RICE UNIVERSITY

THE EQUILIBRIUM CONFIGURATION OF LIQUID HELIUM SURROUNDING CERTAIN EXCITED ATOMIC STATES OF HELIUM AND ITS EFFECT ON ABSORPTION AND EMISSION SPECTRA

by

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The existence of microscopic bubbles in liquid helium surrounding localized electron states has been already established using an effective repulsive potential between the electron and helium atoms. We have found that the same effective potential can be used to calculate He-He* interactions. The potential energy of such a system is viewed as the sum of (1) a He$_2^+$ molecular potential describing the interaction of the ground state atom with the "core ion" of the excited state, and (2) the effective electron-helium repulsion averaged over the excited electron orbital. The relative size of these two terms is shown to explain qualitatively the presence or absence of the characteristic "hump" in helium molecular potentials. The same techniques are extended to computing the perturbation of an excited helium atom by an arbitrary distribution of helium liquid atoms, assuming additivity of the interactions. Stable bubbles are then found to exist around certain atomic states, and the transition energies between excited states in liquid bubbles are shown to be in good agreement with the spectroscopic data of Dennis.
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I. INTRODUCTION

The existence of microscopic bubbles in liquid helium has been a topic of experimental and theoretical investigation for several years. Most of the emphasis has been placed on states of an excess electron in the liquid; such an electron tends to be localized in a microscopic cavity from which about a thousand helium atoms have been displaced.\(^1\)\(^\text{–}^6\) In light of recent experiments, however, it has been postulated that a similar, though smaller, bubble may be formed about excited molecular and atomic states of helium. The present calculations show that such a bubble is indeed the lowest energy configuration of the system for certain atomic helium states, and predict emission and absorption spectra in good agreement with experiment.

Dennis et al.\(^7\) have looked at absorption and emission spectra of electron bombarded liquid helium at 1.7° K and have associated certain lines with atomic and molecular transitions. These lines are shifted only slightly (\(\sim 50\) cm.\(^{-1}\)) from their values for a dilute gas, and hence the bubble model arises as an appealing way to analyze excited states of single helium atoms or molecules in a liquid environment. Simple calculations show that the approximate liquid density\(^8\) of 0.00323 atoms/\(a_0^3\) implies an average interatomic spacing of 7 \(a_0\). The electron cloud of a ground state atom has a radius
of $3 \, \text{a}_0$; the cloud of an excited atom may extend radially perhaps $10 \, \text{a}_0$. Hence considerable overlap and interaction would be expected if there is no redistribution of ground state helium atoms near an excited atom. Since the experimental facts show only a small perturbation of atomic and molecular energy levels, the conclusion is that there is in fact a redistribution of ground state atoms. Furthermore, the observation of vibrational and rotational fine structure in the molecular lines gives further support to the idea that an excited atom or molecule can exist at the center of a small bubble, and be only slightly perturbed by the surrounding fluid.

The basic mechanism which allows an excited atom or molecule to cause a local distortion of the liquid is a strongly repulsive interaction between the orbiting excited electron and the surrounding fluid. Such a repulsion is to be expected. Kestner et al. have shown that low energy electron-helium scattering can be fairly well represented by an effective repulsive potential, and the experimental and theoretical evidence that a free electron injected into liquid helium will repel nearby atoms and thus form a cavity has already been mentioned. In our calculations, an atomic state of helium is pictured as a core ion plus an excited electron, and a single particle wave function is used to describe the electron distribution around this core. The repulsive electron-
helium potential is assumed to be the same whether the electron is bound or free, and the atomic energy level shift is seen as the effect of this perturbing potential on the bound, excited electron wave function.

Crude calculations have been performed on the basis of a bubble model. Assuming a completely static picture of the fluid on the microscopic level, Dennis postulated that the density about an excited molecular state could be described by a step function:

\[ \rho(r) = \begin{cases} 0 & r < R \\ \rho_0 & r \geq R \end{cases} \]

In other words, if an excited atom or molecule is at the origin, there are no other atoms at all within a radial distance R, and for distances greater than R, the normal fluid density \( \rho_0 \) prevails. Dennis was considering a Rydberg \( d \Sigma_u^+ \) state, and he assumed that the orbiting excited electron could be described by a single particle hydrogenic 3s wave function (charge \( Z = 1 \)) whose interaction with the fluid was given by a simple radial potential:

\[ V(r) = \begin{cases} 0 & r < R \\ 1 \text{eV} & r \geq R \end{cases} \]

The electron is not perturbed within the bubble, but
whenever the charge cloud overlaps the bulk fluid, it feels a repulsive potential of 1 eV. (This value is obtained from photoionization experiments).\textsuperscript{11}

For any given bubble radius $R$, the perturbation of the electronic energy is simply

$$E_{\text{overlap}} = \left< \psi_{3s} | \nabla | \psi_{3s} \right>$$

$$= \int_{\infty}^{\infty} \left| \psi_{3s}(r) \right|^2 4\pi r^2 dr$$

and clearly decreases as the bubble expands. The equilibrium bubble radius is found by noting that the formation of a bubble requires the expenditure of work against the external (atmospheric) pressure $p$ and against the surface tension $\gamma$. Thus from a classical, macroscopic point of view, we find the energy of a bubble of radius $R$ to be

$$E_{\text{bubble}}(R) = \frac{4}{3} \pi R^3 p + 4\pi R^2 \gamma$$

The equilibrium radius of the bubble is found such that

$$E_{\text{total}}(R) = E_{\text{bubble}}(R) + E_{\text{overlap}}(R)$$

is a minimum.

Dennis found $R_{eq}$ to be 25 $\text{Å}$ when $p = 1$ atm. and
\[ \gamma = 0.53 \text{ ergs/cm.}^2 \] For this size bubble, the electronic perturbation \( (E_{\text{overlap}}) \) is 101 cm.\(^{-1}\), and this value corresponds essentially to the blue shift in the molecular transition \( \Delta \sum_+^+ b \rightarrow \sum_+^+ \). There is, of course, some perturbation of the lower-lying state, but it turns out to be small for the following reason. The initial fluid configuration about the final state is the same as the equilibrium configuration around the initial state, because the massive fluid atoms cannot redistribute themselves in the short time required for an atomic transition. This redistribution does in time occur, but the transition energy must be computed on the basis of the electronic perturbations of the initial and final states at the instant of the transition, and so we must use the same bubble shape in each case. If we use a hydrogenic 2p wave function \( (Z = 1) \) to represent the excited b \( \sum_+^+ \) Rydberg state, we see that the perturbation of this state is negligible because the 2p wave function \( \psi_{2p}(r) \) has practically vanished for \( r \) as large as \( R_{\text{eq}} \), the original bubble radius. The blue shift of 101 cm.\(^{-1}\) predicted by this very simple model compares favorably with the observed blue shift of 15 cm.\(^{-1}\). This agreement between experiment and theory lends credence to the bubble picture, and offers hope that a more refined model might lead to even better results.

This has indeed been the case. A number of
improvements have been built into the model, and these have served both to make the theory more rigorous (though still admittedly semi-classical), and also to yield better agreement with experiment. We first note that using a step function for the density surrounding the excited atom is clearly a simplification, and the assumption of a round bubble is reasonable only if the excited electron cloud itself is spherical (i.e., an s state). The present model allows a gradual monotonic density change from zero inside the bubble to some $\rho$ outside, and admits a small non-spherical deformation to allow the bubble to follow the contour of a p state electron cloud. Another improvement in the model is the inclusion of terms corresponding to the kinetic energy of the fluid atoms. Dennis' model was entirely static and based on the classical concepts of pressure-volume and surface tension work; in this model these terms as well as kinetic energy terms result from writing a liquid Hamiltonian and assuming a reasonable trial wave function. Perhaps the greatest refinement in the theory has been to examine the interaction of an excited helium atom with individual atoms rather than with bulk fluid. A simple method has been found to calculate the interaction of an excited atom and a nearby ground state atom. This method is reasonably accurate and can be extended using the superposition principle to computing the energy of an excited atom surrounded by an
arbitrary distribution of ground state atoms. Using this technique, we can find the equilibrium bubble shape by minimizing the sum of the energy required to form the bubble, the kinetic energy of the fluid atoms, and the perturbation of the excited atom itself by the fluid. This has been done, and the predicted transition energy shifts are in good agreement with observed atomic emission lines $3^3S \rightarrow 2^3P$, $3^1S \rightarrow 2^1P$, and $2^3P \rightarrow 2^3S$, and with the observed absorption $2^3S \rightarrow 2^3P$. In particular, the observed difference in absorption and emission lines between $2^3S$ and $2^3P$ is seen to result from the different equilibrium bubble shapes formed around the initial state in each of these cases.
II. THE HE--HE* TWO BODY PROBLEM

The assumption is made in this work that the interaction of an excited helium atom with any configuration of ground state atoms surrounding it can be determined by summing each separate two-body interaction. A choice must be made, then, of a procedure to calculate a single He-He* interaction. Accurate potentials are known, and could be used without modification. However, a simplified and more attractive approach has been developed, and will be presented in this section. The basic idea is to view an excited helium atom as a core ion and surrounding excited electron orbital, which interact separately with a nearby ground state atom. A smaller contribution due to the van der Waals interaction of the two atoms is also included. In this way the He-He* potential is pictured as the sum of three terms, each with a clear physical interpretation, and the extension to the He*-helium liquid case is straightforward. Conversely, existing two body potentials depend on variational calculations too complicated to be extended to the many body problem. Were such a potential to be used, there would be no freedom to examine separately the van der Waals effect, or the excited electron--He(1S) interaction, and a great deal of physical insight would be lost. Comparison with very accurate two body potentials shows that our simplified approach is quite good for interatomic separations greater than about 6 \(a_0\), and the
bubble model indicates that ground state fluid atoms seldom approach excited atoms any closer than about $8 \, \text{a}_0$. The method here presented is therefore both conceptually appealing and sufficiently accurate.

Within the framework of the adiabatic approximation, we will assume that some He* is located at an origin, and a ground state atom at a distance $R$ along the $z$ axis as shown in Figure 1. Having separated the excited atom into a core He$^+$ ion and an excited electron orbital $\psi_{\text{excited}}(r)$, we denote the He$^+$ ion-He($1^1S$) interaction by $V_{\text{ion}}$, and by $V_{\text{eff}}$ the effective excited electron-He($1^1S$) potential. $V_{\text{ion}}(R)$ may be either of two potentials, depending on the symmetry of the electronic wave function. These are shown in Figure 2: the $2^1\Sigma_u^+$ curve has an attractive well, the $2^3\Sigma_g^+$ curve is totally repulsive. $V_{\text{eff}}$ depends on $s$, the distance from the electron to the He($1^1S$), and is the primary contribution to the interaction energy as well as the basic mechanism of bubble formation. That this interaction can be described by a local potential is of course an approximation, because the exchange effects present are clearly nonlocal (operator) in character. However, it is found that low energy electron scattering by ground state helium atoms can be adequately described by an effective repulsive potential. This repulsion results from the Pauli principle: the scattered electron wave function must be orthogonal to the bound $1s$ wave functions. Orthogonality
Figure 1:

Representation of He-He* interaction by adding \( V_{\text{ion}}(R) \), the He(1 \( 1S \))-He+ potential, and \( V_{\text{eff}}(s) \), the effective electron-He(1 \( 1S \)) interaction.

