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I. Studies of Cavities Containing One and Two Electrons in Metal-Ammonia Solutions. II. Accurate 'Effective' Intermolecular Pair Potentials in Gaseous Argon.

David Anthony Copeland
Louisiana State University and Agricultural & Mechanical College

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POTENTIALS IN GASEOUS ARGON

A Dissertation
Submitted to the Graduate Faculty of the
Louisiana State University and
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in partial fulfillment of the
requirements for the degree of

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in

The Department of Chemistry

by
David A. Copeland
B.S., University of Alabama, 1965
M.A., University of Alabama, 1966

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ABSTRACT

CHAPTER I

One- and two-electron cavity species of metal-ammonia solutions have been investigated with twelve- and eighteen-molecules in the first coordination shell of molecules and a continuum beyond the first layer. The important electron-molecule and molecule-molecule interactions are considered. The electron-dipole interactions are found to be the greatest stabilizing factor while the hydrogen-hydrogen interactions of the surface molecules determine the cavity size in most cases. The density of the molecules in the first layer is found to be less than the bulk density for the most stable cavities. The energy of a quasi-free electron, V_O, is treated as a parameter. The twelve-molecule models are found to be more stable than the eighteen-molecule models for the values of V_O considered. The two-electron species are found to be unstable relative to two one-electron cavities. Most findings are in reasonable agreement with experimental results although exact agreement is not found. The temperature dependence and asymmetry of the spectra are considered. Several extensions are also proposed. Arguments are given to indicate that the conclusions are general and go beyond the specific models presented.

CHAPTER II

Three-body nonadditive corrections to various assumed argon-argon potentials have been investigated. For intermediate gaseous argon densities, the triple-dipole interaction is shown to be the major correction for many-body interactions and yields very accurate "effective" intermolecular pair potentials. These potentials should lead to the

correct radial-distribution function. The results suggest a density dependence of the minimum of the effective potential of only about $+ 17 \bar{\rho}$ (in degrees Kelvin), where $\bar{\rho}$ is the density in grams per cubic centimeter. The small contribution of the nonadditive effect to the x-ray structure factor of the liquid is briefly examined.

I. STUDIES OF CAVITIES CONTAINING ONE AND TWO ELECTRONS IN METAL-AMMONIA SOLUTIONS

A. INTRODUCTION

1. EXPERIMENTAL BACKGROUND

Since the discovery of the solubility of the alkali metals in liquid ammonia over one hundred hears ago by Weyl,[1] alkali metal-ammonia solutions have sparked considerable experimental and theoretical interest related to the nature of the solutions.[2] The first evidence of the uniqueness of the alkali metal-ammonia solutions was reported in 1897 by Cady. Cady measured the conductance of sodium dissolved in liquid ammonia and noted that these solutions were better conductors than similar solutions of sodium salts.[3] In a series of papers from 1907 to 1922, Kraus confirmed the conclusions of Cady and made similar conclusions about lithium and potassium solutions. Although Weyl reported that alkali metal solutions have a blue color for dilute solutions and a bronze sheen for more concentrated ones, it was Kraus who noted that the blue color moved toward the anode when a voltage was placed across one of the dilute solutions. From the quantitative conductance data of Kraus it follows that the metal atoms are solvated by the ammonia in some manner and yield the positive ions of the metals and stable "solvated electrons".[4] The mobility of the negative charge carrier in the metal-ammonia solutions is the most conclusive evidence for the existence of the "solvated electron". For a solution of high sodium concentration, the specific conductance is found to be about one-sixth that of mercury and for a solution of low sodium concentration, the mobility of the negative charge carrier is found to be

1

seven times greater than the mobility of the positive sodium ion.[4]
Other researchers have reported conductance data,[5,6] and their results
are within one percent of the results obtained by Kraus. The very low
concentration conductance data of Kraus has been questioned by Dewald,
but the discrepancy is no larger than fifteen percent.[7]

Even though the work of Kraus confirmed the existence of
the "solvated electron", it did not indicate the actual structure of
the species present in the metal-ammonia solutions. In 1946, Ogg
postulated that an electron, or possibly an electron pair, resides in
a cavity in the metal-ammonia solutions surrounded by ammonia mole-
cules.[8] Ogg's postulate is based on volume expansion data, $\underline{i.e.}$, the
volume of the metal-ammonia solution is markedly in excess of the
volume of the constituents. Ogg's value for the volume expansion is
incorrect, but the volume expansion has been confirmed,[9-11] The
rupturing of hydrogen bonds and/or the formation of cavities could be
responsible for the volume expansion. If the volume expansion arises
only from the formation of cavities that are assumed to be spherical
and to contain one electron, the radius of a cavity is between 5.7 and
$6.6a_0$[†] for dilute solutions ($\underline{i.e.}$, 10^{-3} M (molar)).[10-13] This result
is obtained by extrapolating volume expansion data to infinite dilu-
tion. Extreme care must be taken in estimating the volume of the
metal ions since electrostriction is important and the ionic radii
of the metal ions are not accurately known. Evers and coworkers[11]
have reported a minimum in the volume expansion in the region 0.01 to

---

[†]Lengths will be given in Bohr radii (1 a_0 = 0.5292 Å) and energies
will be given in Hartrees (27.21 eV).

0.023 M, but more recent data by Gunn[10] indicate that a minimum does not occur.

In dilute solutions of the alkali and alkali-earth metals a very broad asymmetric absorption band is found in the infrared in the neighborhood of 7,000 cm^{-1} and is reported to be independent of the solute.[14-16] This band has only a slight trend toward lower energies with increasing concentrations.[14] This band extends into the visible region of the spectra and gives rise to the observed blue color. The details and trends of this band have been the subject of considerable controversy. Another characteristic of the dilute solutions that is independent of the solute is a single, very narrow spin-resonance line which gives a static spin susceptibility very close to the free spin value when extrapolated to infinite dilution.[17-19] These two properties, as well as the conductance and volume expansion data, have been shown for dilute solutions to be consistent with the cavity model.

As the concentration of the metal-ammonia solutions is increased through the 10^{-3} to .5 M region, a small decrease in the equivalent conductivity and a substantial decrease in the molar magnetic susceptibility are found.[17,20] The decrease in the spin paramagnetism implies that at least one diamagnetic species is being formed as the concentration is increased. Various equilibria have been postulated to explain the decreases, but the equilibrium constants obtained from magnetic data and from conductance data are not consistent.[21] The equilibria that have been most considered are[22,5]

$$(M^+ \cdot e^-) \rightleftharpoons M^+ + (e^-)_{am} \qquad (1)$$

and

$$(M^+ \cdot e^-) \rightleftharpoons \tfrac{1}{2} M_2. \tag{2}$$

We shall denote the "solvated electron" by $(e^-)_{am}$, and a weakly bound electron that is in an "expanded orbital" relative to a metal ion by $(M^+ \cdot e^-)$. This monomer species is similar to the ion-pair species of ionic solutions. The dimer species, M_2, has been described as a pair of ammoniated metal ions held together by two electrons in a molecular orbital situated largely between the two ions. Agreement with susceptibility data has also been obtained by using equilibria (1) and[23]

$$(M^+ \cdot e^-) + (e^-)_{am} \rightleftharpoons M^-. \tag{3}$$

The various species have been chosen because of their diamagnetism, their possible stability, or their conductivity. Another equilibrium that could explain at least part of the decrease in the paramagnetism is[19,24]

$$(e^-)_{am} \rightleftharpoons \tfrac{1}{2} (e_2^=)_{am}. \tag{4}$$

The dielectron species, $(e_2^=)_{am}$, has not been considered important since the theoretical work involving this species supposedly had not found the dielectron species stable relative to two one-electron species.[25,26] Many factors related to the stability of the dielectron species have been assumed without proof and some of these factors are found to be incorrect. This stability will be explored more fully later.

At a concentration of the metal greater than 1 M, the conductivity and magnetic data clearly indicate a nonmetal to metal transition. Dimer formation and dimer clustering have accounted for

some of the metallic properties, but the lack of experimental data and the lack of adequate theories for disordered systems have prevented the determination of an acceptable model for this concentration region. This concentration region will not be considered in this work.

As will be shown in the remainder of this section, no theoretical model has included all of the effects leading to a stable cavity, and only one reasonable theoretical investigation has been carried out for the dielectron species. The agreement with experiment and theory has been obtained _ad_ _hoc_. If a 1s to 2p transition is assumed for the one-electron-in-a-cavity species, the transition energy and solvation energy are found to agree with the experimental values when the radius of the cavity is specified for a dielectric continuum model.[13,26] Before we propose an explicit model for the cavity species at low metal concentrations, we shall review the various calculations that have been executed in order to determine the limitations and reliability of the models.

2. FACTORS LEADING TO CAVITY FORMATION

Let us suppose that we wish to carry out an _a priori_ calculation for the one-electron cavity species in a metal-ammonia solution. For such a calculation we would have to consider the interaction of the electron in the cavity with every molecule in the solution and every molecule-molecule interaction. This would include for each molecule ten electrons as well as four nuclei. If we were not considering the low concentration region, we would also have to consider the various interactions with the metal ions. We will be

interested only in the low concentration region where the electron-ion separations are large and such interactions can be neglected to a first approximation. Even by neglecting the ion interactions we would still be left with an impossible calculation. Clearly some sacrifices have to be made before any calculation can be carried out. Based on assumptions of varying degrees of approximation, models have been proposed. Several models have been based on the assumption that the medium outside the cavity can be considered a continuum. If the stability of the cavity arises from long range interactions or if the penetration of the excess electron into the medium is sufficient to justify the use of the bulk properties of the medium, then the continuum assumption is very good. Two models have been proposed which assume some structure for the first coordination shell of the ammonia molecules. This assumption is very good if the stability arises mainly from short-range interactions.

The previous models did not consider all of the factors necessary for a "realistic" model. The object of this work was to investigate all of the factors and to consider consistently one- and two-electron species by using a simple, complete model.

The total energy of an electron cavity E_T after the re-ordering of the molecules in the liquid is complete can be expressed by the relation

$$E_T = E_e + E_{\mu\mu} + E_{st} + E_{pv} \qquad (5)$$

where $E_{\mu\mu}$ is the dipole-dipole interactions of the molecules in the medium, E_{st} is the energy required to form a surface and is often related to surface tension, and E_{pv} is the energy related to the pressure-volume work.

An $\underline{a}$ $\underline{priori}$ calculation might be considered for obtaining

the electronic energies, E_e, but this procedure would be very diffi-

cult. The exchange interaction of the electron with the molecules on

the surface of the cavity would be a minimal requirement for such a

calculation. Also, the interaction of the electron with the multipole

moments of the ammonia molecules could not be handled simply. Changes

in the molecular structure of each of the molecules would have to be

considered because of the electric field of the excess electron.

Much of the difficulty arises when the electron is close to the mole-

cules, but this region can not be neglected. Because of the diffi-

culty involved in $\underline{a}$ $\underline{priori}$ calculations for the electronic energies

and the difficulty of interpreting these results in terms of the

dominant factors, model systems must also be used for this energy.

The various problems mentioned above must be kept in mind in any

reasonable formulation if any valid comparisons are to be made with

real situations.

We shall now consider what features must be included in a

model for the electron-cavity species of metal-ammonia solutions.

Because ammonia molecules have a rather large dipole moment (1.47

Debye), it is reasonable to assume that this factor must be considered.

A model which includes the first coordination shell of spherical

molecules could take this factor into account by considering each

molecule to have a point dipole at its center. If the reordering of

the molecules in the medium by the electric field of the electron

could be considered as an average effect that can be handled by the

bulk parameters of the liquid, the liquid outside the cavity might be

treated as a continuum. From what has been considered important in previous models and what is now known about the excess electron in polar and non-polar liquids, the electronic energy E_e can be broken down into its various contributions as follows:

$$E_e = T_e + E_{em} + E_{pol} + V_o \qquad (6)$$

where T_e is the kinetic energy of the electron, E_{em} is the sum of the charge-multipole interaction energies, E_{pol} is the charge-induced dipole (polarization) interaction energy, and V_o is the energy of the quasi-free electron. We shall explore the importance of the various energies before we review how they have been handled by other researchers.

The kinetic energy of the electron has obviously been included in all previous models with the common quantum mechanical expressions. The charge-multipole interaction energy has not been included in all of the previous models. Included in this energy, E_{em}, is the interaction of the electron with the multipole moments of the medium molecules with the charge-dipole interaction as the dominant stabilizing contribution. A charge-quadrupole interaction is also included in E_{em} and is a small destabilizing factor. Other multipole interactions might be included, but these interactions make only a minor contribution to the energy. From a simple dimensional analysis it can be seen why the charge-dipole interaction dominates the charge-quadrupole interaction. For the size cavities that we are interested in, the charge-dipole energy decreases (in absolute value) as $1/R_m^2$ while the charge-quadrupole energy decreases as $1/R_m^3$ where R_m is the distance from the center of the cavity to the center

of a molecule in the first coordination shell of molecules on the surface of the cavity (Figure I-A). The only important charge-multipole interactions are the ones where the electron is in the cavity and interacting with the first coordination shell since the other interactions are decreased by distance and by a dielectric screening. Since dipoles orient in electric fields, it is reasonable to assume that the surface molecular dipoles will be oriented by the electric field of the cavity electron. This orientation will yield the maximum charge-dipole stabilizing energy.

Many relations have been used in determining the polarization energy $E_{po\ell}$ and all but one of the calculations has assumed that the dielectric constants, optical and static, characterize the polarizations. The static (or total) polarization accounts for the molecular orientational and all distortional contributions to the energy E_e while the electronic (or optical) polarization accounts for only the electronic distortions of the molecules. The form that the polarization interactions take is based on how the cavities are formed. We shall discuss the assumptions behind the formulations as they are considered in various models. The polarization interactions are important, although they are not the most important interactions leading to stability.

Since an electron in a liquid is not in free space, it only sees differences in the total potential. Because of this characteristic, the energy of a localized electron must be measured relative to a quasi-free electron, the electron in the liquid with no medium rearrangement. The energy V_0 of the quasi-free electron mainly comes from electron-molecular exchange scattering and long range polarization

Figure I.   Radii that are used in model calculations.

    (A)   Radii used in structured models,

    (B)   Radii used in continuum models.

