pi} \int_{0}^{\infty} d\sigma \int_{0}^{\infty} \frac{d\sigma'}{(2\pi)^2} \int_{0}^{2\pi} \frac{4}{\sigma} \frac{1}{\omega_{q}} \left| \frac{\partial \varphi_{q}(z)}{\partial z} \right|^{2} \left( \omega_{q}^{2} \sigma^{2} + k_{q}^{2} \right) \]

expanding the integrand in the angular integration in powers of

\[
\frac{\hbar^{2} k_{q} \cos \theta}{m(E_{B} + \frac{\hbar^{2} \sigma^{2}}{2m} + \frac{\hbar \omega_{q}}{2m} + \frac{\hbar^{2} \sigma^{2}}{2m})}
\]

and maintaining only the first and second terms we obtain:

\[
R_{C} = \frac{\hbar^{4} L}{4 \pi^{2} \sigma_{0} m} \int_{0}^{\infty} \frac{d\sigma}{\sigma} \int_{0}^{\infty} \frac{d\sigma'}{\sigma'} \frac{1}{\omega_{q}} \left( \omega_{q}^{2} \sigma^{2} + k_{q}^{2} \right) \frac{1}{\omega_{q}^{2} \sigma^{2} + k_{q}^{2} + \hbar \omega_{q}}
\]

The integral is calculated numerically using two dimensional Gaussian integration. 

\( \Delta E_{C}^{2}(k) \) is given by:

\[
\int_{0}^{2\pi} \frac{d\theta}{\omega_{q} + \frac{\hbar^{2} \sigma^{2}}{2m} + \frac{\hbar^{2} \sigma^{2}}{2m} + \frac{\hbar^{2} \sigma^{2}}{2m} + \frac{\hbar \omega_{q}}{2m} \cos \theta}
\]

In this case the angular integral has a real and an imaginary part. The imaginary part corresponds to damping, i.e. to the loss of energy to the surface by creating ripplons. We are interested in the real part which is given by:
\[ (66) \quad - \frac{1}{(2\pi)^2} \int_{\mathbf{q}} \frac{d^2 \mathbf{q}}{2 S_0 \omega_0^2 \left[ (\hbar \omega_0 + \hbar^2 q^2 + \frac{\hbar^2 q_{\parallel}^2}{m})^2 - (\frac{\hbar^2 q_{\parallel}^2}{m})^2 \right]^{\frac{1}{2}}} \]

where \( q_{\parallel} \) satisfies \( \hbar \omega_0, + \frac{\hbar^2 q_{\parallel}^2}{m} = \frac{\hbar k}{m} q_{\parallel} \). We notice that in the vicinity of \( q_{\parallel} \), the integrand diverges as \( (q - q_{\parallel})^{-0.5} \) and therefore a special type of Gaussian integration is needed to calculate this integral (see appendix A).

\( \Delta E_B^2(k) \) is calculated numerically for small values of \( k \), and \( R_B \) is obtained by fitting the results to Equation 60.

Using the cut off \( q=1\AA^{-1} \) and the parameters \( \varepsilon=4.48K \)
\( \beta=0.52\AA^{-1} \) and \( Z_0=4.2\AA \) we obtain \( R_C=-0.8 \times 10^{-2} \) and \( R_B=-0.9 \times 10^{-2} \) which give, using Equation 61, \( m^*=1.017m \). For the parameters which correspond to the measured binding energy \( R_C=-1.1 \times 10^{-2} \) and \( R_B=-1.7 \times 10^{-2} \) giving \( m^*=1.029m \). These results show that the renormalized mass is only slightly higher than the free hydrogen mass. Edwards estimated the effective mass on the surface to be \( 1.1m \).

5.3.3 The Ripplon Cloud

We calculate the average number of virtual ripplons moving with a hydrogen atom on the surface. Following Pines we calculate the expectation value of the ripplon number operator

\[ \hat{N} = \sum_{\mathbf{q}} \hat{v}_{\mathbf{q}} \hat{v}_{\mathbf{q}}^\dagger \]

in the perturbed state of the system.
For slow atoms, approximated by taking \( k=0 \), we get:

\[
\langle N \rangle = \frac{1}{A} \sum_{\mathbf{q}} \frac{t_{\mathbf{q} \mathbf{r}}}{2 \omega_{\mathbf{q}}} \sum_{\mathbf{q}'} \frac{|\psi_1 \langle \mathbf{k} - \mathbf{q} | \mathbf{l} \rangle|^2}{(E_{\mathbf{q}} + \frac{t_{\mathbf{q} \mathbf{r}}^2}{2m} + \frac{t_{\mathbf{q} \mathbf{r}}^3}{2m} + t\omega_{\mathbf{q}})}
\]

Performing the integration numerically we obtain:

\[
\langle N \rangle = (0.89 + 2.3) \times 10^{-2} = 3.2 \times 10^{-2}
\]

where the first term is the contribution from the free states and the second from the bound state.

The perturbed wave function is a mixture of a zero ripplon state and one ripplon states. Values for \( \langle N \rangle \) of the order of one or more would not be compatible with such a mixture of states, and would indicate that states containing more ripplons should be included in the state describing the system. However the value of \( \langle N \rangle \) which we obtained, \( \langle N \rangle = 0.03 \), is consistent with a one ripplon approximation.

5.4 Conclusion

In this chapter we showed that no important polaronic effects occur for the bound hydrogen. The effective mass of a hydrogen atom on the surface is only slightly modified by the interaction with the ripplons. Therefore free states with an effective mass \( m^* \) are a good approximation for the bound
hydrogen parallel wave function. Similarly we have shown that a mixture of a zero ripplon state and one ripplon states is an adequate description for the surface state. The small value of $<N>$ and the small difference between the effective mass of a hydrogen atom bound to the surface compared with the mass of a free hydrogen atom indicates that the ripplon-hydrogen coupling should be considered as being weak. We also saw that the two leading terms in the perturbative calculations for the ripplon-atom interaction energy have opposite signs and are of the same order of magnitude as the binding energy, indicating a possible breakdown of perturbation theory. The main contributions to these large shifts comes from the term quadratic in the ripplon variables and from the linear term which couples the virtual states which are not bound to the surface.
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APPENDIX A - NUMERICAL METHODS FOR INTEGRATION

i. One dimensional integrals were calculated by dividing the integration interval into \( N \) equal segments and calculating the integral using 8 point Gaussian integration in each of the segments. The value of \( N \) was fixed so that the desired accuracy would be obtained.

ii. In the same spirit two dimensional integrals were calculated by dividing the integration area into \( M \times N \) parallelograms and performing 8x8 Gaussian Integration in each of them.

iii. Integrals where the integrand \( f(y) \) diverges as \( (y-y_1)^{-0.5} \) at the limit of the integration \( y_1 \) were calculated using a Gaussian-type integration described in Ref. 42 Section 25.4.39. The integration interval was found numerically by solving the algebraic equations defining the limits of the integration.

iv. The thermal average in Equation 33 was calculated by changing the variable \( E \) to \( k^2 \) and \( \theta \) to \( \cos \theta \). Then the \( d(k^2) \) integral was calculated, from zero to infinity, by using the integration method described in Ref. 42 Section 25.4.46 and using \( n=8 \). The \( d(\cos \theta) \) integration was calculated using the method described Section 25.4.33 in Ref. 42 with \( k=2 \) and \( n=4 \).