\( V_{\text{eff}}(s) \) must be averaged over the bound, excited wave function \( \psi(r, \theta, \varphi) \).
Figure 2:
Potential energy as a function of internuclear separation in the He$_2^+$ molecule.
is accomplished at the expense of a node in the wave function a small distance from the helium nucleus. Physically, this gives the scattered electron extra kinetic energy when it is in the region of strong Coulomb attraction. The effect of this positive energy contribution on the motion of the particle described by the orthogonalized wave function is exactly the same as the effect of a repulsive potential on a particle described by a smooth (nodeless) wave function. As stated in the Introduction, we assume that the bound electron in the excited helium atom is perturbed by exactly the same potential that describes the scattering. To calculate this perturbation, $E_{\text{overlap}}$, we must write an explicit form for $V_{\text{eff}}(s)$ and determine appropriate one electron wave functions $\psi_{\text{excited}}(r)$. Formally, then, $E_{\text{overlap}}$ is the value of $V_{\text{eff}}(s)$ averaged over the electron orbital:

$$E_{\text{overlap}}(R) = \int V_{\text{eff}}(s) |\psi_{\text{excited}}(r)|^2 \, d^3 r$$

Conceptually, this term arises as a positive contribution to the energy because the excited electron charge cloud overlaps the effective repulsive potential centered at the ground state atom.

$E_{\text{overlap}}(R)$ and $V_{\text{ion}}(R)$ are the largest terms in our He-He* potential; they represent the separate interaction of the excited electron and the core ion with a nearby
He\(^{(1\,1S)}\). A third term should be included to represent the long range electrostatic energy of our system. This is the van der Waals attraction, given by \(-C/R^6\).

Considerable uncertainty exists in the exact values of \(C\) for various states, particularly in those cases where it shows angular dependence. Calculations by Dalgarno\(^\text{15}\) indicate that for the interaction of He\(^{(1\,1S)}\) with He\(^{(2\,3S)}\), \(C = 29.1\) a.u. A method developed in Appendix A suggests that for He\(^{(1\,1S)}\)–He\(^{(2\,3P_m=0)}\), \(C = 50\left(1 + 2/5 P_2(\cos \theta)\right)\) a.u., where the excited atom is at the origin and \(\theta\) is the polar angle of the location of the ground state atom.

A question might be raised whether the inclusion of a van der Waals term is consistent with the use of \(V_{\text{ion}}\), which might be expected to include a long range polarization interaction \(-\alpha/2R^8\). Fortunately, a comparison of the asymptotic form of both \(V_{\text{ion}}\) curves with \(-\alpha/2R^8\) indicates that neither of them includes significant polarization interaction. This is to be expected: polarization is a second order effect and depends on all possible excited wave functions of the system. The variational wave functions used to calculate \(V_{\text{ion}}\) can include only a small number of excited states, and hence do not fully represent the polarization term. Consequently the use of the van der Waals interaction appears justified, and may be viewed as taking into account second order effects on the wave function.
An analytic form was chosen to represent $V_{\text{eff}}$:

$$V_{\text{eff}}(s) = -\frac{2}{s} e^{-as} + b e^{-s^2/2\sigma^2}$$

(II : 2)

Figure 3 shows the comparison between this form and the potential calculated by Kestner. The Gaussian represents the repulsive barrier of $V_{\text{eff}}$ well and happens to be a convenient form to work with; the screened Coulomb term is added to insure that the potential behaves in the physically expected manner as $s \to 0$. The parameters $a = 4.2$, $b = 0.43$, and $\sigma = 1.5$ give an accurate fit for small and intermediate values of $s$, but the asymptotic form is too large. Adjusting the parameters until the scattering length of $V_{\text{eff}}$ matched the known scattering length for electron-helium collisions gave a much improved asymptotic form but greatly distorted $V_{\text{eff}}$ for smaller values of $s$. Rather than introducing additional parameters or attempting to splice together two different forms, $V_{\text{eff}}$ was simply truncated at an appropriate value of $s$:

$$V_{\text{eff}}(s) = \begin{cases} 
-\frac{2}{s} e^{-as} + b e^{-s^2/2\sigma^2} & s < r_c \\
-\frac{2}{s} e^{-as} & s \geq r_c 
\end{cases}$$

(III : 3)

Since $V_{\text{eff}}$ is always involved in an integral expression, this truncation is not a drastic alteration. The final
Figure 3:

Kestner's $V_{\text{eff}}(s)$ compared with several possible analytic fits. The asymptotic form was chosen to reproduce the electron-helium scattering length; it is much too large for $R \approx 3 a_o$.

Later we will use three forms of $V_{\text{eff}}$:

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>$\sigma$</th>
<th>cutoff</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>......</td>
<td>4.2</td>
<td>0.43</td>
<td>1.5</td>
</tr>
<tr>
<td>(2)</td>
<td>------</td>
<td>3.0</td>
<td>0.544</td>
<td>1.31</td>
</tr>
<tr>
<td>(3)</td>
<td>------</td>
<td>3.0</td>
<td>0.544</td>
<td>1.31</td>
</tr>
</tbody>
</table>
\[ V_{\text{eff}}(s) : \]

- Kestner
- analytic fits
- asymptotic form

\( s \) (\( a_0 \))

\( (\text{eV}) \)
He-He* potentials were in fact improved by a reasonable choice of cutoff, and were insensitive to the exact values of the other parameters.

Two different methods were employed to calculate the excited electron wave functions for the atomic states involved in observed transitions in the liquid. The best results were obtained for states $2^3S$, $2^3P$, and $2^1P$ following the procedure of Morse, Young, and Haurwitz.\textsuperscript{17} Trial single particle excited wave functions were assumed as follows:

\begin{align*}
\text{2S} & : \quad \psi(\vec{r}) = \sqrt{\frac{Z_2^5}{32 \pi^{3/2} N}} \left[ r e^{-\frac{Z_2 r}{2}} - \frac{6A}{Z_2} e^{-\frac{Z_1 r}{2}} \right] \\
\text{2P} (m=0) & : \quad \psi(\vec{r}) = \sqrt{\frac{Z_2^5}{32 \pi}} \quad r e^{-\frac{Z_2 r}{2}} \cos \Theta \\
\text{2P} (m=\pm1) & : \quad \psi(\vec{r}) = \sqrt{\frac{Z_2^5}{64 \pi}} \quad r e^{-\frac{Z_2 r}{2}} \cos \Theta e^{\pm i \psi}
\end{align*}

In the first of these, $N$ is a normalization constant, and $A$ is chosen to make the function orthogonal to the $1s$ ground state. Appropriate symmetric or antisymmetric combinations were made with the ground state (hydrogenic) electron wave function, and the resulting two particle wave functions used to minimize

\begin{equation}
\langle E \rangle = \frac{\langle \psi_{\text{total}} | H | \psi_{\text{total}} \rangle}{\langle \psi_{\text{total}} | \psi_{\text{total}} \rangle} \tag{\text{II}:5}
\end{equation}
The excited p wave functions are characterized by a single parameter, the effective charge. For the singlet case, the result is \( Z = 0.97 \), for the triplet \( Z = 1.09 \). Two parameters define the \( 2^3S \) function; these are \( Z_1 = 3.14 \) and \( Z_2 = 1.22 \). Clearly the asymptotic form of this function, the part which determines \( E_{\text{overlap}} \) in the range of interest, is dominated by the term \( r \exp(-1.22r/2) \). This function may therefore be considered to be essentially hydrogenic with effective charge \( Z = 1.22 \). For completeness, it should now be noted that in each case above, the effective charge of the ground state \( 1s \) function is allowed to vary, but always remains very nearly 2.00. This implies that the approximation of separating the electron orbital and core ion is quite reasonable.

The variational procedure outlined above will not work for the \( 3^1S \) or \( 3^3S \) states because the trial wave functions cannot be made orthogonal to all lower lying states. (The antisymmetric \( 2^3S \) function is clearly orthogonal to the symmetric ground state; the \( p \) state functions are orthogonal to \( s \) states because of the angular factor). In these cases pure hydrogenic \( 3s \) wave
functions were used, and the effective charge found by assuming that the energy difference between the \( \text{He}^+ \) ion and the excited \( (n = 3) \) state could be expressed by the Rydberg formula \( E_n = \frac{1}{2} \frac{Z^2}{n^2} \). This procedure gives \( Z = 1.11 \) for \( 3^3\text{S} \) and \( Z = 1.05 \) for \( 3^1\text{S} \). An estimate of the accuracy of this procedure can be made by applying it to the same states for which the more reliable variational calculation was made. This was done. For \( 2^3\text{S} \), \( Z = 1.18 \); for \( 2^3\text{P} \), \( Z = 1.03 \), and for \( 2^1\text{P} \), \( Z = 1.00 \). Such good agreement suggests that the approximate \( 3^1, 3^3\text{S} \) wave functions probably are quite reasonable, at least asymptotically. One would even expect the results for \( n = 3 \) to be more reliable than for \( n = 2 \), since the shielding of the nucleus by the inner electron is more complete.

Having now considered both the unperturbed wave functions and the perturbing potential, we must evaluate \( E_{\text{overlap}} \), given by

\[
E_{\text{overlap}}(R) = \int V_{\text{eff}}(s) \left| \Psi_{\text{excited}}(r) \right|^2 \, d^3r
\]

\( V_{\text{eff}} \) must be expressed in the same coordinates as \( \Psi_{\text{excited}} \); because of the cylindrical symmetry, \( s = (R^2 + r^2 - 2Rr \cos \theta)^{1/2} \) and it is possible to write

\[
V_{\text{eff}}(s) = V_{\text{eff}}(R, r, \theta) = \sum_{\lambda \neq 0} \sum_{\lambda} v_\lambda (R, r) P_\lambda (\cos \theta)
\]
where

$$V_\lambda (R, r) = \left( \frac{2^{\lambda+1}}{2} \right) \int_0^\pi V_{\text{eff}} (R, r, \theta) P_\lambda (\cos \theta) \sin \theta \, d\theta$$

(II : 7)

Since \( \Psi_{\text{excited}} (r) = \Psi_{\text{excited}} (r, \theta, \phi) \) can be written as the product of a radial function \( g(r) \) (which depends on the state) and a spherical harmonic (which for the states considered here is \( Y_{00} \), \( Y_{10} \), or \( Y_{l+1} \)), \( E_{\text{overlap}} \) takes on the convenient form

$$E_{\text{overlap}} (R) = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 dr$$

\( X \sum_{\lambda=0}^\infty \frac{q_{\text{excited}} (r)^2 \left| Y_{\lambda m} (\theta, \phi) \right|^2}{\sum_{\lambda=0}^\infty} \frac{V_\lambda (R, r) P_\lambda (\cos \theta)}{}$$

$$= \sum_{\lambda=0}^\infty \left\{ \left[ \int_0^{2\pi} \int_0^\pi \sin \theta d\theta \left| Y_{\lambda m} (\theta, \phi) \right|^2 P_\lambda (\cos \theta) \right] \right\}$$

The term in square brackets is zero for most values of \( \lambda \).