(A)

(B)
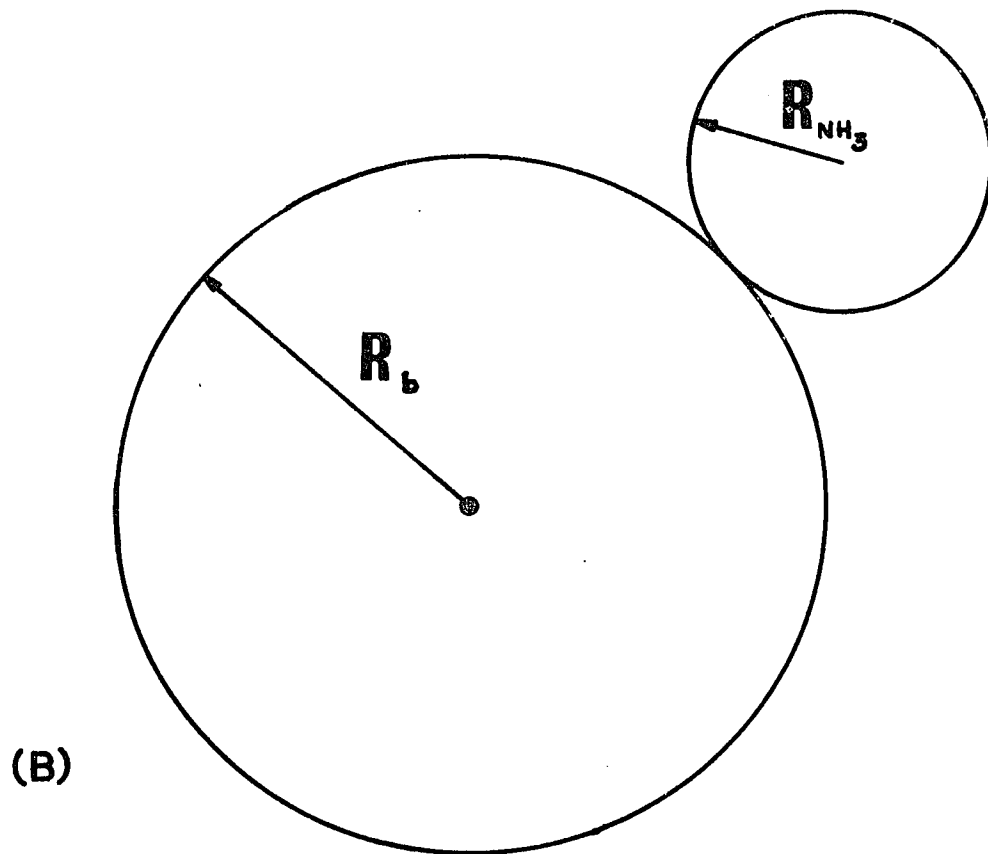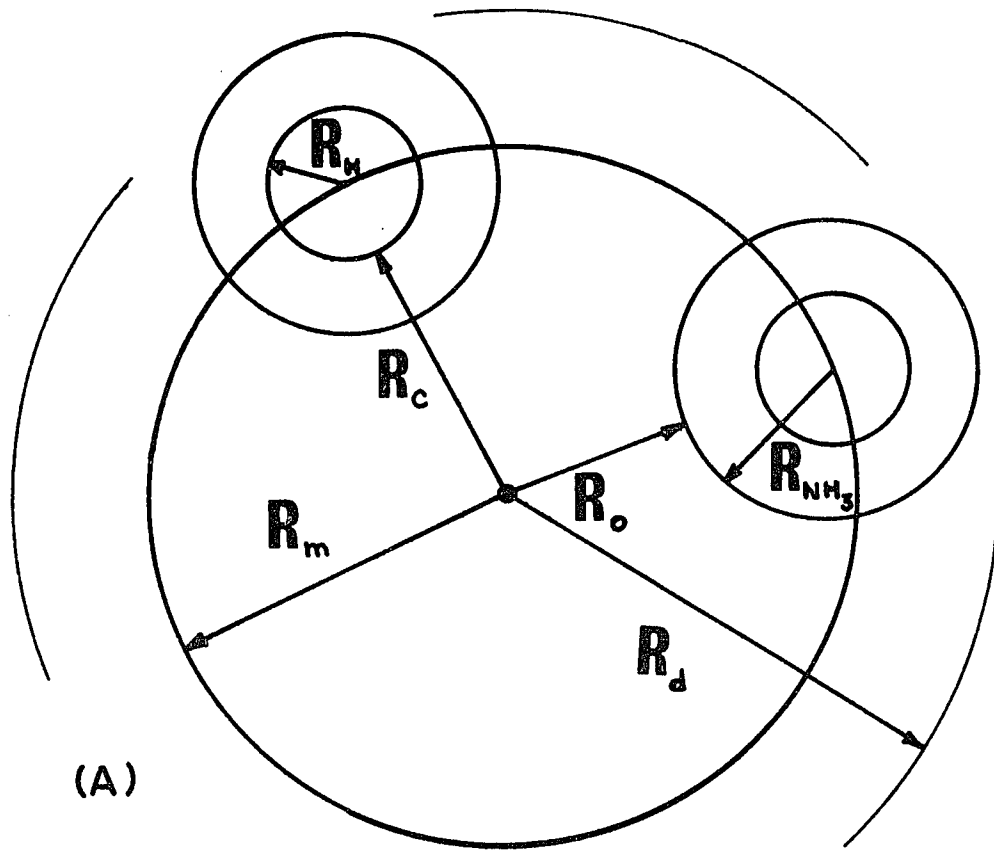
interactions. A small repulsive electron-molecule interaction or a large polarization would favor the quasi-free electron instead of the localized electron (such that $V_0 < E_T$). If an electron is localized in a cavity it would be possible to break V_0 into two parts. One part would consist of the interaction of the electron with the first co-ordination shell of molecules around the cavity. This interaction would take into account the exchange interaction of the electron with the surface molecules. Since NH_3^- is unstable, one can approximate the unperturbed ammonia-electron interaction (neglecting the dipole moment and polarizability) by an effective repulsive potential. This is the pseudo potential which is a result of the antisymmetry principle acting on the total electronic wave function of the electron and ammonia system. Instead of modifying the wave function, one can express this effect in the form of an effective potential. The details and justification for this approach for metal-ammonia solutions have been explored by Jortner and Kestner.[27]

The second part of V_0 would involve the energy of the electron when it is outside the cavity, i.e., when the electron is in the medium and can be considered entirely as a quasi-free electron. Like an electron in a crystal, the electron in the liquid can be considered in the conduction band of the liquid. Because of this similarity, several experimental measurements might be proposed for determining this part of V_0. Photoconduction is one measurement that could yield an experimental value for V_0. Adiabatic ejection of electrons from a photo cathode immersed in a liquid has been shown to give an excess electron in the quasi-free state in liquid rare gases.[28,29] Such a technique might be developed for polar liquids. The photoelectric

effect has also been suggested as a possible avenue of approach, but the magnitude and sign of the surface potentials for polar liquids are unknown.[30] A radial distribution function (or as it is sometimes called, pair correlation function) might be combined with the various interactions of the electron in the liquid to determine the energy of the quasi-free electron as well as the energy of the cavity species.[27] However, the theory of polar liquids is much to primitive at present. The sign and magnitude of V_O is unknown, but it is suspected to be positive because of the first part mentioned above.

We shall now consider the energies that must be combined with the electronic energy to obtain the total energy E_T. Only the unrealistic infinite-well cavity models have tried to determine the total energy of the system. The other calculations have assumed a radius for the cavity ad hoc and then carried out the calculation for the electronic energy. The dipole-dipole repulsion energy $E_{\mu\mu}$ and the surface energy E_{st} could be combined to form one energy relation, but we have divided the contributions to take into account the short-range interactions which are important in systems involving polar liquids. The energy required to form a surface is related to the free energy of the surface which takes into account the kinetic energy of the molecules on the surface and their interactions with the medium as well as the other molecules on the surface. Scaled particle theory as reviewed by Frisch[31] gives the most appropriate choice for determining this energy for cavities in non-polar liquids. A deficiency of the scaled particle theory procedure for polar liquids is found in its neglect of dipole-dipole repulsions (and other multipole interactions) caused by molecules reorienting on the surface of the cavity,

i.e., the polar molecules on the surface of the cavity reorient in the field created by the electron trapped in the cavity. A procedure might be developed that takes these multipole interactions into account. The methods of Hiroike, et al.[32] which used a radial distribution function and a molecular pair potential to take into account the configuration changes of liquid helium caused by an excess electron is probably the most consistent procedure for determining the energy E_{st}. This procedure obtained the correct R_c^2 dependence for the surface energy which is in accord with scaled particle theory. A simpler approach would be to consider in addition only the specific short range interactions between the molecules on the surface of the cavity caused by their orientation and neglect the molecules in the medium. Such a neglect would lead to only a minor error.[33] For the ammonia cavity species the hydrogen-hydrogen interactions must be considered as the most important factor for determining the size of a cavity since the trapped electron forces the hydrogens to be directed into the cavity. We shall discuss such a formulation in Section D.

If $E_{\mu\mu}$ is not taken into account in the determination of E_{st}, it must be considered as a separate contribution to E_T since it is very large. The continuum model calculations of Iguchi,[34] which considered electrons in alcohols, is the only treatment that takes the dipole-dipole repulsion energy into consideration. This model is inappropriate for disordered systems since it assumes that the dipoles form layers. This model can not explain volume expansion data either. By assuming a fixed number of surface molecules this energy can be handled easily. The determination of $E_{\mu\mu}$ will be considered in Section D along with the dipole-quadrupole repulsions between the molecules on the surface of the cavity.

A contribution to E_T from the pressure-volume work E_{pv} can be considered negligible at normal pressures (e.g., less than 10 atmospheres), but is important for studying spectral characteristics at high pressures (e.g., 200 atmospheres or greater). Cohen and Jortner[35] have shown that the quasi-free electron is more stable than the localized electron in solid helium at very high pressures. The pressure volume work arises from the work needed to expand the cavity against the hydrostatic pressure of the liquid. This energy can be obtained from the relation

$$\frac{4\pi}{3} p R^3 \qquad (7)$$

where p is the hydrostatic pressure in the liquid. For a cavity radius R equal to 6 a_0 at normal atmospheric pressure, the energy obtained from equation (7) would be about 10^{-6} Hartrees. We shall therefore neglect any further consideration of E_{pv}.

3. PREVIOUS MODELS OF ONE-ELECTRON CAVITY

We shall now review how the various energies have been handled by other investigators. With the electron totally confined to the cavity, the models of Ogg,[8] Lipscomb,[12] and Stairs[36] assumed that the medium outside the cavity could be treated as a continuum. These three models assumed that the polarization potential of the continuum dielectric medium takes the form (z = 1)

$$- \frac{ze^2}{2R_b} \left(1 - \frac{1}{D_s}\right) \qquad (8)$$

where z is the amount of charge in the cavity, e is the electrostatic charge, R_b (Figure I-B) is the distance from the center of the cavity

to the beginning of the continuum, and D_s (equal to 22 at -33° C.) is the static dielectric constant. The relation given in equation (8) is the well-known Born expression for the total polarization energy of a negative charge surrounded by a liquid medium.[37] This expression is applicable if both the molecular and electronic polarizations contribute to the formation of the cavity. An additional polarization contribution was included in the Lipscomb[12] model by solving a boundary value problem that assumes a constant surface charge at the cavity-continuum boundary. If the electron is not totally confined to the cavity, this additional contribution would be negligible. These three models could be interpreted as having V_0 equal to infinity. Because of the very high transition energies for an electron in a spherical box (Appendix I) and the lack of agreement with experimentally determined characteristics, these models are unrealistic in assuming an infinitely deep well. Nevertheless, no other model considers V_0 to have a value other than zero. The kinetic energy is the only other electronic energy considered by these models.

Jortner[38] has considered a self-consistent field (SCF) continuum dielectric model which also makes use of the Born expression. In this model the polarization energy is given by

$$\frac{e}{2} \left(1 - \frac{1}{D_s}\right) f_{1s}(R_b) \int_0^{R_b} \psi_{1s}^2 \, d\tau + \frac{e}{2} \left(1 - \frac{1}{D_s}\right) \int_{R_b}^{\infty} f_{1s}(r) \psi_{1s}^2 \, d\tau \qquad (9)$$

where ψ_{1s} was taken to be a hydrogen-like 1s wave function, and $f_{1s}(r)$ is defined for a spherically symmetric cavity by the relation

$$f_{1s}(r) = -\int_r^{\infty} \frac{P(t)}{t^2} \, dt \qquad (10)$$

with $P(t)$ defined as the fraction of the electronic charge within the region $r = 0 \rightarrow t$, e.g.,

$$P(t) = e \int_0^t |\psi_{1s}|^2 d\tau \tag{11}$$

For the case considered in this model, $f_{1s}(r)$ takes the form

$$f_{1s}(r) = -\frac{e}{r} + \frac{e(1 + \lambda r)\exp(-2\lambda r)}{r} \tag{12}$$

where λ is a variational parameter, the exponent of the 1s wave function. It should be noted that equation (9) approximates the Born expression if the electron is totally confined to the cavity and if R_b is large. The second integral relation of equation (9) is included because the electron outside the cavity also polarizes the medium. The kinetic energy of the electron and polarization energy given above are the only electronic energies considered in this SCF calculation.

Jortner[13] has also proposed a model that is similar to the polaron model of solid state physics. This polaron model correctly assumed that the electron is localized by the permanent dipoles and not by the optical (electronic) polarization of the liquid. By removing the optical polarization from the Born expression, which includes both optical and molecular polarizations, Jortner obtained the trapping potential

$$V(r) = -\frac{\beta_0 e^2}{R_b} \quad \text{for } r < R_b \tag{13-A}$$

$$= -\frac{\beta_0 e^2}{r} \quad \text{for } r > R_b \tag{13-B}$$

where $\beta_0 = (1/D_0 - 1/D_s)$ and D_0 (equal to 1.76 at $-33°$ C.) is the

optical dielectric constant. After the electron is trapped, a further lowering of the energy is obtained from the optical polarization which was taken into account in this model by the approximate relation

$$- \frac{e^2}{2\bar{r}} \left(1 - \frac{1}{D_0}\right) \tag{14}$$

where $\bar{r}$ is the mean radius of the electron. The kinetic energy was also included in the minimization of the energy with the potential given in equation (13). This model is very successful in explaining all of the qualitative features as well as many of the quantitative ones for the trapped electron.

Davydov[39] and Diegen[40] formulated polaron models similar to the one above but did not truncate the potential $V(r)$ (equation (13-A)) at the cavity boundary. Their formulations have been shown to be incorrect for metal-ammonia systems.[41]

Two models have considered the first coordination shell to be formed by several oriented point dipoles. The model of Land and O'Reilly[23,26] is based on the assumption that from 10 to 15 ammonia molecules will fit on the surface of the cavity with the same density as the bulk medium while a model due to Jortner[42] assumed that there were only 4 molecules on the surface. As in Jortner's[13] polaron model, the model of Land and O'Reilly[23,26] broke the permanent and optical polarizations into two parts, and included the optical polarization after minimizing the energy. The optical polarization was included in this model by a relation, similar to the Born expression,

$$- \frac{ze^2}{2R_m} \left(1 - \frac{1}{D_0}\right) \tag{15}$$

Since this model assumes some structure for the first coordination shell of molecules, the molecular polarization potential of the continuum was divided into regions that omit the first layer as follows:

$$-\beta_0 \int_{R_d}^{\infty} \frac{P(t)}{t^2} \, dt \quad \text{for } r < R_d \tag{16-A}$$

$$-\beta_0 \int_{r}^{\infty} \frac{P(t)}{t^2} \, dt \quad \text{for } r > R_d \tag{16-B}$$

where R_d is the distance from the center of the cavity to the continuum (Figure I-A). Even though this model had a discrete number of molecules on the surface of the cavity, it used dielectric constants which are bulk properties of the liquid.

Jortner[42] also assumed the potential given in equation (13-B) for his model with structure. This model used the molecular approach in handling the polarization when the electron is inside the cavity. The model assumed the potential

$$- \frac{N\alpha_0 e^2}{R_b^4} \quad \text{for } r_1 < R_b \tag{17}$$

for the molecules on the surface of the cavity and

$$- \frac{2\pi \bar{\rho}_d \alpha_0 e^2}{R_b + 2R_{NH_3}} \quad \text{for } r_1 < R_b \tag{18}$$

for the continuum where α_0 is the optical polarizability, $\bar{\rho}_d$ is the number density of the ammonia molecules in the bulk medium, and R_{NH_3} is the radius of the ammonia molecule (Figure I-B). These relations are based on the assumption that the charge is at the center of the cavity. Equation (18) does not contain the Lorentz screening which

has been shown by Lekner[43] to be important. The Lorentz screening

arises from the local field acting on the molecules in the liquid,

which consists of the direct field of the electron and the sum of all

other fields due to the dipoles induced on the neighboring molecules.

The deficiencies can be removed from equation (18) by using the rela-

tion derived by Springett, et al.[44] for excess electrons in helium.

The derivation of that equation and similar equations will be discussed

in Section B.

The structure models of Jortner[42] and Land and O'Reilly[23,26]

used the common charge-dipole potential

$$- \frac{Ne\mu_0}{R_m^2} \text{ for } r_1 < R_m \tag{19}$$

where N is the number of molecules in the first layer, μ_0 is the am-

monia dipole moment, and R_m is the distance from the center of the

cavity to the center of a molecule on the surface of the cavity

(Figure I-A). Although the model of Land and O'Reilly[23,26] did not

have the explicit form given in equation (19), it is in essence the

same if a uniform bulk density is assumed for the surface layer. In

Section D, we shall show that this latter feature is not correct. A

thermal average value of the dipole moment μ_{eff} was approximated from

the Langevin function in this model by the relation

$$\mu_{eff} = \mu_0 \left(1 - \frac{kT}{\mu_0 E_{loc}} \right) \tag{20-A}$$

where k is the Boltzmann constant, T is the absolute temperature of

the system under consideration, and E_{loc} is the local electric field

at the ammonia molecule. All of the reported calculations on this

model assumed that

$$E_{\ell oc} = \frac{ze}{R_m^2} \qquad (20\text{-}B)$$

where z is the amount of charge in the cavity. The value of z for any calculation should be obtained by a self consistent procedure if the electron is not totally confined to the cavity, but the calculations for this model were not obtained by such a procedure. Nevertheless, some of their results are general enough to be interpreted as though the procedure had been followed.

Land and O'Reilly[23,26] also took the charge-quadrupole interaction into account in the calculation of E_{em}. This interaction was obtained from the potential

$$+ \frac{zNQe}{R_m^3} \qquad (21)$$

where Q is the average quadrupole moment of the molecules.

Only the infinite-well cavity models of Lipscomb[12] and Stairs[36] have tried to determine the total energy of the system, E_T. The other calculations have assumed a radius for the cavity ad hoc and then carried out the calculation for the electronic energy. The models of Lipscomb[12] and Stairs[36] assumed that the surface energy E_{st} could be obtained from the relation

$$4\pi R_i^2 \Gamma \quad (R_i = R_b \text{ or } R_c) \qquad (22)$$

where Γ is the surface tension of the surface of the cavity. The proper choice for the value of the surface tension Γ is very difficult.

Scaled particle theory as reviewed by Frisch[31] gives the most appropriate choice of Γ for non-polar liquids by the relation

$$\Gamma = \Gamma_0 \left(1 + \frac{2\delta}{R_i}\right)^{-1} \tag{23}$$

where Γ_0 is the planar surface tension and δ is a parameter which is a measure of the curvature of the surface of a microscopic cavity. An inappropriate value for Γ was used in the Lipscomb[12] calculation and a value of Γ more in line with scaled particle theory was used in the calculation of Stairs.[36] Both models neglected the important structural changes in the first coordination shell of molecules.

From the binding energy E_T of a ground state electron, the solvation energy ΔH_1 of the electron can be obtained from the relation

$$-\Delta H_1 = E_T - \Pi - \Sigma \tag{24}$$

where Σ is the energy required to form the cavity and Π is the energy required to polarize the permanent dipoles of the solvent. From simple electrostatic arguments, the latter is obtained from the relation

$$\Pi = \frac{\beta_0}{8\pi} \int \vec{D} \cdot \vec{D} d\tau \tag{25}$$

where $\vec{D}$ is the electric displacement. A value for Π can also be obtained from the equivalent relation

$$\Pi = \tfrac{1}{2} \int \rho \Phi d\tau = \tfrac{1}{2} \int |\psi_{1s}|^2 \Phi d\tau \tag{26}$$

where ρ is the electron charge density, and Φ is the electrostatic potential resulting from the polarization. We find Φ and $\vec{D}$ from the relations

$$\nabla^2 \Phi = 4\pi e |\psi_{1s}|^2 \qquad (27)$$

and

$$\vec{D} = -\nabla \Phi \qquad (28)$$

where ∇ is the __del__ operator and ∇^2 is the Laplacian operator. The potential obtained from equations (27) and (28) is similar to the potential that is obtained for the interaction of two spherical charge distributions since the ground state wave function ψ_{1s} is spherically symmetric. A relation for obtaining Π was correctly formulated in the model of Land and O'Reilly[23,26] and was given by the relation

$$\Pi = \frac{\beta_o}{2} [\int_{R_d}^{\infty} G_o(r) |\psi_{1s}|^2 r^2 dr + G_o(R_d) P(R_d)] \qquad (29)$$

where $\beta_o G_o$ is the potential and $G_o(r)$ is defined by

$$G_o(r) = \frac{1}{r} \int_o^r |\psi_{1s}|^2 s^2 ds + \int_r^{\infty} |\psi_{1s}|^2 s ds \qquad (30)$$

The truncation of the potential at the continuum boundary is reasonable for the cavity species, but this neglects the orientational energy needed for the first coordination shell. The formula for calculation of Π in Jortner's[13] polaron model is incorrect as given. The relation was reported to be

$$-e \int_{R_b}^{\infty} V(r) \psi_{1s}^2 4\pi r^2 dr \qquad (31)$$

where $V(r)$ is given in equation (13-B). This relation does not take into consideration the polarization arising from the charge in the cavity.

The energy Σ was also included in the model of Land and O'Reilly.[23,26] By creating a cavity in a metal-ammonia solution, the molecules on the surface of the cavity will not be interacting with as many molecules as a molecule in the bulk liquid. Thus Σ is taken as a measure of the energy difference created by the loss of interactions, mainly short range ones. Estimates of this energy were performed by Land and O'Reilly[23,26] with the relation

$$\Sigma = \frac{4\pi}{3} \frac{R_0^3}{V_m} \Delta H_{vap} \tag{32}$$

where ΔH_{vap} (equal to 0.00889 Hartrees at $-33^\circ C$) is the heat of vaporization per molecule, V_m is the volume of an ammonia molecule, and R_0 is the distance from the center of the cavity to a distance R_{NH_3} from the center of the molecules in the first coordination shell (Figure I-A). The expression given in equation (32) takes into account many factors that would be hard to handle separately, but overestimates Σ by over emphasizing long-range interactions. Since the cavity is formed by pushing molecules aside and not by removing molecules from the solution, another procedure is needed. Short range interactions are most important in estimates of Σ. We shall propose an expression intermediate between these in Section D.

4. PREVIOUS MODELS OF TWO-ELECTRON CAVITY

Calculations involving the two-electron cavity have been carried out for only the Ogg[8] and Land and O'Reilly[23,26] models. Applying first-order perturbation theory, Ogg[8] found that the total

energy of the two-electron, infinite-well cavity species was

$$\frac{h^2}{4mR_b^2} - \frac{2e^2}{R_b}\left(1 - \frac{1}{D_s}\right) + \int \frac{e^2}{r_{12}} \psi_{1s}^2 \, d\tau \qquad (33)$$

where h is Planck's constant, m is the electronic mass, the first term is the kinetic energy of the two electrons, the second term is four times the one-electron polarization energy since this term depends on the square of the amount of charge in the cavity, and the integral is the average electron-electron repulsion. The r_{12} in the integral of equation (33) is the distance between the electrons (Figure II). Ogg estimated the value of the integral to be $\frac{e^2}{R_b}$. With this value for the Coulomb integral, the two-electron cavity species is found to be stable relative to two one-electron cavities. Hill[25] showed that the repulsion was actually $\frac{1.79 \; e^2}{R_b}$. This interaction energy makes the two-electron species unlikely at zero concentration and zero temperature. However, Hill was able to show that at finite concentrations and at reasonable temperatures the two-electron species would actually be preferred, e. g. at 0.1 M and $220°K$ he predicted that 72 percent of the electrons could be paired if there were no other competing equilibria. The inadequacy of the one-electron infinite-well cavity species discussed above is also applicable to the Ogg[8] two-electron model.

The binding energies of the two-electron cavity species investigated by Land and O'Reilly[23,26] were taken to be

$$E_{1_s} = 2E_{1s} + \langle G \rangle \qquad (34)$$

and

$$E_{1_P} = E_{1s} + E_{2p} + \langle G \rangle \qquad (35)$$

where E_{1_s} is the energy of the $(1s)^2$ ground state, E_{1_P} is the energy of the lowest ^1P state, and E_{1_s} and E_{2p} are the one-electron 1s and 2p energies respectively. This model combined the repulsive inter-action of the two electrons in the cavity with the polarization interaction that is induced because of the second electron in the cavity to obtain an "effective" repulsive interaction. This "effec-tive" repulsive interaction was reported to be

$$G(r) = G_0(r) - (1 - \frac{1}{D_0})G_0(R_m) \text{ for } r \leq R_m \qquad (36\text{-A})$$

$$= G_0(r)/D_0 \qquad \qquad \text{for } r \geq R_m \qquad (36\text{-B})$$

All of the electron-electron repulsion integrals were expressed in the form given in equation (36) in these calculations. The polariza-tion interaction part of equation (36) was obtained by an expansion of the potential of the addition electron in spherical harmonics. The two-electron calculations of the model were carried out for R_0 equal to 11 a_0 which was chosen __ad__ __hoc__ and will be shown to be inap-propriate in Section D.

The heat of solution ΔH_2 of the two-electron species was obtained in the calculation of Land and O'Reilly[23,26] by the relation

$$-\Delta H_2 = E_{1_s} - \Pi - \Sigma \qquad (37)$$

where Π is four times the relation given in equation (31), and Σ was obtained from equation (34). The heat of the reaction given in

equation (4) was obtained from

$$\Delta H_{21} = \tfrac{1}{2}\Delta H_2 - \Delta H_1 \tag{38}$$

5. GENERAL CONCLUSIONS CONCERNING PREVIOUS MODELS

Of the models considered, the Jortner[13] polaron model

gives the most consistent agreement with experimental quantities

while the model of Land and O'Reilly[23,26] seems to be the most con-

sistent in its formulation of the problem. Because of the emphasis

on long range interactions in Jortner's[13] polaron model and on the

short range interactions in the model of Land and O'Reilly, the

question of which is the more important is still open. The results

of these two calculations are given in Table I so that they can be

compared with the results that we have obtained. The one-electrons s

to p transition energy is denoted by ΔE_{ps} and the two-electron by

ΔE_{ps}^2.

In the models previously considered, polarization inter-

actions have been assumed to be the most important stabilizing factors

of the cavity species. Only in Jortner's[42] structure model was the

short-range electronic polarization considered, explicitly, i.e.,

the polarization of the surface molecules. The calculation of Land

and O'Reilly,[23,26] which included the multipole interactions of the

electron, is a strong indication of the importance of the electron-

dipole interaction. This model assumed that all of the electronic

polarization could be characterized by a bulk property. This assump-

tion is not very good because of the close proximity of the maximum

TABLE I

EXPERIMENTAL AND PREVIOUS THEORETICAL RESULTS[b]

(A) Results obtained by Jortner from his polaron model of the one-electron cavity species in ammonia at -33°C.[a]

$R_0(a_0)$	E_{1s}	E_{2p}	Π	$-\Delta H_1$	ΔE_{ps}
5.67	-0.0796	-0.0482	0.0182	0.0616	0.0313
6.05	-0.0764	-0.0475	0.0175	0.0590	0.0299
6.52	-0.0724	-0.0453	0.0154	0.0572	0.0273

(B) Results obtained by Land and O'Reilly for the one- and two-electron cavity species in ammonia at 27°C. The one-electron cavity was assumed to have $R_0 = 9\ a_0$ and two-electron cavity was assumed to have $R_0 = 11\ a_0$.[c]

	$-\Delta H_1$	ΔE_{ps}	ΔE_{ps}^2	ΔH_{21}
Calculated	0.124	0.042	0.023	-0.033
Experimental[d]	0.062 ± 0.03	0.033	0.030[e]	0.006[e]

[a] Results taken from Reference (13).

[b] Energies are given in Hartree units.

[c] Results taken from Reference (26).

[d] Results taken from Reference (2).

[e] Unconfirmed results. See Reference (24).

electron density to the surface molecules. In addition, all of the models have neglected the energy of a quasi-free electron in the medium. Until a value of V_O is determined, the validity of this assumption is questionable.

The most important feature of the cavity species has in fact been neglected in all of the reasonable models; namely the cavity has not been shown to be stable. Without this latter point, models can always be adjusted to yield the correct experimental parameters without proving the validity of the model or providing insight into the problems of electrons in other solvents. Only when the stability problem is treated correctly can one hope to provide a consistent picture of why the cavity forms as well as how it should be dependent on such factors as temperature and pressure. Only when we have an adequate model can such details as the asymmetry of the band and volume expansion data be discussed.