In an excited s state, only \( \lambda = 0 \) contributes; in a p state there is also a contribution from the \( \lambda = 2 \) term. Writing down the results explicitly, we have
\[ 2^3S : \quad E_{\text{overlap}}(R) = \int_0^\infty |g_{2^3S}(r)|^2 v_o(R,r) r^2 dr \]

\[ = F_{2^3S}(R) \]

\[ 2^3P_{m=0} : \quad E_{\text{overlap}}(R) = \int_0^\infty |g_{2^3P}(r)|^2 v_o(R,r) r^2 dr \]

\[ + \frac{2}{5} \int_0^\infty |g_{2^3P}(r)|^2 v_2(R,r) r^2 dr \]

\[ = F_{2^3P}(R) + G_{2^3P}(R) \]

\[ 2^3P_{m=\pm 1} : \quad E_{\text{overlap}}(R) = \int_0^\infty |g_{2^3P}(r)|^2 v_o(R,r) r^2 dr \]

\[ - \frac{1}{5} \int_0^\infty |g_{2^3P}(r)|^2 v_2(R,r) r^2 dr \]

\[ = F_{2^3P}(R) - \frac{1}{5} G_{2^3P}(R) \]

\[ 3^1S : \quad E_{\text{overlap}}(R) = \int_0^\infty |g_{3^1S}(r)|^2 v_o(R,r) r^2 dr \]

\[ = F_{3^1S}(R) \]

(II : 9)
In all of these integrals, \( V_0(R,r) \) and \( V_2(R,r) \) are evaluated analytically as shown in detail in Appendix B. Here we present the exact results for the case of no cutoff in \( V_{	ext{eff}} \); the general behavior of these functions can be inferred from the graphs in Figure 4.

\[
V_0 (R,r) = -\frac{2 \sinh a r_c e^{-ar_c}}{\alpha R} \quad (II:10)
\]
\[
+ \frac{b\sigma^2}{Rr} e^{-\frac{R^2 + r^2}{2\sigma^2}} \sinh \frac{Rr}{\sigma^2}
\]

\[
V_2 (R,r) = 10 \left[ - \left( 1 + \frac{3}{(ar_c)^2} \right) \frac{\sinh a r_c}{a r_c} + \frac{3 \cosh a r_c}{(ar_c)^2} \right]
\]
\[
\times \left[ \left( 1 + \frac{3}{ar_c} + \frac{3}{(ar_c)^2} \right) \frac{e^{-ar_c}}{r} \right]
\]
\[
+ 15b e^{-\frac{R^2 + r^2}{2\sigma^2}}
\]
\[
\times \left[ \left( \frac{\sigma^2}{2Rr} + \frac{\sigma^6}{R^3 r^3} \right) \sinh \frac{Rr}{\sigma^2} - \frac{\sigma^4}{R^2 r^2} \cosh \frac{Rr}{\sigma^2} \right]
\]
\[
- \frac{5}{2} \frac{b\sigma^2}{Rr} e^{-\frac{R^2 + r^2}{2\sigma^2}} \sinh \frac{Rr}{\sigma^2}
\]
$V_{\text{eff}} (s) = V_{\text{eff}} (R, r, \Theta)$

$$= \sum_{\lambda=0}^{\infty} V_{\lambda} (R, r) P_{\lambda} (\cos \Theta)$$

- $r \ (\text{arbitrary units})$
- $R = 5$
- $R = 10$
- $R = 15$

$V_2$, $V_0$
The functions $F(R)$ and $G(R)$ are evaluated numerically, and the complete energy of interaction is given by

$$E_{\text{total}}(R) = E_{\text{overlap}}(R) + V_{\text{ion}}(R) - \frac{C}{R^6}$$

(II : II)

It is significant that $E_{\text{total}}(R)$ depends implicitly on the parameters of the excited electron wave function through $E_{\text{overlap}}(R)$. Some calculations were done on the $2^3 P$ state in which these parameters were allowed to vary. Increasing the effective charge tends to pull the electron probability distribution in, and hence decreases $E_{\text{overlap}}$. This decrease, however, is balanced by an increase in

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

which must be added in, and the result is that no significant improvement in the interaction potential is gained because $Z$ changes so little for values of $R$ in the range of interest. Therefore all the calculations for the many body problem were performed using completely unperturbed wave functions.

To compare the results presented here with more accurate two body potentials, the effect of molecular symmetry must be included. Precise calculations of molecular potentials depend on whether the total electronic wave function has gerade or ungerade symmetry. Only in the limit of large separation is it rigorously correct to speak of one atom as in some excited state and the other
in the ground state. For smaller separations the excitation must be considered molecular, not atomic, and hence two distinct potential curves result. However, this effect is small for separations of about 6 \( a_0 \) or greater, and the difference between the two possible potential curves is very small. In particular, Evans and Lane \(^{18}\) indicate that for the molecular states \( c^3\Sigma_g^+ \) and \( a^3\Sigma_u^+ \) (which correspond to our potential for \( \text{He}(2^3\text{S})-\text{He}(1^1\text{S}) \)), the two possible curves \( V_+ \) and \( V_- \) are separated by a "difference potential" given for \( R \geq 6 \cdot a_0 \) by

\[
\Delta V(R) = V_+ - V_- = 1.54 \, e^{-1.43R} + 2.93 \, e^{-1.62R} \, \text{a.u.}
\]

The simplest and most reasonable assumption would be that the curve calculated here for \( \text{He}(2^3\text{S})-\text{He}(1^1\text{S}) \) lies approximately halfway between \( V_+ \) and \( V_- \). If this is the case, we should subtract \( \frac{1}{2} \Delta V(R) \) from our curve, and then compare it with an accurate \( V_- \). Fitzsimmons et al. \(^{19}\) suggest upper and lower limits for \( V_- \) on the basis of collision cross sections determined experimentally from diffusion data, and Matsen \(^{20}\) and Buckingham and Dalgarno \(^{21}\) have also calculated \( V_- \). Figure 5 shows that the curve calculated here is in good agreement with these other results.

The procedure discussed in this section for calculating He-He* interactions is not only fairly accurate, but
Figure 5:
Comparison of the present calculation of $V_-$ with other published results. The dashed curve shown is for $V_{\text{eff}}$ number (2) (figure 3). Using instead $V_{\text{eff}}$ number (3) would reduce $V_-$ by less than 5%. The shaded area gives the limits suggested by Walters et al. on the basis of diffusion data.
is also amenable to an appealing physical interpretation. The cases of $\tilde{\Sigma}_u^+$ and $\tilde{\Pi}_u$ are especially illustrative. The former, in the separated atom limit, corresponds to an excited $2^3P$ state at the origin with the electron cloud oriented along the z axis. The ground state atom, located on the z axis, is the center of the repulsive potential felt by the excited p electron. As the ground state atom is brought closer to the excited atom, the repulsive electron-He$(1^1S)$ competes with the attractive, long-range van der Waals force and with the shorter range $V_{\text{ion}}^2$ (which is taken to be the attractive He$_2^+$ $(2\Sigma_u^+)$ curve). Except at very large separations, the van der Waals term is smaller in magnitude than the repulsive interaction. Because the p electron has the highest probability density along the z axis, it begins to overlap the ground state atom at separations so large that the attractive effect of $V_{\text{ion}}$ is still very small. For a range of R around 5 - 8 $a_0$, therefore, the repulsive electron-He$(1^1S)$ term dominates the interaction, and gives the barrier characteristic of He-He* potentials. As R decreases still more, however, the attraction between the He$(1^1S)$ and the core ion becomes larger in magnitude, and accounts for the attractive region of the interatomic potential.

Now consider the interaction of a normal helium atom with a $2\cdot 3^3P_{m=\pm 1}$ state (the $3\Sigma_u^-$ molecular potential). In this state, the excited electron distribution is
concentrated around the equator (xy plane). Hence at long range the potential is predominantly $V_{\text{ion}}$, because the electron does not "see" the ground state atom until the interatomic separation is quite small. This accounts for the lack of a repulsive barrier in the $^3\Sigma_u$ states; the interaction is dominated at all separations by the attractive effect of $V_{\text{ion}}$.

Completely repulsive helium molecular potentials can also be easily understood with the present model. It is only necessary to note that $V_{\text{ion}}$ could just as well be the repulsive $^2\Sigma_g^+$ curve as the attractive $^2\Sigma_u^+$. Then the extreme long range interaction is van der Waals as before, but at intermediate and short range, the repulsive electron-$\text{He}(l\,^1S)$ interaction is reinforced by the repulsive $\text{He}^+-\text{He}(l\,^1S)$ potential.

All of these cases are illustrated graphically in Figures 6-9. They show that the presence or absence of a repulsive barrier at intermediate separations results primarily from the relative size of easily understood repulsive and attractive contributions to the energy. The value of the model here discussed is therefore two-fold: it explains the characteristic features of He-He* two body potentials in an intuitively satisfying manner, and, because of its simplicity, can be easily extended to the liquid many body problem.
Figure 6:
The He($^2\text{S}$) potential represented as the sum of several terms. The van der Waals contribution is too small to be shown clearly on this scale. The final graph shows that the present calculation lies between $V_+$ and $V_-$ for $R \geq 6 a_0$, but becomes less reliable for smaller $R$. 
\[ He^{\kappa} = 2 \ ^3S \]

\[ \text{Diagram: } \]

\[ V_{\text{He}^\kappa - \text{He}} \]
\[ V_{\text{He}^\kappa - \text{He}} \]
\[ (\text{eV}) \]

\[ 10 \]

\[ R (a_0) \]

\[ R (a_0) \]
Figure 7:
A $3\Sigma_u^+$ molecular potential is shown to result from bringing a He ($2 \, ^3P_{m=0}$) from infinity with the electron cloud oriented along the inter-nuclear axis. There is a hump in this case because of the electron-helium repulsion. The van der Waals contribution is too small to be shown clearly.
\[ \text{He}^* = 2^3 P_{n=0} \]

\[ \text{He}^* \quad \text{He} \]

\[ V_{\text{He}_2^+} \]

\[ (\text{eV}) \]

\[ V_{\text{e-He}} \]

\[ \text{R} (\text{a}_0) \]

\[ V_{\text{He}^*-\text{He}} \]

\[ \text{R} (\text{a}_0) \]
Figure 8:
A $^3\Sigma_u^+$ molecular potential is shown to result from bringing a He($^3P_{m=\pm 1}$) from infinity with the electron probability density perpendicular to the internuclear axis. No hump results because the electron-helium repulsion is much smaller than in the previous case. Again, the van der Waals interaction is not shown.
\[ \text{He}^* = 2 \, ^3P_{m = \pm 1} \]

\[ V_{\text{He}_2^+} \]

\[ V_{e \cdot \text{He}} \]

\[ V_{\text{He}^* \cdot \text{He}} \]
Figure 9:

A purely repulsive He-He* potential results by setting $V_{\text{ion}} = a \sum q^*$. 
\[ \text{He}^* = 2^3 S \]

\[ V_{\text{He}_2^+} \]

\( (eV) \)

\[ V_{e-\text{He}} \]

\[ V_{\text{He}^*-\text{He}} \]

\( R (\alpha_o) \)
This chapter will develop the formalism necessary to calculate the total energy of a system composed of an excited helium atom located inside an arbitrary cavity in liquid helium. We can write

\[
E_{\text{system}} = E_{\text{atom}}^0 + \int \Delta E(R, \Omega) \rho(R, \Omega) \, dV + E_{\text{bubble}}
\]

where \( E_{\text{atom}}^0 \) is the energy of the unperturbed excited atom; \( \rho(R, \Omega) \) is the fluid density at distance \( R \) and angular coordinate \( \Omega = \theta, \phi \); \( \Delta E(R, \Omega) \) gives the perturbation of the central excited atom due to a He\((1\, ^1S)\) at \((R, \Omega)\), and \( E_{\text{bubble}} \) is the energy of the fluid configuration described by \( \rho \). The integral term in this expression shows explicitly that we are viewing the perturbation of the excited atom by the distribution of He\((1\, ^1S)\) atoms as simply additive. In the preceding chapter we derived \( \Delta E \) for the special case \( \Theta = 0 \) and found

\[
\Delta E(R, \Theta = 0) = E_{\text{overlap}}(R) + V_{\text{ion}}(R) - \frac{c}{R^6}
\]