B. FORMULATION OF THE HAMILTONIANS

To expect realistic numbers from a model calculation requires that the model be brought as close to reality as possible. We have assumed a very dilute metal-ammonia solution so that ion-electron interactions can be neglected. In studying the problem of electrons in polar as opposed to non-polar liquids one faces many rather serious problems which limit the accuracy one can expect. The most serious aspect involves hydrogen bonding. At the level of a semi-empirical study one can only pay a limited amount of attention to this vital

problem. In what follows we have considered its influence to be weak, at least weaker than electrostatic effects acting on the <u>first</u> layer of polar molecules surrounding the electron cavity. We have assumed that beyond the first layer hydrogen bonding and statistical effects dominate over electrostatic orienting effects especially since electrostatic effects are rapidly screened by the dielectric constant. In this model such assumptions are probably adequate for ammonia but possibly suspect for strongly hydrogen bonded liquids like water.[27] Another aspect that might be considered serious is the distortion of the molecules in the first layer caused by the electrostatic field of the electron in the cavity, but this distortion has been shown to be adequately taken into account by a (linear) polarization.[44]

In this section we will formulate the model for the one- and two-electron cavity species of metal-ammonia solutions. We have taken a very molecular point of view and used molecular parameters whenever possible. The model that we have considered consists of N polarizable, spherical molecules symmetrically distributed on the surface of a spherical cavity with a polarizable continuum outside the first coordination shell of molecules. At the center of each molecule we have assumed that there is a point dipole which has its dipole moment oriented toward the center of the cavity. We have also assumed that at the center of each molecule there is a point quadrupole which is cylindrically symmetric along the dipole moment axis. With these multipole moments we have been able to specify the moments with scalar quantities.[46] Each molecule will be assumed to have a hard core radius

R_H (Figure I-A) which would be characteristic of an electron scattering

cross section with polarization and multipole interactions removed. As

is the usual case, this hard-core radius R_H is less than the average

radius R_{NH_3} (approximately equal to 3.66 a_0 at -33°C) of the molecule

in the bulk liquid.[47,48] The electronic polarization of each molecule

is assumed to be characterized by the optical polarizability α_0. For

lack of a molecular counter part, the β_0 used in the previous models

has been used to account for the molecular polarization in the con-

tinuum beyond the first layer.

The hard-core radius R_H mentioned above defines the region

in which one must worry about the internal structure of the ammonia

molecule. Based on many molecules Bader, Henneker, and Cade[48] have

defined a criterion for such a hard core. Using the ammonia molecule

charge distributions of Bader and Jones[49] a value of 1.85 a_0 is obtained.

Since such charge distributions can be poor, a value of 2.0 a_0 was also

tried with but a slight effect.

We shall now formulate the Hamiltonian that we have used

for the one-electron cavity species. The various parts of the

Hamiltonian will be expressed in Hartree units. With the electron

at an arbitrary point in the cavity, the electron-dipole potential

takes the form

$$V_{e\mu}^i = -\frac{\mu_{eff} \cos \theta_a}{\rho_1^2} \tag{39}$$

where $\underline{i}$ indicates that the electron is interacting with the $\underline{i}$th mol-

ecule, and ρ_1 and θ_a are defined as shown in Figure II. We have

Figure II. Coordinates used in the
            various potentials.

31
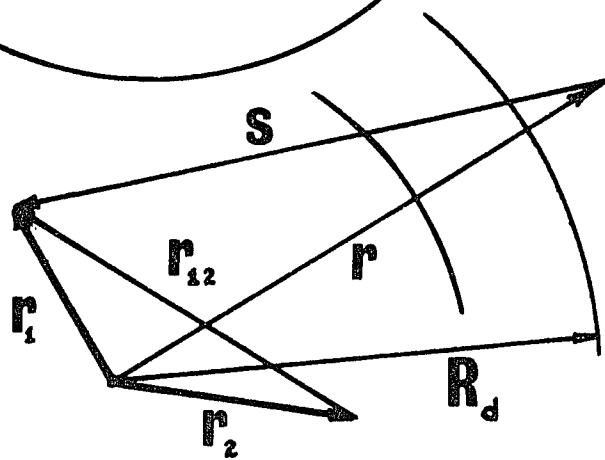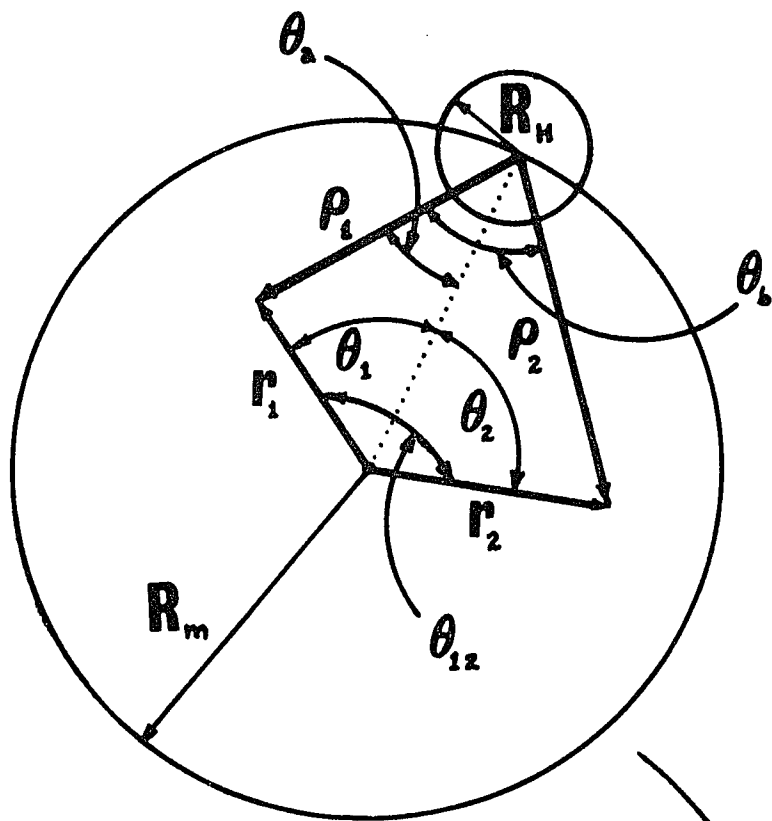
assumed that the thermal average magnitude of the dipole moment can be

obtained from the high field limit as expressed in equation (20-A)

with the amount of charge, z, used in determining E_{loc} (equation (20-B)),

taken as the amount of charge in the region 0.0 to R_c (Figure I-A).

This region will be referred to as the void region. The value of z

was obtained through a self consistent procedure. We have taken the

gas phase dipole moment for μ_0 equal to 0.574 a_0 (1.47 Debye).[49]

With the electron at an arbitrary point in the cavity, the

electron-quadrupole potential takes the form

$$V_{eQ}^i = + \frac{Q}{\rho_1^3} \tfrac{1}{2}(3\cos^2\theta_a - 1) \tag{40}$$

where ρ_1 and θ_a are the same as defined above. A thermal average

was not considered for the magnitude of the quadrupole moment since

this term makes only a small contribution (less then twenty percent)

to the total energy and the actual electron-quadrupole interaction

would be very difficult to handle. We have taken a theoretical value

for the quadrupole moment Q equal to 0.82 a_0^2.[49] This quadrupole

moment is smaller than some of the experimental values but the

difference makes only a minor contribution to the final energies.[46]

The potential energy of an induced dipole (polarization)

in an electric field $\vec{\mathcal{E}}$ is

$$-\tfrac{1}{2} \vec{\mathcal{E}} \cdot \overset{\leftrightarrow}{\alpha}_0 \cdot \vec{\mathcal{E}} \tag{41}$$

where $\overset{\leftrightarrow}{\alpha}_0$ is the polarizability tensor of a molecule under considera-

tion.[46] Because the ammonia molecule has an almost uniform

polarizability tensor we have approximated the tensor with a scalar

polarizability α_0 (equal to 15.3 a_0^3) times a unit tensor.[46] With

this assumption equation (41) reduces to

$$- \frac{\alpha_0}{2} \vec{\mathcal{E}} \cdot \vec{\mathcal{E}} \tag{42}$$

For the one-electron cavity species we have assumed that the electric

field is the one-electron field

$$\vec{\mathcal{E}}_1 = - \frac{\vec{\rho}_1}{\rho_1^3} \tag{43}$$

Thus we have found that the induced dipole potential for each of the

molecules for the one-electron cavity species takes the form

$$V_{pol}^i = - \frac{\alpha_0}{2\rho_1^4} \tag{44}$$

The contribution of the long range electronic polarization potential

exerted by the molecules in the continuum can be expressed in the form[44]

$$V_{pol}^c = - \frac{\alpha_0 \bar{\rho}_d}{2} \int g(r) \frac{1}{s^4} L(r) d\tau \tag{45}$$

where r is the distance from the center of the cavity to an arbitrary

point in the medium, s is the distance from the electron to the point

in the medium (Figure II), $\bar{\rho}_d$ is the number density of the bulk dielec-

tric continuum, and the integration over the volume includes the volume

of the continuum only. The c superscript denotes an electron-continuum

interaction. Here, g(r) is the radial distribution function relative

to the center of the cavity which we shall approximate by the relation

$$g(r) = 0 \qquad r < R_d (= R_m + R_{NH_3}) \qquad (46)$$

$$= 1 \qquad r > R_d$$

To provide a rough estimate of the screening function $L(r)$ we have taken the form that Lekner[35] has shown to be adequate for liquid argon, i.e.,

$$L(r) = 1 \qquad \text{for } r < R_d \qquad (47)$$

$$= \frac{1}{(1 + \frac{8\pi\alpha_o\bar{\rho}_d}{3})} \text{ for } r > R_d$$

Combining equations (45), (46) and (47) yields the integral relation

$$V^c_{po\,\ell} = - \frac{\alpha_o\bar{\rho}_d}{(1 + \frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \int_{R_d}^{\infty} \frac{1}{s^4} d\tau \qquad (48)$$

which yields on integrating over the region R_d to infinity

$$V^c_{po\,\ell} = - \frac{\pi\alpha_o\bar{\rho}_d}{2(1 + \frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \left[\frac{2R_d}{(R_d^2 - r_1^2)} + \frac{1}{r_1}\ell n \left\{ \frac{r_1 + R_d}{R_d - r_1} \right\} \right]$$

$$\text{for } r_1 < R_d - R_H \quad \text{and if} \qquad (49)$$

the electron is in the continuum region equation (49) is not applicable. To determine the electronic polarization for this region we have assumed that the potential is determined by the amount of charge enclosed in a spherical region. To keep in line with the molecular approach we have assumed that we can use the Clausius-Mossotti relation to convert $(1 - \frac{1}{D_o})$ to molecular parameters. The resulting

potential for the electronic polarization for the electron in the con-
tinuum is found to be for the region not considered by equation (49)

$$V^c_{po\ell} = - \frac{2\pi\alpha_o\bar{\rho}_d}{(1 + \frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \frac{1}{r_1} \qquad \text{for } r_1 > R_d - R_H \qquad (50)$$

The molecular polarization of the continuum has been included by using
the potential that was used in Jortner's[13] polaron model and approximately
equal to the potential used by Land and O'Reilly[23,26]:

$$V^c_{mpo\ell} = - \frac{\beta_Q}{R_d} \qquad \text{for } r_1 < R_d \qquad (51)$$

$$= - \frac{\beta_Q}{r_1} \qquad \text{for } r_1 > R_d$$

In some of the preliminary calculations we considered V_O
as the two separate effects mentioned in the Introduction, but later
abandoned this approach since an experimental investigation would not
be able to distinguish between the amount of contribution that each
would make separately to the total energy. It is of interest to con-
sider how we handled the determination of the electron-molecule inter-
action for the surface since such a technique might be used if the
external contribution to V_O is ever evaluated. We have tried to
approximate the repulsion by fitting electron-neon (no polarization
included) scattering cross sections to a simple $B e^{-A\rho_1}$ potential
since neon is isoelectric with the ammonia molecule. Some adjustment was
made for the larger size of the ammonia molecule relative to neon.
The stability of the cavity, however, was not very sensitive to the
parameters A and B for the case where the external V_O was assumed to
be zero. In our final calculations we have assumed that V_O can be

approximated with one empirical parameter. We have assumed that the electron will interact with a barrier of height V_0 defined by the relation

$$V_0(r_1) = 0 \qquad \text{for } r_1 < R_c \qquad (52)$$

$$= V_0 \qquad \text{for } r_1 > R_c$$

For the two-electron species we must consider several additional potentials. The electron-electron interaction potential takes the familiar form $1/r_{12}$ but several cases must be considered since each of the electrons has a probability of being outside the cavity where the dielectric screening must be considered. With the screening taken into account from a molecular point of view and remembering that only the electronic polarization responds to the instantaneous positions of the electrons, the repulsive potential takes the form

$$V_{Coul.} = \frac{1}{r_{12}} \qquad r_1 < R_c; \; r_2 < R_c \qquad (53)$$

$$= \frac{(1 - \frac{4\pi}{3}\alpha_0\bar{\rho}_\ell)}{(1 + \frac{8\pi}{3}\alpha_0\bar{\rho}_\ell)} \frac{1}{r_{12}} \qquad \begin{array}{l} \text{for } r_1 < R_c, \; r_2 > R_c; \\ \quad\quad r_1 > R_c, \; r_2 < R_c \end{array}$$

$$= \frac{(1 - \frac{4\pi}{3}\alpha_0\bar{\rho}_d)}{(1 + \frac{8\pi}{3}\alpha_0\bar{\rho}_d)} \frac{1}{r_{12}} \qquad \text{for } r_1 \text{ and } r_2 > R_c$$

where we have expressed $1/D_{op}$ in terms of polarizability which is obtained from the Clausius-Mossotti relation in the manner shown to be appropriate by Lekner.[43] We have assumed that the number density of the first layer $\bar{\rho}_\ell$ is appropriate for the screening when one of the electrons is outside of the void region and the number density

of the bulk medium $\bar{p}_d$ is appropriate when both electrons are outside

of the void region.