The first section of this chapter will generalize this result to arbitrary \( \Theta \). The second section will discuss the energy required to distort the fluid into a bubble configuration, and the specific variational form of the bubble shape will be presented in the third section.
A. Derivation of $\Delta E(R, \Omega)$

Recalling the definition of $E_{\text{overlap}}$, we may write

\begin{equation}
\Delta E(R, \Omega) = \langle \psi_{\text{excited}} | V_{\text{eff}} | \psi_{\text{excited}} \rangle + V_{\text{ion}}(R) - \frac{C(\Theta)}{R^6} \tag{III:3}
\end{equation}

Since $V_{\text{ion}}$ is the interaction of two spherical bodies, the core He$^+$ ion and the He(1 $^1S$), it does not depend on $\Theta$. If $\psi_{\text{excited}}$ is an s state, the van der Waals term will not depend on $\Theta$, but for a p state it will. In the latter case Appendix A shows that the expected $\Theta$ dependence is

$$C(\Theta) \propto 1 + \frac{2}{5} P_2(\cos \Theta)$$

It should be clear that for $\Theta \neq 0$, Legendre polynomials are not sufficient to express $V_{\text{eff}}$ in terms of $r$, $\Theta$, and $\varphi$. However, the full expansion in spherical harmonics is easily obtained by noting

\begin{equation}
V_{\text{eff}} = \sum_{\lambda=0}^{\infty} V_{\lambda}(R, r) P_{\lambda}(\cos \gamma) \tag{III:4}
\end{equation}

$\gamma$ is the angle between $(R, \Omega)$ and $(r, \Omega)$ as shown in Figure 10, and the $V_{\lambda}$ are exactly the same as before. Then $P_{\lambda}(\cos \gamma)$ can be written using its known expansion in spherical harmonics:
Figure 10:
Interaction of a He* with a He(l \textsuperscript{1}S) at an arbitrary location (R, θ, φ). $V_{\text{eff}}(s)$ must be expressed in spherical harmonics.
\[ V_{\text{eff}} = \sum_{\lambda=0}^{\infty} V_\lambda (R,r) \frac{4\pi}{2\lambda+1} \sum_{\lambda=0}^{\infty} Y^*_{\lambda\beta} (\Omega) Y_{\lambda\beta} (\Omega) \quad (\text{III}: 5) \]

Substituting this into (III:3), and assuming \( \psi_{\text{excited}} = g_{\text{excited}}(r) Y_{1m}(\Omega) \), we find

\[ \Delta E (R,\Omega) = \int_{4\pi} d\Omega \int_{0}^{\infty} r^2 dr \left| g_{\text{excited}} (r) Y_{1m} (\Omega) \right|^2 \]
\[ \times \left[ \sum_{\lambda=0}^{\infty} V_\lambda (R,r) \frac{4\pi}{2\lambda+1} \sum_{\lambda=0}^{\infty} Y^*_{\lambda\beta} (\Omega) Y_{\lambda\beta} (\Omega) \right] \]
\[ + V_{\text{ion}} (R) - \frac{C(\Theta)}{R^6} \]

\( Y_{\lambda\beta} (\Omega) \) does not depend on the coordinates over which the integration is performed. Bringing it outside the integral and regrouping terms then yields

\[ \Delta E (R,\Omega) = \sum_{\lambda=0}^{\infty} \frac{4\pi}{2\lambda+1} Y^*_{\lambda\beta} (\Omega) \]
\[ \times \int_{4\pi} d\Omega \left| Y_{1m} (\Omega) \right|^2 Y_{\lambda\beta} (\Omega) \int_{0}^{\infty} r^2 dr \left| g_{\text{excited}} (r) \right|^2 V_\lambda (R,r) \]
\[ + V_{\text{ion}} (R) - \frac{C(\Theta)}{R^6} \]

This sum is easily evaluated for the excited states of interest. Not surprisingly, for an s state \((l = m = 0)\), only the term \( \lambda = \beta = 0 \) contributes, and \( \Delta E \), as required by symmetry, does not depend on \( \Theta \) :
\[ \Delta E_{2^3S} (R, \Omega) = F_{2^3S} (R) + V_{1on} (R) - \frac{C_{2^3S}}{R^6} \quad (\text{III}: 8) \]

\[ \Delta E_{3^1S} (R, \Omega) = F_{3^1S} (R) + V_{1on} (R) - \frac{C_{3^1S}}{R^6} \]

The functions \( F(R) \) are exactly the same as those derived in the previous chapter.

If \( \psi_{\text{excited}} \) is a \( p \) state, the result obviously will depend on orientation. Suppose the electron cloud is oriented along the \( z \) axis \((l = 2, m = 0)\). Since the only \( \varphi \) dependence of \( \Delta E \) is \( \int_{0}^{2\pi} e^{i \varphi} d\varphi \), we must have \( q = 0 \).

Then orthogonality relations enable us to eliminate all terms except \( \lambda = 0, q = 0 \) and \( \lambda = 2, q = 0 \) from the sum, leaving

\[ \Delta E_{2^3p} (R, \Omega) = \quad (\text{III}: 9) \]

\[ 4\pi Y_{00}^* (\Omega) \int_{4\pi} \cos \vartheta d\vartheta \left| Y_{10} \right|^2 Y_{00} \int_{0}^{\infty} r^2 dr \left| g_{2^3p} (r) \right|^2 V_0 (R, r) \]

\[ + \frac{4\pi}{5} Y_{20}^* (\Omega) \int_{4\pi} \cos \vartheta d\vartheta \left| Y_{10} \right|^2 Y_{20} \int_{0}^{\infty} r^2 dr \left| g_{2^3p} (r) \right|^2 V_2 (R, r) \]

\[ + V_{1on} (R) - \frac{C (\Theta)}{R^6} \]

Doing the integrals and using the relation between \( Y_{20} (\Omega) \) and \( P_2 (\cos \Theta) \), we can write
\[ \Delta E_{2sp} (R, \Omega) = F_{2sp} (R) + P_2 (\cos \Theta) G_{2sp} (R) \]
\[ + V_{10h} (R) - \frac{C_{2sp} (\Theta)}{R^6} \]  
(III:10)

This is the desired result, which may be substituted into equation (III:1).

B. The Bubble Energy

The classical definition of \( E_{\text{bubble}} \) discussed in the Introduction had only two terms, the work against surface tension and pressure volume work. Hiroike et al.\(^4\) have shown that these static terms arise, after many approximations, from a quantum mechanical approach to the fluid, but that another term should also be included, which can be interpreted as a kinetic energy contribution.

Let the fluid consist of \( N \) bosons of mass \( M \) without internal structure. If they interact pairwise according to a potential \( u(r) \) depending only on relative separation, then an appropriate Hamiltonian is

\[ H = -\frac{1}{2M} \sum_{\omega}^{N} \nabla_\omega^2 + \sum_{j<k} u (r_{jk}) \]  
(III:11)

This can be solved approximately for the ground state by assuming a fully symmetric trial wave function

\[ \psi (\vec{r}_i, \ldots, \vec{r}_N) = e^{\frac{i}{2} \sum_{j<k} \omega (r_{jk})} \]  
(III:2)
\( \omega(r) \) has been found fairly accurately by variational calculations;\(^{22}\) however, its general behavior is easily inferred. It will be small for large values of its argument, and must approach \(-\infty\) as \( r \to 0 \). This insures that the probability that two atoms will be very close to each other will be small.

In the present situation, the fluid is not in the ground state. Hiroike therefore adds another term to the trial wave function:

\[
\psi(\vec{r}_1, \ldots, \vec{r}_N) = e^{\frac{i}{\hbar} \left[ \sum_{j<k} \omega(\vec{r}_{jk}) + \sum_{m=1}^{N} \chi(\vec{r}_m) \right]} \tag{III : 13}
\]

For a typical bubble configuration, \( \chi(r) \) will be large and negative for \( r \) less than the bubble radius. Thus the probability that an atom finds itself inside the bubble is small. Hiroike assumes that \( \omega(r) \) is the same as in the liquid ground state, and that \( \chi(r) \) bears a simple relation to the density. Then he defines

\[
E_{\text{bubble}} = \langle E \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \tag{III : 14}
\]

To calculate \( \langle E \rangle \) we must write it in terms of quantities that can be measured or are known. It is helpful to note that the one and two particle density functions are given by
\[ \rho(\vec{r}) = \frac{N \int |\psi(\vec{r}, \vec{r}_1, \ldots, \vec{r}_N)|^2 d^3 r_1 \ldots d^3 r_N}{\int |\psi(\vec{r}, \vec{r}_1, \ldots, \vec{r}_N)|^2 d^3 r_1 \ldots d^3 r_N} \quad (III:15) \]

\[ \rho^{(a)}(\vec{r}, \vec{r}') = \frac{N(N-1) \int |\psi(\vec{r}, \vec{r}', \vec{r}_3, \ldots, \vec{r}_N)|^2 d^3 r_3 \ldots d^3 r_N}{\int |\psi(\vec{r}, \vec{r}_3, \ldots, \vec{r}_N)|^2 d^3 r_3 \ldots d^3 r_N} \]

Using these, Hiroike writes

\[ \langle KE \rangle = \frac{1}{\delta M} \int \vec{v} \cdot \nabla \rho^{(a)}(\vec{r}_1, \vec{r}_2) d^3 r_1 d^3 r_2 \]

\[ + \frac{1}{BM} \int \nabla \cdot \vec{f}(\vec{r}_1) \cdot \nabla \rho^{(a)}(\vec{r}) d^3 r_1 \]

\[ \langle PE \rangle = \frac{1}{2} \int \rho(\vec{r}_1, \vec{r}_2) u(\vec{r}_{12}) d^3 r_1 d^3 r_2 \quad (III:16) \]

In order to find the energy of a bubble of radius \( R \), Hiroike assumes a density function \( \rho(r) \) with the following properties

\[ \rho(r) = 0 \quad r \leq R \]

\[ \rho(r) \approx \rho_0 \quad r \geq R + \delta R \]

\[ \delta R \ll R \]

\( \delta R \) is the width of the region where the transition from zero density to equilibrium density takes place. With such a density, the potential energy plus the first term of the kinetic energy are shown to be approximately

\[ \frac{4}{3} \pi R^3 \rho + 4 \pi R^2 \left[ \text{complicated function of } R, \rho, \omega, u \right] \quad (III:17) \]
The crucial point is that the quantity in brackets happens to be fairly constant for a wide variety of bubble sizes. This enables Hiroike to consider that quantity to be an effective surface tension, and he computes it to be 0.52 ergs/cm. This \( \gamma \) is in reasonably good agreement with an experimental value\(^{23} \) of 0.36 ergs/cm.\(^2 \) \((1^\circ K)\) and another theoretical prediction\(^{24} \) of 0.58 ergs/cm.\(^2 \)

We are still left with the additional term

\[
\frac{1}{2M} \int \vec{V}_i \chi(r_i) \cdot \vec{V}_i \rho(r_i) d^3 r_i.
\]