When both electrons are inside the cavity, the electron-

electron interaction is mediated by the polarization of the ammonia

molecules in the liquid. In the model that we have considered, this

mediation comes from the interaction of the electrons with the

first layer and with the continuum. If the electric field is defined

for the two-electron species by

$$\vec{\mathcal{E}}_2 = -\frac{\vec{p}_1}{p_1^3} - \frac{\vec{p}_2}{p_2^3} \tag{54}$$

where p_1 and p_2 are shown in Figure II, the potential is found by

using equation (42) to be

$$-\frac{\alpha_o}{2p_1^4} - \frac{\alpha_o}{2p_2^4} - \frac{\alpha_o \cos\theta_b}{p_1^2 p_2^2} \tag{55}$$

where θ_b is shown in Figure II. The first two terms of this

equation are the polarization of each of the electrons while the

third term

$$V_{2po\ell}^i = -\frac{\alpha_o \cos\theta_b}{p_1^2 p_2^2} \tag{56}$$

is the polarization interaction arising from an additional electron

in the cavity. Equation (56) has been converted to coordinates

relative to the center of the cavity to yield the following relation

for the polarization interaction with a molecule in the first

layer (Appendix II):

$$V_{2po\ell}^{i} = -\frac{\alpha_o}{2} \sum_{n=o}^{\infty} \sum_{m=o}^{\infty} \frac{r_1^n r_2^m}{R_m^{n+m+2}} \{ \frac{(2m+1)}{(R_m^2-r_2^2)} + \frac{(2n+1)}{(R_m^2-r_1^2)} - \frac{r_{12}^2(2n+1)(2m+1)}{(R_m^2-r_1^2)(R_m^2-r_2^2)} \} P_n(\cos\theta_1)P_m(\cos\theta_2)$$

$$(57)$$

where $P_n(\cos\theta)$ is a Legendre polynomial in terms of $\cos\theta$. The

polarization interaction with the continuum arising from equation

(56) is found to be given by (Appendix III)

$$V_{2po\ell}^{c} = -\frac{4\pi\alpha_o\bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \sum_{n=o}^{\infty} \frac{(n+1)}{(2n+1)} \frac{r_1^n r_2^n}{R_d^{2n+1}} P_n(\cos\theta_{12}) \qquad (58)$$

If we were to combine equations (53),(57) and (58) we would have

an expression similar to the "effective" repulsion used in the model

of Land and O'Reilly[23,26] (equation (36)).

The kinetic energies of the one- and two-electron species

were obtained from the common kinetic energy operators

$$T_1 = -\frac{1}{2}\nabla_1^2 \qquad (59)$$

for the one electron species and

$$T_2 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 \qquad (60)$$

for the two-electron species. Combining the various one-electron

potentials with the kinetic energy we obtain the Hamiltonian for the

one-electron species

$$\mathcal{H}_1 = T_1 + \sum_{i=1}^{N} \{V_{e\mu}^i + V_{eQ}^i + V_{po\ell}^i\} + V_{po\ell}^c + V_{mpo\ell}^c + V_o \tag{61}$$

where N is the number of molecules in the first layer. The
two-electron Hamiltonian is given by

$$\mathcal{H}_2 = T_2 + \sum^{electrons} [\sum_{i=1}^{N} \{V_{e\mu}^i + V_{eQ}^i + V_{po\ell}^i\} + V_{po\ell}^c + V_{mpo\ell}^c + V_o] + V_{Coul.} + \sum_{i=1}^{N} V_{2po\ell}^i + V_{2po\ell}^c$$

$$\tag{62}$$

In the next section we present trial wavefunctions and
evaluate the integrals of the various potentials to obtain the
electronic energies.

C. METHOD OF CALCULATION AND RESULTS FOR THE ELECTRONIC ENERGIES

To begin this calculation, some assumptions had to be made
about the liquid structure. Since little is known of this even in
the pure liquid, we have based this model on what is known about the
solid. We have assumed that there are twelve or eighteen molecules
in the first coordination shell of molecules since the solid crystalizes
in a slightly distorted cubic-close-packed (ccp) structure.[50] This
structure for the first layer would be analogous to having a vacant
lattice site at which the electron is confined. The structure of
twelve-molecule first layer is shown in Figure III. Since a ccp
structure has only twelve nearest neighbors for each site in the
lattice, we have assumed that an additional molecule could reside
on each of the six faces of the ccp structure and give rise to the

eighteen-molecule first layer. One of the additional molecules for the 18 molecule configuration is shown in Figure IV-A. Other numbers of surface molecules might be considered, but for the size cavities suggested by volume expansion data this seems unlikely. Cavities could exist with from six to twenty molecules in the first layer, but the most probable number is between eight and eighteen. A distribution of cavities with different numbers of molecules on the surface could explain some of the asymmetry of the spectra of the one-electron species.

For the one-electron species the lowest S state wavefunction was assumed to be of the form (unnormalized)

$$1S_A = (1 + \alpha r + \beta r^2)e^{-\gamma r} Y_{oo}(\theta,\phi) \tag{63}$$

and the first P state wavefunction was assumed to be of the form

$$2P_{Alm} = re^{-\xi r} Y_{1m}(\theta,\phi) \tag{64}$$

where α, β, γ and ξ are variational parameters and $Y_{\ell m}(\theta,\phi)$ is a spherical harmonic. The notation 1s and 2p is used in analogy with atomic calculations. In the case of the two-electron species the ground state wavefunction was

$$\psi_{SCF} = 1S_B(1)1S_B(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{65}$$

where the subscript B refers to a different set of parameters than those obtained for the one-electron species and $\alpha(i)$ and $\beta(i)$ are spin functions. The two model calculations that have previously

Figure III.   Positions of molecules in ccp structure
that are used in the 12 molecule model.
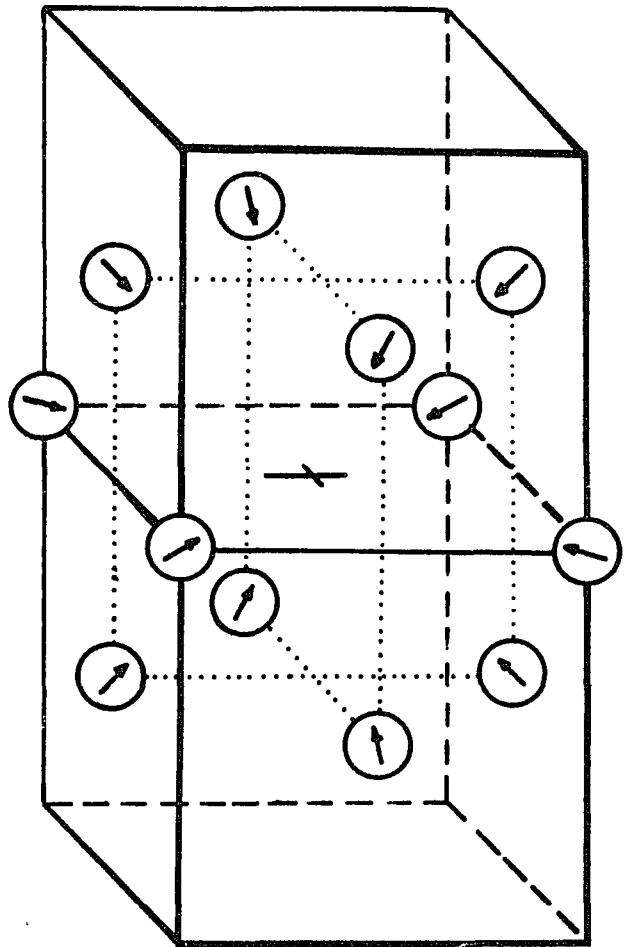The arrows indicate centrally oriented
point dipoles.

Figure IV. Possible positions for additional molecules on the ccp structure. The arrows with crosses indicate the additional molecule.

    (A) Position of one of six additional molecules. This structure is used in the 18 molecule model.

    (B) Position of one of eight additional molecules.

(A)
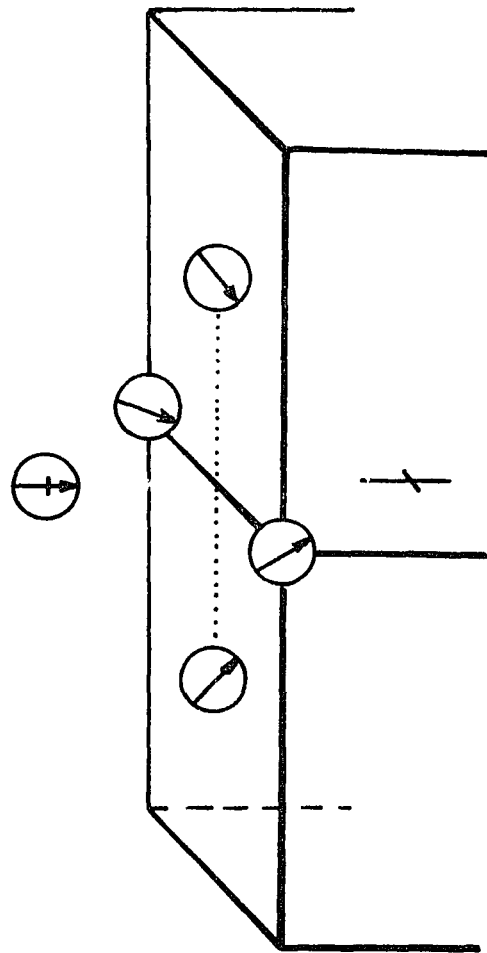
(B)
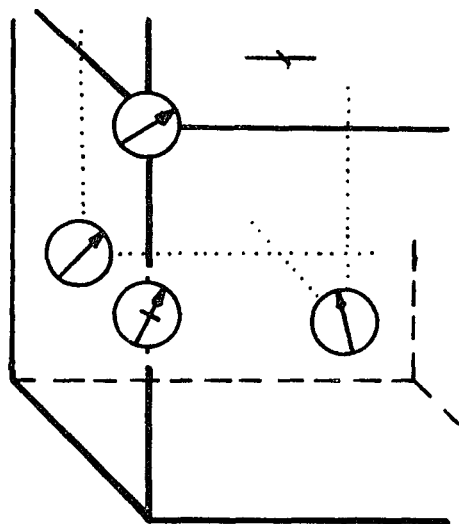
considered the two-electron species (Section A) have neglected electron correlation effects, namely the reduction of the electron repulsion when the electrons are allowed to avoid one another. We have determined that the correlation energy δE_2 is almost one electron volt for the system used in the Ogg[8] model (Appendix I). Because correlation energy is an unknown factor that should be considered in determining the stability of the two-electron species, we have carried out a configuration interaction (CI) procedure to determine the correlation energy. The correlation energy δE_2 for the system considered is defined as the difference between the energy obtained for the configuration interaction and the energy obtained with the uncorrelated ground state wavefunction. The correlated wavefunction was assumed to be of the form

$$\psi_{CI} = c_1 \psi_{SCF} + \frac{c_2}{\sqrt{3}} [2p_{B11}(1) 2p_{B1-1}(2) + 2p_{B1-1}(1) 2p_{B11}(2)$$

$$- 2p_{B10}(1) 2p_{B10}(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \qquad (66)$$

where $2p_{B1m}$ is the appropriate 2p excited orbital with appropriately optimized parameters. The $2p_{B1m}$ was obtained by optimizing the first excited ^1P state wavefunction

$$\psi_{1_P} = \frac{1}{\sqrt{2}} \{1S_B(1) 2p_{B10}(2) + 1S_B(2) 2p_{B10}(1)\} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$(67)$$

where $1S_B(1)$ was obtained by optimizing the wavefunction given in equation (65).

For the trial functions given above we may compute the
quantity

$$E = \int \Phi_j^* \mathcal{H}_j \Phi_j \, d\tau \,, \tag{68}$$

the expectation value of the energy of the system in a normalized
state Φ_j where the subscript j denotes a one- or two-electron
state. By applying the variational method to equation (68) we have
obtained the energies of the systems under consideration. Since the
excited state wavefunctions are orthogonal to the ground state
wavefunctions for a given j, the variational method is also applicable
for determining the energies for excited states. We have minimized
the energies by a brute force technique since several of the expressions
involved are not simple. Since the angular dependence of the various
potentials can be readily integrated out of equation (68), we shall
give the resulting radial integrals that we have evaluated to determine
the electronic energies.

For the centrally oriented dipoles of the 12 and 18 molecule
models, the electron-dipole interaction energy is given by

$$\langle \Phi_1 \mid \sum_{i=1}^{N} V_{e\mu}^i \mid \Phi_1 \rangle = \frac{-N\mu_{eff}}{R_m^2} \int_o^{R_c} |\psi|^2 \, r^2 dr \tag{69}$$

where ψ is a normalized one-electron radial wavefunction. This result is
obtained by simply converting the coordinate system of equation (39)
to bicentric coordinates and integrating.[51] Because we have assumed
that the molecules of the first layer are spherically distributed on
the surface of the cavity, equation (69) is also valid for the p state

wavefunctions. Similarly we have obtained the electron-quadrupole

interaction energy of equation (40):

$$\langle \Phi_1 | \sum_{i=1}^{N} V_{eQ}^i | \Phi_1 \rangle = \frac{+NQ}{R_m^3} \int_0^{R_c} |\psi|^2 r^2 dr \tag{70}$$

When an electron is in the layer of molecules, i.e., in the region

R_c to $R_m + R_H$, the electron still interacts with the multipole moments.

The electron-dipole interaction for this region is

$$\frac{-N\mu_{eff}}{4R_m} \frac{(1-\frac{4\pi}{3}\alpha_o\bar{\rho}_\ell)}{(1+\frac{8\pi}{3}\alpha_o\rho_\ell)} \left[\frac{2}{R_m} \int_{R_c}^{R_m+R_H} |\psi|^2 r^2 dr + \frac{R_m^2 - R_H^2}{R_H \, R_m} \int_{R_c}^{R_m+R_H} |\psi|^2 r dr \right.$$
$$\left. - \frac{1}{R_m R_H} \int_{R_c}^{R_m+R_H} |\psi|^2 r^3 dr \right] \tag{71}$$

The dielectric screening (polarization screening) is included in this

expression since the molecules will screen the electron-dipole

interactions. The energy arising from equation (71) is only a minor

contribution to the total electronic energy. We have neglected the

electron-dipole interaction for the continuum region and have neglected

the electron-quadrupole interaction except in the region considered

by equation (70) for reasons considered in the early part of Section B.

The electronic polarization of the first layer of molecules

was obtained from the relations

$$\langle \Phi_1 | \sum_{i=1}^{N} V_{pol}^i | \Phi_1 \rangle = - \frac{N\alpha_o}{2} \int_0^{R_c} \frac{|\psi|^2 r^2}{(R_m^2 - r^2)^2} dr \tag{72-A}$$

$$- \frac{N\alpha_o}{8(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_\ell)} \frac{1}{R_m R_H^2} \int_{R_c}^{R_m+R_H} |\psi|^2 r\, dr \qquad (72\text{-}B)$$

$$- \frac{N\alpha_o}{2(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \int_{R_m+R_H}^{\infty} \frac{|\psi|^2 r^2}{(r^2-R_m^2)^2}\, dr \qquad (72\text{-}C)$$

where equation (72-B) is approximated from

$$- \frac{N\alpha_o}{8(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_\ell)} \frac{1}{R_m}\left[\frac{1}{R_H^2}\int_{R_c}^{R_m+R_H} |\psi|^2 r\, dr - \int_{R_c}^{R_m+R_H} \frac{|\psi|^2 r\, dr}{(R_c+r)^2}\right] \qquad (73)$$

Three regions are used to evaluate equation (44) since the polarization interaction of the electron with a molecule is not appropriate inside the hard core of the molecule.[44] The results given in equations (72) and (73) are obtained from simple bicentric coordinate integrations. We have included the appropriate Lorentz screening factors in equations (72) and (73). The electronic polarization of the continuum is easily obtained from equations (49) and (50):

$$\langle \Phi_1 | V_{po\ell}^c | \Phi_1 \rangle = - \frac{\pi\alpha_o\bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)}\left[\int_0^{R_d-R_H} |\psi|^2 \left\{ \frac{R_d r}{(R_d^2-r^2)} + \frac{1}{2}\ell n\left[\frac{r+R_d}{R_d-r}\right]\right\} r\, dr\right] \qquad (74\text{-}A)$$

$$- \frac{2\pi\alpha_o\bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \int_{R_d-R_H}^{\infty} |\psi|^2 r\, dr \qquad (74\text{-}B)$$

Equation (51) yields for the molecular polarization the simple result:

$$\langle \Phi_1 | V_{mpo\ell}^c | \Phi_1 \rangle = - \frac{\beta_o}{R_d} \int_0^{R_d} |\psi|^2 r^2\, dr \qquad (75\text{-}A)$$

$$- \beta_o \int_{R_d}^{\infty} |\psi|^2 r\, dr \qquad (75\text{-}B)$$

From equation (52) we obtain the repulsive interaction of an electron with the medium molecules, i.e., with the first layer and the continuum:

$$\langle \Phi_1 | V_o | \Phi_1 \rangle = V_o \int_{R_c}^{\infty} |\psi|^2 \, r^2 dr \tag{76}$$

Using the appropriate one-electron wavefunction ψ we have determined the electronic energies, E_e, for the s and 2p states for the values of the parameter V_o equal to 0.0, 0.01838, 0.03675, and 0.07350 Hartrees (which are respectively 0.0, 0.5, 1.0, and 2.0 eV). The 12 molecule results are given in Tables II and III, and the 18 molecule results in Tables IV and V.

We have also obtained the oscillator strengths for the various transitions from the relation

$$O_{ps} = \frac{2}{3} \Delta E_{ps} \, |\langle 1s_A | z | 2p_{A10} \rangle|^2 \tag{77}$$

where ΔE_{ps} is the 1s to 2p transition energy and $\langle 1s_A | z | 2p_{A10} \rangle$ is the value of the transition dipole. Values of the oscillator strength were found to be fairly constant for the cavities considered for a given value of V_o. Some values of the oscillator strengths will be given in the next section.

We shall now consider how we have obtained the electronic energies for the two-electron species. With the Hamiltonian $\mathcal{H}_2$ in equation (68) we have taken the parameters α and β from the one-electron calculations and have minimized the ^1S and ^1P energies

TABLE II

ELECTRONIC ENERGIES AND WAVE FUNCTION PARAMETERS FOR

ONE-ELECTRON-TWELVE-MOLECULE CAVITY

R_c	α	β	γ	E_{1s}^a	ξ	E_{2p}	ΔE_{ps}
$V_0 = 0.00$ eV							
5.00	2.01	-0.141	0.36953	-0.19328	0.37734	-0.12902	0.06427
5.25	2.02	-0.136	0.35234	-0.18245	0.36328	-0.12328	0.05917
5.50	2.07	-0.134	0.33672	-0.17262	0.34922	-0.11793	0.05469
5.75	2.10	-0.131	0.32266	-0.16365	0.33828	-0.11293	0.05072
6.00	2.09	-0.126	0.30859	-0.15540	0.32578	-0.10824	0.04716
6.25	2.17	-0.126	0.29766	-0.14787	0.31641	-0.10388	0.04399
6.50	2.21	-0.124	0.28672	-0.14092	0.30547	-0.09979	0.04112
6.75	2.21	-0.120	0.27578	-0.13447	0.29609	-0.09595	0.03853
7.00	2.28	-0.120	0.26641	-0.12854	0.28828	-0.09236	0.03618
$V_0 = 0.50$ eV							
5.00	1.91	-0.139	0.38359	-0.18620	0.38984	-0.11721	0.06900
5.25	1.90	-0.133	0.36641	-0.17550	0.37578	-0.11168	0.06382
5.50	1.88	-0.127	0.35078	-0.16576	0.36328	-0.10652	0.05925
5.75	1.87	-0.122	0.33672	-0.15688	0.35078	-0.10169	0.05519
6.00	1.91	-0.120	0.32578	-0.14877	0.33984	-0.09719	0.05158
6.25	1.89	-0.115	0.31328	-0.14131	0.33047	-0.09298	0.04833
6.50	1.88	-0.111	0.30234	-0.13445	0.32109	-0.08904	0.04541
6.75	1.89	-0.108	0.29297	-0.12814	0.31172	-0.08536	0.04278
7.00	1.89	-0.105	0.28359	-0.12229	0.30234	-0.08191	0.04038

[a]Energies are in Hartree units.

TABLE III

ELECTRONIC ENERGIES AND WAVE FUNCTION PARAMETERS FOR
ONE-ELECTRON-TWELVE-MOLECULE CAVITY

R_c	α	β	γ	E_{1s}^a	ξ	E_{2p}	ΔE_{ps}
$V_0 = 1.00$		eV					
5.00	1.87	-0.141	0.39766	-0.17973	0.40234	-0.10583	0.07389
5.25	1.83	-0.133	0.38047	-0.16914	0.38828	-0.10053	0.06861
5.50	1.84	-0.129	0.36641	-0.15954	0.37578	-0.09558	0.06395
5.75	1.83	-0.124	0.35234	-0.15078	0.36484	-0.09096	0.05981
6.00	1.80	-0.118	0.33984	-0.14277	0.35391	-0.08665	0.05612
6.25	1.74	-0.111	0.32734	-0.13544	0.34453	-0.08262	0.05281
6.50	1.75	-0.108	0.31797	-0.12872	0.33516	-0.07888	0.04984
6.75	1.71	-0.103	0.30703	-0.12251	0.32578	-0.07536	0.04714
7.00	1.73	-0.101	0.29922	-0.11680	0.31797	-0.07210	0.04470
$V_0 = 2.00$		eV					
5.00	1.85	-0.149	0.42422	-0.16825	0.42734	-0.08435	0.08390
5.25	1.85	-0.144	0.40703	-0.15795	0.41484	-0.07956	0.07839
5.50	1.82	-0.137	0.39297	-0.14866	0.40234	-0.07512	0.07354
5.75	1.78	-0.130	0.37891	-0.14021	0.39141	-0.07099	0.06922
6.00	1.75	-0.124	0.36641	-0.13250	0.38203	-0.06714	0.06536
6.25	1.74	-0.120	0.35547	-0.12548	0.37266	-0.06358	0.06190
6.50	1.68	-0.113	0.34453	-0.11898	0.36328	-0.06023	0.05875
6.75	1.65	-0.108	0.33516	-0.11314	0.35391	-0.05720	0.05594
7.00	1.61	-0.103	0.32578	-0.10771	0.34766	-0.05434	0.05336

[a]Energies are in Hartree units.

TABLE IV

ELECTRONIC ENERGIES AND WAVE FUNCTION PARAMETERS FOR
ONE-ELECTRON-TWELVE-MOLECULE CAVITY

R_c	α	β	γ	E_{1s}[a]	ξ	E_{2p}	ΔE_{ps}
V_O = 0.00		eV					
7.50	2.50	−0.134	0.27656	−0.15704	0.30234	−0.11763	0.03940
7.75	2.50	−0.131	0.26406	−0.15130	0.29453	−0.11404	0.03726
8.00	2.50	−0.128	0.25469	−0.14604	0.28672	−0.11071	0.03533
8.25	2.49	−0.124	0.24844	−0.14130	0.28047	−0.10767	0.03363
8.50	2.49	−0.121	0.24219	−0.13690 ·	0.27422	−0.10482	0.03208
8.75	2.49	−0.118	0.23594	−0.13268	0.26797	−0.10203	0.03065
9.00	2.50	−0.116	0.22969	−0.12916	0.26172	−0.09972	0.02944
9.25	2.49	−0.113	0.22656	−0.12581	0.25703	−0.09749	0.02832
9.50	2.50	−0.110	0.22656	−0.12301	0.25391	−0.09566	0.02735
V_O = 0.50		eV					
7.50	2.43	−0.137	0.28906	−0.15216	0.31641	−0.10899	0.04317
7.75	2.44	−0.134	0.27969	−0.14656	0.30859	−0.10560	0.04096
8.00	2.37	−0.127	0.27031	−0.14139	0.30078	−0.10242	0.03897
8.25	2.49	−0.130	0.26406	−0.13671	0.29453	−0.09952	0.03719
8.50	2.49	−0.127	0.25781	−0.13242	0.28828	−0.09683	0.03559
8.75	2.49	−0.124	0.25156	−0.12832	0.28203	−0.09421	0.03410
9.00	2.50	−0.122	0.24531	−0.12484	0.27734	−0.09201	0.03283
9.25	2.50	−0.120	0.23906	−0.12154	0.27266	−0.08989	0.03165
9.50	2.49	−0.117	0.23594	−0.11872	0.26797	−0.08809	0.03063

[a]Energies are in Hartree units.

TABLE V

ELECTRONIC ENERGIES AND WAVE FUNCTION PARAMETERS FOR

ONE-ELECTRON-EIGHTEEN-MOLECULE CAVITY

R_c	α	β	γ	E_{1s}[a]	ξ	E_{2p}	ΔE_{ps}
V_o = 1.00		eV					
7.50	2.19	-0.129	0.30156	-0.14791	0.32891	-0.10094	0.04697
7.75	2.16	-0.124	0.29219	-0.14237	0.32109	-0.09770	0.04468
8.00	2.12	-0.119	0.28281	-0.13729	0.31484	-0.09468	0.04260
8.25	2.14	-0.117	0.27656	-0.13268	0.30703	-0.09193	0.04075
8.50	2.21	-0.118	0.27031	-0.12846	0.30078	-0.08939	0.03907
8.75	2.22	-0.116	0.26406	-0.12459	0.29609	-0.08704	0.03755
9.00	2.22	-0.114	0.25781	-0.12111	0.28984	-0.08492	0.03619
9.25	2.16	-0.109	0.25156	-0.11791	0.28516	-0.08296	0.03495
9.50	2.28	-0.113	0.24844	-0.11518	0.28203	-0.08132	0.03387
V_o = 2.00		eV					
7.50	2.14	-0.135	0.32656	-0.14080	0.35391	-0.08642	0.05438
7.75	1.97	-0.122	0.31406	-0.13540	0.34609	-0.08349	0.05192
8.00	1.88	-0.114	0.30469	-0.13050	0.33984	-0.08082	0.04968
8.25	1.91	-0.113	0.29844	-0.12607	0.33203	-0.07841	0.04766
8.50	1.97	-0.114	0.29219	-0.12203	0.32578	-0.07620	0.04582
8.75	1.96	-0.111	0.28594	-0.11835	0.32109	-0.07420	0.04415
9.00	1.94	-0.108	0.27969	-0.11506	0.31484	-0.07243	0.04263
9.25	2.06	-0.112	0.27656	-0.11214	0.31016	-0.07088	0.04126
9.50	1.98	-0.106	0.27031	-0.10957	0.30547	-0.06955	0.04002

[a]Energies are in Hartree units.

with respect to the parameters γ and ξ where E_{1_S} and E_{1_P} are the corresponding energies. This procedure was used so that some comparison could be made with the other wavefunctions and so that an enormous amount of computer time would not be required. The energy contributions arising from the repulsive Coulomb potential given in equation (53) were evaluated by converting the integrals to the F and G integrals that are common to atomic calculations.[52,53] Coulomb integrals in the off-diagonal elements of the CI calculation were also evaluated with the F and G integrals (See Appendix I for the basic ideas concerning CI calculations).

General relations have not been obtained for the two-electron polarization interactions given in equations (57) and (58). We shall therefore give the specific result. For the diagonal elements of the CI matrix obtained with the basis set $\{\psi_{SCF}, \psi_{1_{S-2p_B}}\}$ we have found that

$$\langle \psi_{SCF} | \sum_{i=1}^{N} V_{2po\ell}^{i} | \psi_{SCF} \rangle = -\frac{N\alpha_o}{R_m^4} \{\int_o^{R_c} |\psi_{1s_B}(r)|^2 r^2 dr\}^2 \tag{78}$$

and

$$\langle \psi_{SCF} | V_{2po\ell}^{c} | \psi_{SCF} \rangle = -\frac{4\pi\alpha_o \bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o \bar{\rho}_d)} \frac{1}{R_d} \{\int_o^{R_d - R_H} |\psi_{1s_B}(r)|^2 r^2 dr\}^2 \tag{79}$$

for the polarization contributions to H_{11} and

$$\langle \psi_{1_{S-2p_B}} | \sum_{i=1}^{N} V_{2po\ell}^{i} | \psi_{1_{S-2p_B}} \rangle = -\frac{N\alpha_o}{R_m^4} \left[\{\int_o^{R_c} |\psi_{2p_B}(r)|^2 r^2 dr\}^2 + \frac{6}{5R_m^4} \{\int_o^{R_c} |\psi_{2p_B}(r)|^2 r^4 dr\}^2 \right] \tag{80}$$

and

$$\langle \psi_{1_{S-2p_B}} | \sum_{i=1}^{N} V_{2pol}^{i} | \psi_{1_{S-2p_B}} \rangle = - \frac{4\pi\alpha_o\bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \frac{1}{R_d} \left[\{\int_o^{R_d-R_H} |\psi_{2p_B}(r)|^2 r^2 dr\}^2 \right.$$

$$\left. + \frac{18}{125R_d^4} \{\int_o^{R_d-R_H} |\psi_{2p_B}(r)|^2 r^4 dr\}^2 \right] \tag{81}$$

for the polarization contributions to H_{22} where ψ_{2p_B} is the normalized, radial wavefunction for $2p_{Blm}$ which is obtained from minimizing the ^1P energy, E_{1_P}, and $\psi_{1_{S-2p_B}}$ is the $2p_B-^1S$ part of equation (66) (i.e., the part of equation (66) which is multiplied times C_2). The polarization contributions to the off-diagonal elements H_{12} and H_{21} were found to be

$$\langle \psi_{SCF} | \sum_{i=1}^{N} V_{2pol}^{i} | \psi_{1_{S-2p_B}} \rangle = - \frac{N2\alpha_o}{\sqrt{3}R_m^6} \{\int_o^{R_c} \psi_{1s_B}^*(r) \psi_{2p_B}(r) r^3 dr\}^2 \tag{82}$$

and

$$\langle \psi_{SCF} | V_{2pol}^{c} | \psi_{1_{S-2p_B}} \rangle = - \frac{4\pi\alpha_o\bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \frac{2}{3\sqrt{3}R_d^3} \{\int_o^{R_d-R_H} \psi_{1s_B}^*(r) \psi_{2p_B}(r) r^3 dr\}^2 \tag{83}$$

We have omitted all of the integrals that are zero because of the orthogonality of Legendre polynomials.