\( \rho \) has already been specified; the assumption is now made that

\[
\rho(r) = e^{\chi(r)} = |e^{\frac{i}{\hbar} \chi(r)}|^2 = |\psi(r)|^2
\]

\[
\vec{V}_\rho = (\vec{\nabla} \chi) \rho
\]

This is equivalent to neglecting all correlation between particles and assuming that each moves independently. In this case the extra term is

\[
\frac{1}{2M} \int \frac{(\vec{V}_\rho)^2}{\rho} d^3 r
\]

and is easily evaluated (numerically) for any \( \rho \). Some insight into the meaning of this term may be gained by noting that it is the kinetic energy of a particle described by the wave function \( \psi(r) = e^{\frac{i}{\hbar} \chi(r)} \).
\[ \langle KE \rangle = \frac{1}{2M} \int e^{\frac{i}{\hbar} \chi(r)} \frac{i}{\hbar} \nabla \cdot \frac{i}{\hbar} \nabla e^{\frac{i}{\hbar} \chi(r)} \, d^3 r \]  

But by the hermiticity of the momentum operator,

\[ \langle KE \rangle = \frac{1}{2M} \int \frac{i}{\hbar} \nabla e^{\frac{i}{\hbar} \chi(r)} \cdot \frac{i}{\hbar} \nabla e^{\frac{i}{\hbar} \chi(r)} \, d^3 r \]

\[ = \frac{1}{8M} \int \nabla X e^{\frac{i}{\hbar} \chi(r)} \cdot \nabla X e^{\frac{i}{\hbar} \chi(r)} \, d^3 r \]  

(III : 19)

Using \( \nabla X = \frac{\nabla \rho}{\rho} \), this is clearly

\[ \langle KE \rangle = \frac{1}{8M} \int \frac{(\nabla \rho)^2}{\rho} \, d^3 r \]  

(III : 20)

In summary, Hiroike shows that the bubble energy can be represented by

\[ E_{\text{bubble}} = E_{\text{pv}} + E_{\text{surf}} + \frac{1}{8M} \int \frac{(\nabla \rho)^2}{\rho} \, d^3 r \]  

(III : 21)

We have shown that the added term is basically a single particle term; all the correlation effects are assumed to be accounted for in the evaluation of \( E_{\text{pv}} \) and \( E_{\text{surf}} \). The behavior of the extra term is evident: it diverges for the case of an infinitely sharp bubble. Physically, this is reasonable. If a sharp bubble is formed, the natural tendency of the fluid configuration would be to relax. Mathematically, the infinite density gradient corresponds to a discontinuity in the wave function.
C. The Bubble Shape

A two parameter variational function was chosen to represent a spherical bubble:

\[
\rho(R) = \begin{cases} 
\rho_0 & R < R_0 \\
\rho_0 \left[1 - (1 + \alpha(R-R_0))e^{-\alpha(R-R_0)}\right] & R \geq R_0
\end{cases}
\]

This is in fact the same function used by Hiroike and referred to in the last section. The approximate length of the transition region, in which the density is gradually increasing is \(4/\alpha\). (At \(R = R_0 + 4/\alpha\), \(\rho = 0.915 \rho_0\)). One of the conditions for the validity of equation (III:17) is that the transition region be narrow compared to the bubble radius; if this is true there is no ambiguity in defining a bubble radius. The system energy, however, proves typically to be a minimum for \(\alpha = 1 \, a_0^{-1}\). For a \(2^3S\) state at the center of the bubble, \(R_0 \approx 9 \, a_0\). The density therefore increases from zero at \(9 \, a_0\) to about \(\rho_0\) at \(13 \, a_0\); clearly \(E_{pv}\) and \(E_{surf}\) will depend on which radius is used to compute them.

The choice was made to define an effective sharp bubble of radius \(R'_0\) such that

\[
4\pi \int_0^{R'_0} \rho(R) R^2 dR = \int_0^\infty \left[\rho_0 - \rho(R)\right] R^2 dR
\]

(III:23)
This sharp bubble could be transformed into the bubble described by $\rho(R)$ by a continuous flow of mass inward through the surface $R = R'_o$. In short, the effective bubble radius is defined as the "center of mass" of the transition region. Carrying out the integral in (III:23) and solving for $R'_o$ gives

$$\left( R'_o \right)^3 = \frac{1}{\alpha^3} \left[ 24 + 18 \alpha R_o + 6 (\alpha R_o)^2 + (\alpha R_o)^3 \right]$$

Note that as $\alpha \to \infty$, the bubble becomes increasingly sharp, and $R'_o \to R_o$, as it must.

The only remaining task is to compute the kinetic energy term, denoted now by $E_{\text{kin}}$. Since

$$\nabla \rho = \frac{\partial \rho}{\partial R} \hat{R} = \alpha^2 \rho_o (R-R_o) e^{-\alpha(R-R_o)} \hat{R} \quad \text{for } R > R_o$$

we have

$$E_{\text{kin}} = \frac{4 \pi}{8 M} \int_{R_o}^{\infty} \frac{\alpha^4 \rho_o^2 (R-R_o)^2 e^{-\alpha(R-R_o)}}{\rho_o \left[ 1 - (1 + \alpha(R-R_o)) e^{-\alpha(R-R_o)} \right]} \, dR$$

$$= \frac{4 \pi \alpha \rho_o}{8 M} \int_0^{\infty} \frac{y^2 e^{-y} \left( \frac{y}{\lambda} + R_o \right)^2}{1 - (1+y) e^{-y}} \, dy$$

$$= \frac{\pi \alpha \rho_o}{2 M} \left[ \frac{1}{\alpha^2} \int_0^{\infty} \frac{y^4 e^{-y} \, dy}{1 - (1+y) e^{-y}} + \frac{2 R}{\alpha} \int_0^{\infty} \frac{y^3 e^{-y} \, dy}{1 - (1+y) e^{-y}} + R_o^2 \int_0^{\infty} \frac{y^2 e^{-y} \, dy}{1 - (1+y) e^{-y}} \right]$$

$$= \frac{1}{\alpha} \left[ A + B \alpha R_o + C (\alpha R_o)^2 \right]$$
The integrals were done numerically using the constants \( \rho_o = 0.0032 \text{ gm./cm.}^3 \) and \( M = 6.7 \times 10^{-24} \text{ gm.} \). The result is \( A = 2.68 \times 10^{-5}, B = 3.90 \times 10^{-5}, C = 2.68 \times 10^{-5} \).

The complete energy of a spherical bubble surrounding an excited s state can now be written:

\[
E_{\text{system}} = E_{\text{atom}}^0 + 4\pi \int_{\rho_o}^{\infty} \rho(R) A E(R) R^2 dR + E_{\text{bubble}}
\]

\[
E_{\text{bubble}} = E_{p\nu} + E_{\text{surf}} + E_{\text{kin}}
\]

\[
= \frac{1}{3} \frac{1}{\pi} \rho_o^3 \rho + \frac{4}{9} \pi \rho_o^2 \rho + \frac{1}{\alpha} \left[ A \rho_o + B \rho_o^3 + C (\rho_o)^4 \right]
\]

This expression for \( E_{\text{system}} \) was minimized as a function of \( \alpha \) and \( R_o \), and the results are given in the next chapter.

A more general bubble shape is expected if the excited atom is not spherically symmetric. We have argued that the bubble is formed by a repulsive interaction between He(1\(^1\)S) atoms and the excited electron orbital. Hence the variational function describing the fluid distribution around a p state should have the freedom to constrict at the equator, where the electron probability density is least. We assume that the cross section of such a nonspherical bubble is given by \( R(\Theta) = R_o (1 + \beta P_2 (\cos \Theta)). \) Then the complete density function is
\[ \rho(R, \Theta) = \begin{cases} 0 & R < R(\Theta) \\ \rho_0 \left[ 1 - (1 + \alpha (R - R(\Theta)) e^{-\alpha (R - R(\Theta))} \right] & R \geq R(\Theta) \end{cases} \]  

When \( \beta = 0 \), this reduces exactly to the spherically symmetric density function (III:22). For \( \beta \neq 0 \), the inner boundary of the transition region is \( R(\Theta) \), and successive equi-density contours are given by

\[ R'(\Theta) = R'_0 + R_0 \beta P_2(\cos \Theta). \]

As in the case of the round bubble, the transition region turns out to be so large that care must be taken to define an effective sharp bubble to use in computing \( E_{PV} \) and \( E_{surf} \). The boundary of this sharp bubble is taken to be the equidensity contour at the center of mass of the transition region. If this effective bubble has cross section \( R'_0 + R_0 \beta P_2(\cos \Theta) = R'_0 (1 + \beta' P_2(\cos \Theta)) \), then

\[ 2\pi \int_0^\pi \int_0^{\pi'} \rho_0(R, \Theta) R^2 dR \quad \text{(III:29)} \]

\[ = 2\pi \int_0^\pi \int_0^{\pi'} \int_0^{\pi'} \left[ \rho_0 - \rho(R, \Theta) \right] R^2 dR \]

The solution turns out not to be as simple as before:

\[ (R'_0)^3 = \left( \frac{1}{\alpha^3} \left[ 2^4 + 16 \alpha R_0 + 6 (\alpha R_0)^2 \left( 1 + \frac{1}{5} \beta^2 \right) + (\alpha R_0)^3 \right] - \frac{3}{5} \rho_0 R_0^2 \rho (R'_0 - R_0) \]
R_o' is found by iteration using the fact that the first term on the right hand side of the equation is much larger than the second.

Care must be taken to distinguish between R_o and R_o', and β and β'. The inner bubble radius, where the density first begins to increase from zero, is given by R(®) = R_o(1 + β P_2). The cross section of the effective sharp bubble, used to compute E_{pv} and E_{surf}', is R'(®) = R_o'(1 + β' P_2), where R_o' is determined from equation (III:30) and β' = R_o β / R_o'. Given this sharp, nonspherical bubble, the question arises of exactly how to compute the work required to form it. The pressure volume term is straightforward, just one atmosphere times the volume of the nonspherical cavity. But it is not clear how to express the surface energy of a nonspherical bubble, since the local energy could be expected to depend on curvature. We assume that this is not true, however, and let E_{surf} be the same constant surface tension times the surface area of the bubble. For the surface area and volume of the deformed bubble, we use the results of Rayleigh^{27} (good to first order in β^2):

\[ E_{pv} = \frac{4}{3} \pi R_o' \beta^2 \left( 1 + \frac{3}{5} \beta^2 \right) \quad (III : 3) \]

\[ E_{surf} = 4 \pi R_o' \gamma \left( 1 + \frac{4}{5} \beta^2 \right) \]
The evaluation of $E_{\text{kin}}$ is also more difficult for the generalized density function. The analysis is carried out in Appendix C, and gives

$$E_{\text{kin}} = \frac{1}{\alpha} \left[ A + B \alpha R_o + C (\alpha R_o)^2 \left( 1 + \frac{1}{5} \beta^2 \right) \right] \quad (\text{III} : 32)$$

Now we can summarize the results of this section for the most general bubble shape:

$$E_{\text{system}} = E_{\text{atom}}^0 + 2 \pi \int_0^{\pi} \int_0^1 \int_0^{\infty} \rho(R, \theta) \Delta E(R, \theta) R^2 dR + E_{\text{bubble}} \quad (\text{III} : 33)$$

$$E_{\text{bubble}} = \frac{4}{3} \pi R_o' \rho \left( 1 + \frac{2}{5} \beta^2 \right)$$

$$+ \frac{4}{5} \pi R_o'^2 \rho \left( 1 + \frac{4}{5} \beta^2 \right)$$

$$+ \frac{1}{\alpha} \left[ A + B \alpha R_o + C (\alpha R_o)^2 \left( 1 + \frac{7}{5} \beta^2 \right) \right]$$

Chapter IV will give the results of the variational calculation carried out according to this formula.
IV. RESULTS AND DISCUSSION

The results of the calculations described in the last chapter will be presented in the first two sections of this chapter, followed by a few general conclusions. A division is made between the results for the absorption and emission between $2^3S$ and $2^3P$, and the emission lines $3^1S \rightarrow 2^1P$ and $3^3S \rightarrow 2^3P$. For the former calculations we have a high degree of confidence in the wave functions and other parameters, and the results show clearly how the effect of the fluid environment causes these two transition lines to differ. The results for the $3S \rightarrow 2P$ transitions are dealt with separately because of uncertainties in the long range electrostatic interaction (van der Waals forces) involved.

A. Absorption and Emission Between $2^3S$ and $2^3P$

Before discussing in detail the results for these transitions, the qualitative behavior of the model will be analyzed. In the case of emission, the equilibrium bubble formed around the $2^3P$ is distorted, slightly pinched in at the equator where the dumbbell shaped p electron probability is a minimum. When the transition to the $2^3S$ state occurs, there is a great deal of perturbation of the s electron where its spherical probability density overlaps the pinched in portion of the bubble. The positive perturbation of the lower lying state is much greater than that of the
higher state, and therefore the transition line is red shifted. Conversely, if the initial state is $2^3S$, the equilibrium bubble is spherical, with a radius comparable to the average radius of the nonspherical bubble. In this case both states are only slightly perturbed, and the prediction of a small blue shift is in accord with experimental results. Both of these transitions are illustrated schematically in figures 11 and 12.

With this qualitative picture in mind, consider the exact theoretical results of Tables 1 and 2. These show agreement with experiment within $\sim 25$ cm.$^{-1}$ for a range of surface tensions and effective electron-helium potentials ($V_{\text{eff}}$). (It should be noted that these small shifts are measured relative to the free atom transition energy of $1.08 \mu = 9231$ cm.$^{-1}$) An appreciation of the behavior of these results can be gained by considering their sensitivity to the major factors which determine them. We therefore examine their dependence on the wave functions, the van der Waals term, the bubble energy expression, and the effective electron-helium potential.

Unperturbed free atom wave functions were used throughout the calculations. A posteriori, the small perturbations obtained afford justification for this, but some trials were made using perturbed wave functions. In the two body interaction described in chapter II, it was found that increasing the effective charge of the wave
Figure 11:
Schematic representation of the difference in perturbation of He\((2\,^3P)\) and He\((2\,^3S)\), depending on the bubble shape, as explained in the text.
EMISSION
\[2^3P \rightarrow 2^3S\]

ABSORPTION
\[2^3S \rightarrow 2^3P\]
Figure 12:
Graphical calculation of the transition energy for absorption and emission. The $2^3P \rightarrow 2^3S$ emission takes place between the minimum of the top dashed curve and the corresponding position of the lower dashed curve. Note that distortion lowers the energy of the bubble around the He($2^3P$) state, and raises the energy of the spherically symmetric He($2^3S$) state. The absorption takes place between the minimum of the lower solid curve and the corresponding position of the upper solid curve.

These calculations are done for $\gamma = 0.52$ ergs/cm$^2$, $V_{\text{eff}}$ number (2), and the distortion parameter $\beta$ is fixed at 0.3 for the dashed curves.
$$A E = 22 \text{ cm}^-1$$

**ABSORPTION**

$$A E = 4.8 \text{ cm}^-1$$

**EMISSION**

(\text{DISTORTED BUBBLE})

(\text{ROUND BUBBLE})
Table 1:
Final results for emission, $2^3\text{P} \rightarrow 2^3\text{S}$, over a range of surface tensions and effective potentials.
$$\text{Experimental Value: } -68 \text{ cm}^{-1}$$
Table 2:
Final results for absorption, $2 \, ^3S \rightarrow 2 \, ^3P$, over a range of surface tensions and effective potentials.
$2^3S \rightarrow 2^3P$

**Effective $e^- - \text{He Potential}$**

<table>
<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_o$</td>
<td>10.0</td>
<td>9.75</td>
<td>9.5</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\beta$</td>
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<td>0.0</td>
</tr>
<tr>
<td>shift</td>
<td>21 cm.$^{-1}$</td>
<td>29 cm.$^{-1}$</td>
<td>22 cm.$^{-1}$</td>
</tr>
</tbody>
</table>

**Experimental Value:** 0 cm.$^{-1}$
function "pulled in" the electron probability distribution and hence reduced $E_{\text{overlap}}$. This energy reduction was largely cancelled by the increased repulsion between the excited electron and the inner ls electron. For this reason, and because trials in the liquid case would require a great deal of computation, it was felt that unperturbed wave functions were completely adequate to within the accuracy of the model.

A cause of greater concern than the wave functions was the choice of van der Waals coefficient. For the $2^3S$ state, Dalgarno's value of 29.1 a.u. is based on an accurate calculation and is undoubtedly adequate. For the $2^3P$ state, however, no published calculations or measurements exist. The value of $50(1 + \frac{2}{5}P_e)$ found in Appendix A is certainly a reasonable estimate, and does have the virtue of producing good agreement with experiment. It was found that the particular choice of van der Waals constant had a noticeable effect on how much the bubble distorted at the equator, for there the electron probability density is low and the electrostatic attraction is dominant. Using $C = 35(1 + \frac{2}{5}P_e)$ led to a slightly larger bubble and hence to less red shift on emission.

An appealing feature of the calculations was an insensitivity to the exact definition of the bubble energy, as shown in Tables 1 and 2. This insensitivity is pleasing because so little is known about calculating the energy.
of a fluid configuration. The surface tension energy is the largest contribution to the bubble energy, and is most sensitive to variation of bubble parameters. And the idea of a bubble with surface tension is certainly an approximation when the bubble diameter is only a few times larger than the average separation of the fluid atoms. It appears that the long range van der Waals attraction may be important in limiting the size of the local fluid distortion around an excited atom, so that the dependence on an exact choice of surface tension is minimized.

Somewhat greater sensitivity to the specific form of $V_{\text{eff}}$ was observed. For the emission lines, it is surprising that forms (1) and (2) of $V_{\text{eff}}$ give such similar results, while the results of (3) differ markedly. The explanation seems to rest on the fact that $\rho = 0.4$ in the equilibrium cases for (3), while $\rho = 0.3$ for (1) and (2). In all three cases the total energy of the $2^3P$ state in the bubble is very close for $\rho = 0.3$ and $\rho = 0.4$. After the transition, however, the perturbation of the $2^3S$ is very much greater for $\rho = 0.4$, and this accounts for the sensitivity in emission. The sensitivity to $V_{\text{eff}}$ is much less in absorption. This is because small changes in the shape of the equilibrium bubble do not greatly affect this calculation: the perturbations of the upper and lower states tend to move up or down together, with little net change. This contrast in sensitivity is heightened by the fact that we are quite
sure that the absorption transition takes place in a spherical bubble, whereas the emission occurs in a distorted bubble. The uncertainty over exactly how to compute the distortion energy is therefore compounded by the critical dependence on the exact amount of distortion.

Several other features and limitations of the model are worthy of mention. One is that the dependence on $V_{\text{ion}}$ does not seem to be critical. In the $2^3S$ bubble, $V_{\text{ion}}(R)$ is essentially zero for $R$ as large as the inner bubble radius. In the $2^3P$ bubble, it is important to use the averaged form of $V_{\text{ion}} = \frac{1}{2}(V(\Sigma^+_a) + V(\Sigma^+_q))$ so that it will be slightly repulsive at small $R$. This prevents the electrostriction effect from causing the bubble to collapse (as it does if $V_{\text{ion}} = V(\Sigma^+_a)$).

A possible limitation of the model is that the monotonic density function assumed to describe the bubble cross section does not reflect the behavior of a liquid radial distribution function. On an atomic level, the density might be expected to have a maximum at the bubble radius, followed by several small oscillations before approaching the equilibrium density. Nonetheless, the intent of this calculation was to try to use a simple model, and a more complicated density function would require additional variational parameters. A second limitation to be mentioned is that no form of screening was included. The interaction of the central atom with any
other atom was assumed not be be influenced by any intervening fluid. For $V_{\text{ion}}$ and the averaged electron-helium repulsion this produces no problem since they fall off very rapidly with distance. The van der Waals term does have a significant long range effect, but it was felt that any attempt to include dielectric or screening effects would only introduce additional uncertainty.

B. The $3^1S \rightarrow 2^1P$ and $3^3S \rightarrow 2^3P$ Transitions

These results are treated in a separate section because the combined uncertainties in the wave function and van der Waals coefficients made it more difficult to obtain results in agreement with experiment. Also, the physical picture is different in this case in several respects. First, the transition energy shift is essentially determined by the perturbation of the higher $(3^1,3^3S)$ state. The cavity formed around the large $n = 3$ state is so large that there is virtually no overlap of the $2^1,3^3P$ wave functions. Because of this, we would expect the transition shift to be blue, due to the repulsive interaction of the electron wave function with the surrounding fluid. This is certainly part of the story, but equally important is the distortion of the large, loosely bound $3^1,3^3S$ wave function. It appears that the observed small shifts (10 and 15 cm.$^{-1}$ for triplet and singlet) result from the near cancellation of these two effects.
The discussion in chapter II indicated that the \( n = 3 \) hydrogenic wave function with an appropriate effective charge has a fairly accurate asymptotic form. This, however, is only for the case of a free atom. The \( 3\,^1S \) wave function would be expected to become more distorted in the liquid environment, and in this case we have no variational formula to compute the increase in atomic energy caused by distorting ("pulling in") the electron cloud.