A CI procedure was not carried out for the ^1P excited state since correlation is not expected to be large for this state (See Appendix I). The polarization contribution of the two-electron potentials for the ^1P state were found to be given by

$$\langle \psi_{1_p} | \sum_{i=1}^{N} V_{2po\ell}^{i} | \psi_{1_p} \rangle = -\frac{N\alpha_o}{R_m^4} \left[\{\int_o^{R_c} |\psi_{1s_B}(r)|^2 r^2 dr\} \{\int_o^{R_c} |\psi_{2p_B}(r)|^2 r^2 dr\} \right.$$

$$\left. + \frac{2}{3R_m^2} \{\int_o^{R_c} \psi_{1s_B}^*(r) \psi_{2p_B}(r) r^3 dr\}^2 \right] \qquad (84)$$

and

$$\langle \psi_{1_p} | V_{2po\ell}^c | \psi_{1_p} \rangle = -\frac{4\pi\alpha_o\bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \frac{1}{R_d} \left[\{\int_o^{R_d-R_H} |\psi_{1s_B}(r)|^2 dr\} \{\int_o^{R_d-R_H} |\psi_{2p_B}(r)|^2 \right.$$

$$\left. r^2 dr\} + \frac{2}{9R_d^2} \{\int_o^{R_d-R_H} \psi_{1s_B}^*(r) \psi_{2p_B}(r) r^3 dr\}^2 \right]$$

$$(85)$$

where ψ_{1_p} is given in equation (67).

We have considered the same values of V_o for the two-electron species that were used for the one-electron species. The results for the 12 molecule calculations are given in Tables VI through VIII and the results for the 18 molecule calculations are given in Tables IX through XI. Oscillator strengths have also been calculated for the two-electron species by using $1s_B$ and $2p_B$ in equation (77) with the uncorrelated ^1S and ^1P transition energy. Several of these values will be given in the next section.

TABLE VI

ELECTRONIC ENERGIES AND WAVE FUNCTION PARAMETERS FOR

TWO-ELECTRON-TWELVE-MOLECULE CAVITY

R_c	α	β	γ	$E_{1_s}^a$	ξ	E_{1_p}	ΔE_{ps}^2	$-\delta E_2$
V_0	= 0.00	eV						
4.50	2.09	-0.126	0.42578	-0.43537	0.45000	-0.31226	0.12311	0.01760
4.75	2.09	-0.126	0.39453	-0.40408	0.41875	-0.29187	0.11221	0.01736
5.00	2.09	-0.126	0.36641	-0.37629	0.39063	-0.27336	0.10292	0.01698
5.25	2.09	-0.126	0.33984	-0.35106	0.36250	-0.25686	0.09420	0.01618
5.50	2.09	-0.126	0.31797	-0.32877	0.34062	-0.24131	0.08745	0.01566
5.75	2.09	-0.126	0.29922	-0.30869	0.32187	-0.22705	0.08164	0.01522
6.00	2.09	-0.126	0.28203	-0.29045	0.30625	-0.21384	0.07662	0.01489
6.25	2.09	-0.126	0.26797	-0.27346	0.29062	-0.20193	0.07152	0.01435
6.50	2.09	-0.126	0.25703	-0.25843	0.28125	-0.19057	0.06786	0.01457
V_0	= 0.50	eV						
4.50	1.89	-0.115	0.42422	-0.43283	0.44687	-0.30128	0.13154	0.01564
4.75	1.89	-0.115	0.39297	-0.40123	0.41562	-0.28049	0.12074	0.01519
5.00	1.89	-0.115	0.36484	-0.37314	0.38750	-0.26158	0.11155	0.01462
5.25	1.89	-0.115	0.33984	-0.34804	0.36250	-0.24431	0.10373	0.01400
5.50	1.89	-0.115	0.31797	-0.32551	0.34062	-0.22850	0.09701	0.01338
5.75	1.89	-0.115	0.29922	-0.30520	0.32187	-0.21401	0.09119	0.01284
6.00	1.89	-0.115	0.28359	-0.28680	0.30625	-0.20073	0.08607	0.01245
6.25	1.89	-0.115	0.26953	-0.26997	0.29375	-0.18841	0.08156	0.01226
6.50	1.89	-0.115	0.26016	-0.25467	0.28437	-0.17706	0.07761	0.01242

[a]Energies are in Hartree units.

TABLE VII

ELECTRONIC ENERGIES AND WAVE FUNCTION PARAMETERS FOR
TWO-ELECTRON-TWELVE-MOLECULE CAVITY

R_c	α	β	γ	E_{1_s}[a]	ξ	E_{1_p}	ΔE^2_{ps}	$-\delta E_2$
V_0 = 1.00		eV						
5.00	1.83	-0.129	0.34766	-0.37064	0.37187	-0.25172	0.11892	0.01140
5.25	1.83	-0.129	0.32578	-0.34494	0.35000	-0.23364	0.11130	0.01087
5.50	1.83	-0.129	0.31016	-0.32185	0.33437	-0.21711	0.10473	0.01078
5.75	1.83	-0.129	0.29609	-0.30011	0.31875	-0.20192	0.09819	0.01051
6.00	1.83	-0.129	0.28516	-0.28029	0.30937	-0.18767	0.09262	0.01084
6.25	1.83	-0.129	0.27734	-0.26157	0.30000	-0.17452	0.08705	0.01114
6.50	1.83	-0.129	0.26953	-0.24408	0.29375	-0.16191	0.08218	0.01177
V_0 = 2.00		eV						
5.25	1.78	-0.130	0.32891	-0.34162	0.35625	-0.20813	0.13349	0.00915
5.50	1.78	-0.130	0.31328	-0.31758	0.34062	-0.19127	C.12631	0.00902
5.75	1.78	-0.130	0.30234	-0.29511	0.32656	-0.17582	0.11929	0.00893
6.00	1.78	-0.130	0.29297	-0.27402	0.31562	-0.16143	0.11259	0.00905
6.25	1.78	-0.130	0.28516	-0.25443	0.30937	-0.14790	0.10653	0.00963
6.50	1.78	-0.130	0.27891	-0.23581	0.30312	-0.13519	0.10062	0.01020

[a]Energies are in Hartree units.

TABLE VIII

RESULTS OF CONFIGURATION INTERACTION FOR

TWO-ELECTRON-TWELVE-MOLECULE CAVITY

R_c	$E_{1_s}^a$	$-\delta E_2$	C_1	C_2
V_o = 0.00 eV				
4.50	−0.43537	0.01760	−0.95431	0.29883
4.75	−0.40408	0.01736	−0.95022	0.31158
5.00	−0.37629	0.01698	−0.94669	0.32214
5.25	−0.35106	0.01618	−0.94458	0.32827
5.50	−0.32877	0.01566	−0.94223	0.33495
5.75	−0.30869	0.01522	−0.93997	0.34126
6.00	−0.29045	0.01489	−0.93744	0.34816
6.25	−0.27346	0.01435	−0.93574	0.35270
6.50	−0.25843	0.01457	−0.93095	0.36514
V_o = 0.50 eV				
4.50	−0.43283	0.01564	−0.96289	0.26991
4.75	−0.40123	0.01519	−0.96060	0.27794
5.00	−0.37314	0.01462	−0.95892	0.28367
5.25	−0.34804	0.01400	−0.95778	0.28750
5.50	−0.32551	0.01338	−0.95698	0.29014
5.75	−0.30520	0.01284	−0.95624	0.29258
6.00	−0.28680	0.01245	−0.95517	0.29604
6.25	−0.26997	0.01226	−0.95344	0.30157
6.50	−0.25467	0.01242	−0.95037	0.31113
V_o = 1.00 eV				
5.00	−0.37064	0.01140	−0.97126	0.23801
5.25	−0.34494	0.01087	−0.97087	0.23962
5.50	−0.32185	0.01078	−0.96930	0.24587
5.75	−0.30011	0.01051	−0.96823	0.25005
6.00	−0.28029	0.01084	−0.96510	0.26188
6.25	−0.26157	0.01114	−0.96180	0.27376
6.50	−0.24408	0.01177	−0.95692	0.29036
V_o = 2.00 eV				
5.25	−0.34162	0.00915	−0.98015	0.19827
5.50	−0.31758	0.00902	−0.97936	0.20212
5.75	−0.29511	0.00893	−0.97843	0.20659
6.00	−0.27402	0.00905	−0.97686	0.21386
6.25	−0.25443	0.00963	−0.97382	0.22732
6.50	−0.23581	0.01020	−0.97048	0.24119

[a]Energies are in Hartree units.

TABLE IX

ELECTRONIC ENERGIES AND WAVE FUNCTION PARAMETERS FOR

TWO-MOLECULE-EIGHTEEN-MOLECULE CAVITY

R_c	α	β	γ	$E_{1_s}^a$	ξ	E_{1_p}	ΔE_{ps}^2	$-\delta E_2$
V_0 = 0.00		eV						
7.00	2.50	-0.128	0.26172	-0.30920	0.27734	-0.24062	0.06857	0.01054
7.25	2.50	-0.128	0.25078	-0.29604	0.26797	-0.22981	0.06623	0.01067
7.50	2.50	-0.128	0.23984	-0.28368	0.25859	-0.21974	0.06394	0.01066
7.75	2.50	-0.128	0.23203	-0.27239	0.25078	-0.21056	0.06184	0.01079
8.00	2.50	-0.128	0.22578	-0.26150	0.24141	-0.20204	0.05946	0.01061
8.25	2.50	-0.128	0.21797	-0.25139	0.23516	-0.19386	0.05753	0.01075
8.50	2.50	-0.128	0.21328	-0.24170	0.22734	-0.18641	0.05528	0.01061
8.75	2.50	-0.128	0.20859	-0.23264	0.22109	-0.17938	0.05326	0.01062
9.00	2.50	-0.128	0.20391	-0.22364	0.21328	-0.17275	0.05090	0.01023
V_0 = 0.50		eV						
7.00	2.43	-0.137	0.26641	-0.29500	0.28359	-0.22302	0.07198	0.01063
7.25	2.43	-0.137	0.25547	-0.28155	0.27422	-0.21220	0.06935	0.01073
7.50	2.43	-0.137	0.24766	-0.26898	0.26484	-0.20230	0.06668	0.01076
7.75	2.43	-0.137	0.23984	-0.25718	0.25703	-0.19297	0.06421	0.01088
8.00	2.43	-0.137	0.23359	-0.24600	0.24922	-0.18431	0.06169	0.01091
8.25	2.43	-0.137	0.22891	-0.23539	0.24141	-0.17627	0.05911	0.01086
8.50	2.43	-0.137	0.22578	-0.22532	0.23359	-0.16885	0.05647	0.01071
8.75	2.43	-0.137	0.22109	-0.21584	0.22734	-0.16171	0.05413	0.01069
9.00	2.43	-0.137	0.21797	-0.20692	0.22109	-0.15515	0.05177	0.01060

[a]Energies are in Hartree units.

TABLE X

ELECTRONIC ENERGIES AND WAVE FUNCTION PARAMETERS FOR

TWO-ELECTRON-EIGHTEEN-MOLECULE CAVITY

R_c	α	β	γ	$E_{1_s}^a$	ξ	E_{1_p}	ΔE_{ps}^2	$-\delta E_2$
V_0 = 1.00		eV						
7.00	2.19	-0.129	0.27578	-0.28167	0.29141	-0.20586	0.07581	0.01111
7.25	2.19	-0.129	0.26328	-0.26826	0.28203	-0.19508	0.07318	0.01118
7.50	2.19	-0.129	0.25547	-0.25567	0.27266	-0.18525	0.07042	0.01121
7.75	2.19	-0.129	0.24922	-0.24400	0.26484	-0.17614	0.06785	0.01138
8.00	2.19	-0.129	0.24297	-0.23284	0.25703	-0.16757	0.06528	0.01142
8.25	2.19	-0.129	0.23828	-0.22257	0.25078	-0.15964	0.06293	0.01164
8.50	2.19	-0.129	0.23359	-0.21246	0.24297	-0.15218	0.06028	0.01145
V_0 = 2.00		eV						
7.00	1.88	-0.114	0.29141	-0.25838	0.30859	-0.17348	0.08490	0.01232
7.25	1.88	-0.114	0.28047	-0.24554	0.29922	-0.16319	0.08236	0.01248
7.50	1.88	-0.114	0.27109	-0.23374	0.29141	-0.15368	0.08006	0.01276
7.75	1.88	-0.114	0.26328	-0.22270	0.28359	-0.14494	0.07777	0.01294
8.00	1.88	-0.114	0.25703	-0.21262	0.27734	-0.13690	0.07572	0.01330
8.25	1.88	-0.114	0.25234	-0.20290	0.26953	-0.12954	0.07336	0.01329
8.50	1.88	-0.114	0.24766	-0.19395	0.26328	-0.12268	0.07127	0.01343

[a]Energies are in Hartree units.

TABLE XI

RESULTS OF CONFIGURATION INTERACTION FOR

TWO-ELECTRON-EIGHTEEN-MOLECULE CAVITY

R_c	$E_{1_s}^a$	$-\delta E_2$	C_1	C_2
V_o = 0.00 eV				
7.00	-0.30920	0.01054	-0.95289	0.30333
7.25	-0.29604	0.01067	-0.95037	0.31114
7.50	-0.28368	0.01066	-0.94845	0.31694
7.75	-0.27239	0.01079	-0.94580	0.32476
8.00	-0.26150	0.01061	-0.94472	0.32787
8.25	-0.25139	0.01075	-0.94177	0.33625
8.50	-0.24170	0.01061	-0.94037	0.34015
8.75	-0.23264	0.01062	-0.93798	0.34670
9.00	-0.22364	0.01023	-0.93785	0.34704
V_o = 0.50 eV				
7.00	-0.29500	0.01063	-0.95537	0.29542
7.25	-0.28155	0.01073	-0.95302	0.30292
7.50	-0.26898	0.01076	-0.95100	0.30920
7.75	-0.25718	0.01088	-0.94838	0.31712
8.00	-0.24600	0.01091	-0.94609	0.32391
8.25	-0.23539	0.01086	-0.94416	0.32949
8.50	-0.22532	0.01071	-0.94265	0.33378
8.75	-0.21584	0.01069	-0.94032	0.34028
9.00	-0.20692	0.01060	-0.93835	0.34569
V_o = 1.00 eV				
7.00	-0.28167	0.01111	-0.95603	0.29326
7.25	-0.26826	0.01118	-0.95390	0.30014
7.50	-0.25567	0.01121	-0.95196	0.30623
7.75	-0.24400	0.01138	-0.94933	0.31429
8.00	-0.23284	0.01142	-0.94716	0.32076
8.25	-0.22257	0.01164	-0.94397	0.33002
8.50	-0.21246	0.01145	-0.94272	0.33358
V_o = 2.00 eV				
7.00	-0.25838	0.01232	-0.95638	0.29213
7.25	-0.24554	0.01248	-0.95426	0.29897
7.50	-0.23374	0.01276	-0.95163	0.30724
7.75	-0.22270	0.01294	-0.94935	0.31423
8.00	-0.21262	0.01330	-0.94629	0.32332
8.25	-0.20290	0.01329	-0.94471	0.32792
8.50	-0.19395	0.01343	-0.94239	0.33453

[a]Energies are in Hartree units.