The procedure adopted was to adjust the van der Waals constant until the calculated shifts were in agreement with experiment. The lack of accurate calculations of the long range attraction between He(\( 3\,^1S \)) and He(\( 1\,^1S \)) affords a certain latitude in assigning \( C \), and the final perturbation of the \( 3\,^1S \) states as a function of \( C \) is plotted in figures 13 and 14. The near linearity may be at first surprising, but is easily explained by noting the bubble parameters corresponding to the shifts as listed in Table 3. A large increase in \( C \) (from zero to its final value) changes the bubble shape only slightly, and small changes in \( C \) about this final value essentially do not affect the bubble parameters. This is because the long range van der Waals interaction is competing with the electron-helium repulsion, which is very sharply increasing for \( R \) less than the bubble radius. In other words, it is very difficult to make the bubble even a
Figure 13:
The emission shift of $3^1S \rightarrow 2^1P$ as a function of van der Waals constant $C$. The dotted line marks the effective $C$ chosen.
SHIFT (cm\(^{-1}\))

EMISSION

3 \( ^1S \rightarrow 2 \( ^1P \)

\( y = 0.52 \)

\( y = 0.36 \)

C
(units of 188 a.u.)
Figure 14:
The emission shift of $3^3S \rightarrow 2^3P$ as a function of van der Waals constant $C$. The dotted line marks the effective $C$ chosen.
EMISSION

$3^3 \text{S} \rightarrow 2^3 \text{P}$

SHIFT (cm$^{-1}$)

$\gamma = 0.52$

$\gamma = 0.36$

C (units of 168 a.u.)
Table 3:
Equilibrium bubble parameters for $3^{1,3}{\text{s}}$, for several surface tensions and van der Waals constants.
\[ 3^1S: \quad C \text{ (a.u.)} \]

| \( \gamma \) | 0  | 4.5 \( \times \) 188 | 5.5 \( \times \) 188 | 6.5 \( \times \) 188 |
|----------------|----------------|----------------|----------------|
| 0.58           | \( R_0 = 22.0 \) | \( R_0 = 21.0 \) | \( R_0 = 21.0 \) | \( R_0 = 20.5 \) |
| 0.52           | \( R_0 = 22.0 \) | \( R_0 = 21.0 \) | \( R_0 = 21.0 \) | \( R_0 = 21.0 \) |
| 0.36           | \( R_0 = 22.5 \) | \( R_0 = 21.0 \) | \( R_0 = 21.5 \) | \( R_0 = 21.5 \) |

\[ 3^3S: \quad C \text{ (a.u.)} \]

| \( \gamma \) | 0  | 4.5 \( \times \) 168 | 5.0 \( \times \) 168 | 5.5 \( \times \) 168 |
|----------------|----------------|----------------|----------------|
| 0.58           | \( R_0 = 21.0 \) | \( R_0 = 20.0 \) | \( R_0 = 20.0 \) | \( R_0 = 20.0 \) |
| 0.52           | \( R_0 = 21.0 \) | \( R_0 = 20.0 \) | \( R_0 = 20.0 \) | \( R_0 = 20.0 \) |
| 0.36           | \( R_0 = 21.5 \) | \( R_0 = 20.5 \) | \( R_0 = 20.5 \) | \( R_0 = 20.5 \) |

In all cases, \( \alpha = 0.67; \beta = 0.0 \)
little bit smaller because of this repulsion. Increasing C therefore causes a nearly proportional decrease in the perturbation.

The values of C finally adopted for the $3^{1,3}S$ states are indicated by dotted lines in figures 13 and 14, and the final shifts thereby obtained are shown in Table 4. The values of C chosen are both about five times larger than those calculated in Appendix A, and this discrepancy deserves some comment. First, the derivation in the Appendix does not take into account second order effects on the wave functions. For the large $3^{1,3}S$ states, this could cause a serious underestimate of C. Secondly, the adjustment of C may be viewed as empirically taking into account unknown effects. Since the bubbles are larger around the $n = 3$ states than around $n = 2$ ones, more atoms are displaced and the configuration energy becomes more difficult to calculate. In this context, C enables us to represent very complicated interactions within the framework of a simple model.

C. Conclusions

We have attempted to show that certain atomic transitions of helium in a liquid helium environment can be explained on the basis of a simple bubble model, and have calculated transition energies in reasonable agreement with experiment. From our results, we can say with
Table 4:
Final $3^1S$ 2 $1P$ and $3^3S$ 2 $3P$ transition energy shifts, calculated for effective van der Waals constants

\[ c = 5.5 \times 10^8 \text{ a.u.} \quad (3^1S) \]

\[ c = 5.0 \times 10^8 \text{ a.u.} \quad (3^3S) \]
$$3 \, ^1S \rightarrow 2 \, ^1P$$

$$C = 5.5 \times 188 \text{ a.u.}$$

<table>
<thead>
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<th>$\gamma$</th>
<th>Shift</th>
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<tr>
<td>0.58</td>
<td>26 cm.$^{-1}$</td>
</tr>
<tr>
<td>0.52</td>
<td>26 cm.$^{-1}$</td>
</tr>
<tr>
<td>0.36</td>
<td>1 cm.$^{-1}$</td>
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</tbody>
</table>

Experimental Value = 15 cm.$^{-1}$

$$3 \, ^3S \rightarrow 2 \, ^3P$$

$$C = 5.0 \times 168 \text{ a.u.}$$

<table>
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<td>0.58</td>
<td>18 cm.$^{-1}$</td>
</tr>
<tr>
<td>0.52</td>
<td>18 cm.$^{-1}$</td>
</tr>
<tr>
<td>0.36</td>
<td>-6 cm.$^{-1}$</td>
</tr>
</tbody>
</table>

Experimental Value = 10 cm.$^{-1}$
confidence that a local distortion of the liquid around an excited atom does occur, and we can compute with some success the perturbation of the excited atom by the surrounding liquid. The major difficulty lies in calculating the exact nature of the distortion. It seems likely that subtle many body effects may play an important role in the liquid configuration energy, and we have shown that uncertainty in the exact liquid configuration can sometimes affect the final results.

The theory and calculations described herein indicate the strengths and limitations of a simple model. For small bubbles around atomic states, we can draw on a number of fairly accurate wave functions, and hope that the uncertainty involved in estimating other parameters and many body effects is not too great. As we progressed from s states to p states, and from \( n = 2 \) to \( n = 3 \), it was clear that the problems increased. The extension from atoms to molecules will involve even greater difficulty, for more accurate wave functions will have to be found, and directionally dependent forces examined more closely. This work ends at the point where present uncertainties begin to prohibit meaningful calculations. It is hoped that we have shown just how much information can be gleaned from a very simple model of liquid structure.
APPENDIX A

Calculation of van der Waals Coefficients

The van der Waals interaction is a small but important factor in the present calculations. The only published results for the cases we are interested in is the long range interaction of He (1\textsuperscript{1}S) with He (2\textsuperscript{3}S).\textsuperscript{15} Estimates of the other necessary coefficients were therefore made using original calculations. The approach is to find the average polarization energy of a He (1\textsuperscript{1}S) caused by some He\textsuperscript{*}. As usual, we consider He\textsuperscript{*} = He\textsuperscript{+} plus bound, excited orbital \(\psi(r,\theta,\varphi)\). The field at the ground state atom is the vector sum of the separate Coulomb fields of the electron and core ion as shown in figure 15. Because of this field, the He (1\textsuperscript{1}S) is polarized and has an energy

\[
E_{\text{pol}} = -\frac{1}{2} \alpha \left[ \frac{\mathbf{E}_B}{E_B} \right]^2 = -\frac{1}{2} \alpha E_B^2
\]

Averaging \(E_{\text{pol}}\) over the probability density of the excited electron and keeping terms to order \(R^{-6}\) enables us to write

\[
U = -\frac{C}{R^6}
\]

where \(C\) is the van der Waals constant and may depend on \(\Theta\).

We first approximate the reciprocal of the distance from the excited electron to the He(1\textsuperscript{1}S):
$$\frac{1}{X} = \sum_{L=0}^{\infty} \frac{r_L^L}{r_{L+1}^{L+1}} \ P_L(\cos \eta)$$

$$\approx \sum_{L=0}^{\infty} \frac{r^L}{R^{L+1}} \ P_L(\cos \eta)$$

$$\approx \frac{1}{R} + \frac{r \cos \eta}{R^2}$$

$$\frac{1}{X^2} \approx \frac{1}{R^2} + \frac{2r \cos \eta}{R^2}$$

The field at B due to the electron is \(-\frac{1}{X^2} \hat{X}\). The component of this vector along \(\hat{R}\) is \(-\frac{1}{X^2} \cos \theta\) and the component perpendicular to \(\hat{R}\) is \(-\frac{1}{X^2} \sin \beta\). Adding this to the field of the core ion, \(+\frac{1}{R^2} \hat{R}\), we have for the magnitude of the total field at B:

$$E_B^2 = \left( \frac{1}{R^2} - \frac{\cos \beta}{X^2} \right)^2 + \left( \frac{\sin \beta}{X^2} \right)^2$$

$$= \frac{1}{R^4} - \frac{2 \cos \beta}{R^2 X^2} + \frac{1}{X^4}$$

By the law of sines

$$\sin \beta = r \left( \frac{1}{X} \right) \sin \eta$$

$$= r \left( \frac{1}{R} + \frac{r \cos \eta}{R^2} \right) \sin \eta$$

$$\approx \frac{r \sin \eta}{R}$$
Hence

\[
\cos \beta = \sqrt{1 - \sin^2 \beta} \\
\approx 1 - \frac{1}{2} \frac{r^2 \sin^2 \eta}{R^2}
\]

Inserting this back into the expression for \( E_B^2 \) gives

\[
E_B^2 = \frac{1}{R^4} - \frac{2}{R^2} \left( \frac{1}{R^2} + \frac{2 \Gamma \cos \eta}{R^3} \right) \left( 1 - \frac{1}{2} \frac{r^2 \sin^2 \eta}{R^2} \right)
\]

\[
+ \left( \frac{1}{R^2} + \frac{2 \Gamma \cos \eta}{R^3} \right) + o(R^{-7})
\]

\[
= \frac{r^2}{R^6} \left( 4 \cos^2 \eta + \sin^2 \eta \right) + o(R^{-7})
\]

\[
= \frac{r^2}{R^6} \left( 3 \cos^2 \eta + 1 \right) + o(R^{-7})
\]

\[
= 2 \frac{r^2}{R^6} \left( 1 + \frac{3 \cos^2 \eta - 1}{2} \right) + o(R^{-7})
\]

\[
E_B^2 \approx 2 \frac{r^2}{R^6} \left[ 1 + P_2(\cos \eta) \right]
\]
This gives a formal expression for \( U \):

\[
U = -\frac{1}{2} \alpha \left< E^2 \right>
\]

\[
\alpha = -\frac{\alpha}{R^6} \left< \psi \left| r^2 \left[ 1 + \frac{2}{3} \frac{\partial}{\partial \theta} \left( \cos \eta \right) \right] \right| \psi \right>
\]

Suppose \( \psi = R(x) Y_{lm}(\theta, \phi) \). We know

\[
P_2(\cos \eta) = \frac{4\pi}{5} \sum_{\mu=-2}^{+2} Y_{2\mu}^*(\theta, \phi) Y_{2\mu}(\Theta, \Omega)
\]

Hence

\[
U = -\frac{\alpha}{R^6} \int_0^\infty r^2 |R(r)|^2 r^2 dr
\]

\[
x \int d\Omega |Y_{lm}(\theta, \phi)|^2 \left\{ 1 + \frac{4\pi}{5} \sum_{\mu=-2}^{+2} Y_{2\mu}^*(\theta, \phi) Y_{2\mu}(\Theta, \Omega) \right\}
\]

\[
= -\frac{\alpha}{R^6} \left[ \int_0^\infty |R(r)|^2 r^4 dr \right]
\]

\[
x \left[ 1 + \frac{4\pi}{5} Y_{20}(\Theta, \Omega) \int d\Omega |Y_{lm}(\theta, \phi)|^2 Y_{20}(\Theta, \Omega) \right]
\]
For the cases of interest, $l = m = 0$ or $l = 1, m = 0$:

$s$ state ($l = m = 0$):

$$ U = -\frac{\alpha}{R^6} \left[ \int_0^\infty |R(r)|^2 r^4 dr \right] $$

$p$ state ($l = 1, m = 0$):

$$ U = -\frac{\alpha}{R^6} \left[ \int_0^\infty |R(r)|^2 r^4 dr \right] $$

$$ \times \left[ 1 + \frac{2}{5} P_2 (\cos \Theta) \right] $$

Naturally the evaluation of these integrals will depend on the choice of radial function $R(r)$. Using the same radial functions as discussed in chapter II, and substituting the polarizability of ground state helium ($\alpha = 1.38$ a.u.$^{25}$), we can tabulate the final results:

$$ 2^3 S $$

$$ R(r) = 0.357 r e^{-\frac{1.22 r}{2}} - 1.05 e^{-1.57 r} $$

$$ U = -\frac{2.2}{R^6} \text{ a.u.} $$

$$ 2^3 P_{m=0} $$

$$ R(r) = \frac{1}{\sqrt{24}} (1.09)^{5/2} r e^{-\frac{1.09 r}{2}} $$
\[ U = \frac{-35 \left( 1 + \frac{2}{5} R P_2 (\cos \Theta) \right)}{R^6} \text{ a.u.} \]

\[ R(r) = \frac{1}{40.5 \sqrt{3}} Z^{3/2} (27 - 18Zr + 2Z^2r^2) e^{-\frac{Zr}{3}} \]

**Singlet**: \[ Z = 1.05 \]

\[ U = \frac{-188}{R^6} \text{ a.u.} \]

**Triplet**: \[ Z = 1.11 \]

\[ U = \frac{-168}{R^6} \text{ a.u.} \]

In chapter II Dalgarno's value \( C = 29.1 \text{ a.u.} \) was quoted for the interaction of \( \text{He}(2 \, ^3S) \) with \( \text{He}(1 \, ^1S) \). This is reasonably close to the result \( C = 22 \text{ a.u.} \) obtained here; the difference is easily understood physically. The method here used a first order unperturbed wave function for the excited state. Second order effects could be expected to distort this wave function in such a way as to lower \( U \). For this reason we also adopt a slightly larger value of \( C \) for the \( ^3P \) state than the one calculated:

\[ C = 50 \left( 1 + \frac{2}{5} P_2 (\cos \Theta) \right) \text{ a.u.} \]
The value of 50 was chosen also on the grounds that it yields good agreement with experiment.

Van der Waals constants for the \( n = 3 \) excited states as calculated here did not produce agreement with experiment; the procedure by which these constants were adjusted has already been discussed (chapter IV).
APPENDIX B

Expansion of $V_{\text{eff}}$ in Legendre Polynomials

Having made the analytic approximation

$$V_{\text{eff}}(s) = -\frac{2}{s} e^{-as} + b e^{-\left(\frac{s^2}{2\sigma^2}\right)} \quad s < r_c$$

$$V_{\text{eff}}(s) = -\frac{2}{s} e^{-as} \quad s \geq r_c$$

and knowing

$$s = \left| \frac{\hat{R} - \hat{r}}{R} \right| = \sqrt{R^2 + r^2} - 2Rr \cos \Theta$$

we wish to express

$$V_{\text{eff}}(s) = V_{\text{eff}}(R, r, \Theta)$$

$$= \sum_{\lambda=0}^{\infty} V_{\lambda}(R, r) P_{\lambda}(\cos \Theta)$$

where

$$V_{\lambda}(R, r) = \frac{2\lambda+1}{2} \int_{0}^{\pi} V_{\text{eff}}(R, r, \Theta) P_{\lambda}(\cos \Theta) \sin \Theta \, d\Theta$$
In this Appendix we shall explicitly evaluate $v_o(R,r)$ and $v_2(R,r)$.

The first term of $V_{\text{eff}}$ is independent of cutoff and is the familiar case:

$$
e^{-a |\vec{r}_i - \vec{r}_o|} = \frac{ia}{|\vec{r}_i - \vec{r}_o|} \sum_{\lambda=0}^{\infty} (2\lambda+1) j_{\lambda}(iar_{<}) h_{\lambda}^{+}(iar_{>} \, P_{\lambda}(\cos \Theta)

Here $\Theta$ is the angle between $\vec{r}_1$ and $\vec{r}_2$, $r_{<}$ ($r_{>}$) is the greater (lesser) of $|\vec{r}_1|$ and $|\vec{r}_2|$, and $j_{\lambda}$ and $h_{\lambda}^{+}$ are spherical Bessel and Hankel functions. Specifically,

$$j_{0} = \frac{\sinh ar_{<}}{ar_{<}}$$

$$j_{2} = - \left( 1 + \frac{3}{(ar_{<})^2} \right) \frac{\sinh ar_{<}}{ar_{<}} + \frac{3 \cosh ar_{<}}{(ar_{<})^2}$$

$$h_{0}^{+} = \frac{e^{-ar_{>}}}{iar_{>}}$$

$$h_{2}^{+} = - \left( 1 + \frac{3}{ar_{>}^2} + \frac{3}{(ar_{>)^2}} \right) \frac{e^{-ar_{>}}}{iar_{>}}$$

In the case of no cutoff ($r_{c} \to \infty$), the Gaussian part of $V_{\text{eff}}$ leads to the integrals

$$\frac{1}{2} \int_{0}^{\pi} e^{-\frac{R^2 + r^2 - 2rr \cos \Theta}{2 \sigma^2}} \sin \Theta \, d\Theta$$

The effect of a finite cutoff is to change the upper limits of integration from $\pi$ to some angle $\theta_\circ(R,r)$. The diagram shows that for fixed $R$ and $r$, $\theta_\circ$ is chosen such that the point $P$ is just at the cutoff distance of $V_{\text{eff}}$:

If $R$, $r$, and $r_c$ are the sides of a possible triangle, $\theta_\circ$ is given by the law of cosines:

$$\cos \theta_\circ = \frac{R^2 + r^2 - r_c^2}{2 R r}$$

For general values of $R$, $r$, and $r_c$ a suitable definition is

$$\cos \theta_\circ = \min\left[1, \max\left[-1, \frac{R^2 + r^2 - r_c^2}{2 R r}\right]\right]$$
The evaluation of the integrals is more tedious than subtle. The reader is asked to accept the final results:

\[ V_0 (R,r) = \frac{-2 \sinh a r < e^{-a r} }{a R r} \]

\[ + \frac{b \sigma^2}{R r} \ e^{-\frac{R^2 + r^2}{2 \sigma^2}} \ F (R, r, \cos \Theta_0) \]

\[ V_2 (R,r) = 5 i a J_2 (i a r_c) \ h^+_2 (i a r_c) \]

\[ + 15 b e^{-\frac{R^2 + r^2}{2 \sigma^2}} \ \left\{ \left( \frac{\sigma^2}{2 R r} + \frac{\sigma_0^4}{R^3 r^3} \right) F (R, r, \cos \Theta) \right\} \]

\[ - \frac{\sigma^4}{R^2 r^2} \ G (R, r, \cos \Theta) \}

\[ - \frac{5}{2} \frac{b \sigma^2}{R r} \ e^{-\frac{R^2 + r^2}{2 \sigma^2}} \ F (R, r, \cos \Theta_0) \]

\[ + \frac{\sigma^2 \sin^2 \Theta_0}{4 R r} \ e^{\frac{R r \cos \Theta_0}{\sigma^2}} \]
Here we define

\[
F(R, r, \cos \theta) = \frac{1}{2} \left( e^{\frac{Rr}{\sigma^2}} - e^{\frac{Rr \cos \theta}{\sigma^2}} \right)
\]

\[
G(R, r, \cos \theta) = \frac{1}{2} \left( e^{\frac{Rr}{\sigma^2}} - \cos \theta e^{\frac{Rr \cos \theta}{\sigma^2}} \right)
\]

Clearly in the limit \( r_c \to \infty \), \( \cos \theta_o \to -1 \), and

\[
F(R, r, -1) = \sinh \frac{Rr}{\sigma^2}
\]

\[
G(R, r, -1) = \cosh \frac{Rr}{\sigma^2}
\]

In this limit the general result reduces to the formulas (II: 9).
We wish to evaluate

$$E_{\text{kin}} = \frac{\rho_0}{\Theta M} \int \frac{(\nabla \rho)^2}{\rho} \ d^3r$$

for $\rho(R, \Theta)$ as given by equation (III: 28). Since

$$\nabla \rho = \hat{R} \frac{\partial \rho}{\partial R} + \hat{\Theta} \frac{1}{R} \frac{\partial \rho}{\partial \Theta}$$

we can write for $R > R(\Theta)$

$$\frac{\partial \rho}{\partial R} = \alpha^2 \rho_0 (R - R(\Theta)) e^{-\alpha (R - R(\Theta))}$$

$$\frac{\partial \rho}{\partial \Theta} = \rho_0 \alpha^2 (R - R(\Theta)) \frac{dR(\Theta)}{d\Theta} e^{-\alpha (R - R(\Theta))}$$

Since $\hat{R} \cdot \hat{\Theta} = 0$, $(\nabla \rho)^2 = (\frac{\partial \rho}{\partial R})^2 + \frac{1}{R^2} (\frac{\partial \rho}{\partial \Theta})^2$.

$$E_{\text{kin}} =$$

$$\frac{\pi n \alpha}{4M} \int_{\sin \Theta}^{\pi} d\Theta \int_{R(\Theta)}^{\infty} dR \frac{(R - R(\Theta))^2 e^{-2\alpha (R - R(\Theta))}}{1 + [1 + \alpha (R - R(\Theta))] e^{-\alpha (R - R(\Theta))}} [R^2 + (\frac{dR(\Theta)}{d\Theta})^2]$$
$$= \frac{\rho_0 \pi a^+}{4M} \int_0^\pi \sin \Theta \ d\Theta$$

$$\times \int_0^\infty \frac{y^{3/2} e^{-2y}}{1-(1+y)e^{-y}} \left[ \left( \frac{y}{\alpha} + R(\Theta) \right)^2 + \left( \frac{dR(\Theta)}{d\Theta} \right)^2 \right] \frac{dy}{\alpha}$$

Changing variables to $y = \alpha (R - R(\Theta))$ we can express the radial integral in terms of the previously used $A$, $B$, and $C$ integrals (cf. equation (III:26)):

$$A = \frac{\rho_0 \pi}{2M} \int_0^\infty \frac{y^{3/2} e^{-2y} \ dy}{1-(1+y)e^{-y}}$$

$$B = \frac{\rho_0 \pi}{2M} \int_0^\infty \frac{y^{3} e^{-2y} \ dy}{1-(1+y)e^{-y}}$$

$$C = \frac{\rho_0 \pi}{2M} \int_0^\infty \frac{y^{2} e^{-2y} \ dy}{1-(1+y)e^{-y}}$$
Figure 15:
The polarization of a He(1 $^1S$) at B caused by
He* = He+ plus excited electron orbital centered
at the origin.
The remaining integrals are over $\Theta$:

\[
E_{\text{kin}} = \frac{1}{2\alpha} \left[ A \int_0^\pi \sin \Theta \ d\Theta \\
+ B\alpha \int_0^\pi R(\Theta) \sin \Theta \ d\Theta \\
+ C \int_0^\pi \left[ \alpha^2 R(\Theta)^2 + \left( \frac{dR(\Theta)}{d\Theta} \right)^2 \right] \sin \Theta \ d\Theta \right]
\]

Substituting $R(\Theta) = R_o(1 + \beta P_2(\cos \Theta))$, the final result is readily obtained:

\[
E_{\text{kin}} = \frac{1}{\alpha} \left[ A + B \alpha R_o + C (\alpha R_o)^2 \left( 1 + \frac{7}{5} \beta^2 \right) \right]
\]
REFERENCES


14. $V_{\text{eff}}$ is usually called a pseudopotential. For additional information, see references 4,5,9, and B.J. Austin, V. Heine, and L.J. Sham, Phys. Rev., 127, 276 (1962).


16. This calculation was performed by Robert Shelton, Rice University.