D. STABILITY OF CAVITIES

The primary reason the cavity exists is because the molecules oriented on the surface of the cavity by the enclosed charge repel one another. Two factors must be taken into account in addition to the electronic energy in order to determine the most stable cavity. As was mentioned in the Introduction, E_{pv} is negligible and E_{st} is not adequately handled by scaled particle theory. Most of the surface energy can be determined by considering the short-range interactions between the molecules of the first coordination shell. Of prime importance are the dipole-dipole and hydrogen-hydrogen repulsions. With the dipoles on the surface of the cavity centrally oriented, every dipole will repel the other dipoles. This orientation will also place the three hydrogen atoms of the ammonia molecule on the inner surface of the cavity. Because of their orientation, a hydrogen atom of one surface molecule could be as much as 3.5 a_o closer to a hydrogen atom of another surface molecule than the centers of the two molecules. This situation renders the normal molecular pair potentials considered in terms of a distance between centers of the molecules invalid.

With the point dipole approximation the dipole-dipole repulsion between two molecules can be written in the form

$$\frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5} \tag{86}$$

where $\vec{\mu}_1$ and $\vec{\mu}_2$ are the dipole moment vectors and $\vec{r}$ is the interdipole vector of magnitude r. Since the dipoles are symmetrically distributed on the surface of the cavity and the angles obtained from the dot products of the vectors do not change as the size of the cavity is increased, the dipole-dipole interaction for a given configuration of molecules can be written in the form

$$\frac{\epsilon\mu^2}{R_m^3} \qquad (87)$$

where ϵ is a constant that is determined by the molecular configuration. For the twelve dipole ccp structure ϵ is equal to 41.04 and for the eighteen dipole structure ϵ is 906.6. The value of the dipole moment μ might be taken as μ_{eff} of equation (20) but this assumes that the dipoles are not polarizable. Since they are, μ is replaced by[46]

$$\mu = \mu_{eff} + \frac{z\alpha_o}{R_m^2} \qquad (88)$$

This factor is extremely important for cavities with larger z values.

Since the exact hydrogen-hydrogen distances are difficult to determine and the magnitude of the repulsion between these atoms is not accurately known, some assumptions will have to be made. We shall assume that the hydrogen-hydrogen potential for water molecules is adequate for ammonia molecules and shall use the one obtained by Eisenberg and Kauzman[53]

$$\phi_{H-H} = \{15.94e^{-2.43r_h} - \frac{3.56}{r_h^6}\} \text{ (Hartrees)} \qquad (89)$$

which has a minimum at the hydrogen-hydrogen distances, r_h, of 4.69 a_o. An estimate is now needed for the interatomic distance as a function R_c (or R_m). By using the charge densities of Bader and Jones[49] as a model it is easily seen that a circle drawn in the plane of the three hydrogen atoms that passes through the atomic nuclei would have a radius of about 1.76 a_o. With $R_H = 1.85$ a_o and using the charge densities we find that the distance from the center of the cavity to the center of one of the circles is approximately $R_c + 1.11$ a_o. By using several trigonometric relations, the distance between the centers of the circles for the nearest neighbor molecules is $R_c + 1.11$ a_o for the twelve molecule cavities and $[0.765(R_c + 1.11\ a_o)]$ for the eighteen molecule cavities. From these relations we can approximate the hydrogen-hydrogen separations as a function of R_c and the radius of the circle in the hydrogen plane R_p by

$$R_c + 1.11\ a_o - 2R_p \tag{90}$$

for the twelve molecule model and

$$0.765(R_c + 1.11\ a_o) - 2R_p \tag{91}$$

for the eighteen molecule model. The most important part of equation (89) is the repulsive interaction since the attractive part is cancelled, in part at least, by the dipole-quadrupole repulsions between the molecules. From the calculations of

Buckingham[55] for an octahedral configuration of molecules, the dipole-quadrupole repulsions for the models that we have considered are estimated to be about fifteen percent of the dipole-dipole result without polarization. From the size and R_c dependence of the dipole-quadrupole repulsion (which goes as $1/R_c^5$) and of the attractive part of equation (89), it seems reasonable to neglect both of these contributions. Before such a calculation was carried out, we had to decide on a reasonable value for R_p since the hydrogen atoms are not always along the intermolecular axis. Since the molecules are relatively free to rotate around the dipole axis, we have estimated that a smaller value for R_p than the maximum 1.76 a_o would represent some average effect. The value should not be very much smaller than the maximum since the number of hydrogen-hydrogen interactions that are important would increase as the separation distance increases on rotating the molecules. As an example let us consider two ammonia molecules with their hydrogen atoms in a plane. If we now place the molecules so that two hydrogen atoms are very close we would have a strong repulsive interaction. If we now hold one of the molecules fixed but rotate the other molecule to a position where a hydrogen atom bisects a hydrogen-hydrogen bond angle, we have to consider two interactions which are not very much different from the one interaction considered above. With these relations in mind we have assumed that R_p can have a value in the range 1.25 to 1.50 a_o. Because of the rapid decrease in the repulsive potential as R_c is

increased, only nearest neighbor interactions have been considered.

A value of R_p equal to 1.35 a_o was used to determine E_T. The values

for the minimum of E_T for the species considered are given in

Table XII and XIII. The choice of R_p used is probably not optimal for

obtaining agreement with experimental results (Table I), but it

illustrates one of the most important features which must be present

in the actual species. These features will be elaborated on in the

Discussion (Section E).

The heat of solution must be evaluated by using equation

(24), but the proper calculation of Σ is difficult. From simple

structural considerations, Σ should include the loss of total

interactions of only one molecule. This energy lost from the

decrease of molecule-molecule interactions was estimated to be

about the energy needed to evaporate one molecule from the surface

of the liquid, i.e., the heat of evaporation of one molecule,

ΔH_{vap} (= 0.00889 Hartrees). We have neglected the surface energy

in   minimizing the cavity energy since this energy is not the

determining factor as regards cavity size. We have therefore

included the surface energy in the energy Σ. By using the surface

energy we will compensate for the neglect of long-range interactions

of the surface molecules and their kinetic energy changes. We

obtained the surface energy from equation (22) using the surface

tension of equation (23). The experimental planar surface tension[56]

of 40 dynes/cm was used with a δ equal to 2.46 a_o, obtained from heat

of evaporation data.[31,57] The decrease in the number of hydrogen

bonds that a surface molecule could form might be included in Σ, but this energy would have a great uncertainty. We have tried to account for some of this energy in the calculation of Π.

To calculate Π we have used a relation similar to the one given by Land and O'Reilly[23,26] (equation (29)). The relation used is

$$\Pi = \frac{\beta_o}{2}[\int_{R_c}^{\infty} G_o(r) |\psi_{1s_A}|^2 r^2 dr + G_o(R_c)P(R_c)] \tag{92}$$

where we have included the first coordination shell of molecules in the determination of Π. This seems to be a reasonable procedure for obtaining the energy required to polarize all of the permanent dipoles in the solvent. The energy Π for the two electron species was obtained by using ψ_{1s_B} instead of ψ_{1s_A} in equation (92) and multiplying the result by four. This procedure accounts for the additional electron in the cavity.

In Table XII are the combined results obtained for the solvation energies, transition energies, and oscillator strengths of the most stable cavity for the one-electron species using the values of V_o considered. The results for the two-electron species are given in Table XIII. The interpretation of these results will be given in the next section.

TABLE XII

RESULTS FOR MOST STABLE ONE-ELECTRON CAVITIES OF

THE TWELVE- AND EIGHTEEN-MOLECULE MODELS[a]

V_o(eV)	$R_c(a_o)$	E_{1s}	0_{ps}	ΔE_{ps}	E_{st}	Π	E_T	$-\Delta H_1$
12 Molecule Model								
0.0	6.25	-0.1479	0.39	0.044	0.0101	0.0296	-0.1136	0.0650
0.5	6.30	-0.1400	0.38	0.048	0.0103	0.0298	-0.1052	0.0562
1.0	6.35	-0.1327	0.38	0.051	0.0104	0.0294	-0.0976	0.0489
2.0	6.40	-0.1203	0.38	0.059	0.0105	0.0287	-0.0853	0.0372
18 Molecule Model								
0.0	8.75	-0.1326	0.42	0.031	0.0189	0.0264	-0.0987	0.0445
0.5	8.75	-0.1283	0.41	0.034	0.0189	0.0271	-0.0921	0.0372
1.0	9.25	-0.1179	0.42	0.035	0.0211	0.0262	-0.0868	0.0306
2.0	9.50	-0.1026	0.42	0.040	0.0223	0.0262	-0.0795	0.0221

[a]V_o is the parameter which defines the energy of a quasi-free electron. The cavity size is R_c and the total energy, E_T, is the sum of the electronic energy, E_{1s}, and the surface molecule-molecule interactions. The energy to orient the permanent dipoles is given by Π. The Franck-Condon transition energy is ΔE_{ps} with oscillator strength 0_{ps}. The heat of solution is ΔH_1. All energies are in Hartrees.

TABLE XIII

RESULTS FOR MOST STABLE TWO-ELECTRON CAVITIES OF

THE TWELVE- AND EIGHTEEN-MOLECULE MODELS[a]

V_o(eV)	$R_c(a_o)$	E_{1_s}	O_{ps}	ΔE^2_{ps}	E_{st}	Π	E_T	$-\Delta H_2$	ΔH_{21}
12 Molecule Model									
0.0	5.75	-0.3087	1.11	0.082	0.0088	0.1261	-0.2320	0.0882	0.0209
0.5	5.75	-0.3052	1.29	0.091	0.0088	0.1261	-0.2276	0.0838	0.0143
1.0	5.75	-0.3001	1.12	0.098	0.0088	0.1267	-0.2160	0.0716	0.0131
2.0	5.75	-0.2951	1.34	0.119	0.0088	0.1270	-0.2081	0.0634	0.0055
18 Molecule Model									
0.0	8.25	-0.2514	1.12	0.056	0.0168	0.1064	-0.1812	0.0491	0.0200
0.5	8.25	-0.2354	0.90	0.059	0.0168	0.1096	-0.1612	0.0250	0.0243
1.0	8.25	-0.2257	0.88	0.063	0.0168	0.1120	-0.1547	0.0170	0.0221
2.0	8.50	-0.1940	0.96	0.071	0.0178	0.1120	-0.1229	-0.0158	0.0300

[a] V_o is the parameter which defines the energy of a quasi-free electron. The cavity size is R_c and the total energy, E_T, is the sum of the electronic energy E_{1_s}, and the surface molecule-molecule interactions. The energy to orient the permanent dipoles is given by Π. The Franck-Condon transition energy ΔE^2_{ps} with oscillator strength O_{ps}. The heat of solution is ΔH_2 while the enthalpy per electron relative to two one electron cavities is ΔH_{21}. All energies are in Hartrees.

E. DISCUSSION AND CONCLUSIONS

Although exact agreement with experimental results
(Table I-B) has not been obtained with this calculation, many
questions concerning the cavity species have been answered. For
all of the values of V_o considered, the twelve-molecule cavity
is found to be more stable than the eighteen-molecule cavity
(Tables XII and XIII). This was found for both the one- and two-
electron species. Preliminary calculations with a six-molecule
cavity indicate that the twelve-molecule cavity is still the most
stable species. Since similar calculations could be carried out for
an eight- and a fourteen-molecule cavity, no firm conclusions can
be made as to the actual number of molecules on the surface of the
most stable cavity. Nevertheless, most of the results point to a
number around twelve.

The most revealing aspects of these calculations are the
factors which determine the size of the cavity. These factors indicate
that an <u>ad hoc</u> choice for the radius of the cavity is not justified.
Hydrogen-hydrogen repulsions force the molecules on the surface
of the cavity apart to a greater extent than might be expected from
using an average molecule-molecule interaction. This indicates that
the bulk molecular density for the first layer as assumed by Land
and O'Reilly[23,26] is incorrect. This repulsion is the most important
single factor in determining the cavity sizes for the one- and

two-electron twelve-molecule cavities and the two-electron eighteen-molecule cavities. These cavities are approximately the same sizes that would be expected if the structures were held fixed but the electronic energies neglected. The most important factor involved in the one-electron eighteen-molecule cavities is the induced dipole-induced dipole repulsions. Because of the greater number of first layer molecules and the larger size of the cavities, a larger percent (approximately 80 percent) of the charge is in the void region (0 to R_c). The Coulomb repulsion between the electrons in the two-electron species causes the electrons to have a lower charge density in the void region and thereby reduces the induced dipole repulsions.

The major stabilization of the cavity species is the electron-dipole interaction. This stabilization and the repulsions between the molecules on the surface of the cavity are the primary reasons for the existence of a cavity. The greatest destabilizing factor for the two-electron species is the energy required to polarize the permanent dipoles in the liquid. The question of relative stability must be related to the heats of solution of the one- and two-electron species. By comparing the energies ΔH_1 and ΔH_{21} given in Tables XII and XIII, the results mentioned in the first paragraph of this section are confirmed.

Because the transition energies of the one-electron species calculations are higher for the most stable cavities than the

experimental ones, a negative value for the energy of the quasi-free electron, V_o, would give better agreement as is indicated by the trend to lower transition energies as V_o is decreased. The p states are affected by V_o to a greater extent than the ground state since the p states have a higher charge density outside the cavities. With a negative V_o of the size that is suggested by the other transition energies, the p states would be totally delocalized. However, this would also give an unrealistic concentration of the quasi-free electrons. Thus it appears that the twelve-molecule cavities do not have the correct number of molecules on the surface. Because of the apparent agreement between the calculated heats of solution and the experimental ones for the twelve-molecule cavities and because the ground state is affected only slightly by V_o, the ground state energies are probably very accurate. A thorough treatment of V_o might bring the excited state energy down and thus give transition energies in accord with experimental ones.

Although the transition energies are somewhat higher than the experimental values, several general features of the transitions seem to be common for the species considered. The total energy E_T is very flat at the minimum energies (Figure V) which is in accord with the broad experimental band. If the allowed s to p transitions are determined by the thermal energy of the system, the extent that the energy can deviate from the minimum of the total energy E_T might be estimated by the energy kT.

Figure V. Energy diagrams for E_T versus R_c in the vicinity of the
minima for the one-electron twelve-molecule model with
V_o = 0.0, 0.5, and 1.0 eV where V_o is the energy of the
quasi-free electron. The upper curve in each of the
three plots is E_T for the excited p state and the
lower curve is E_T for the ground state.
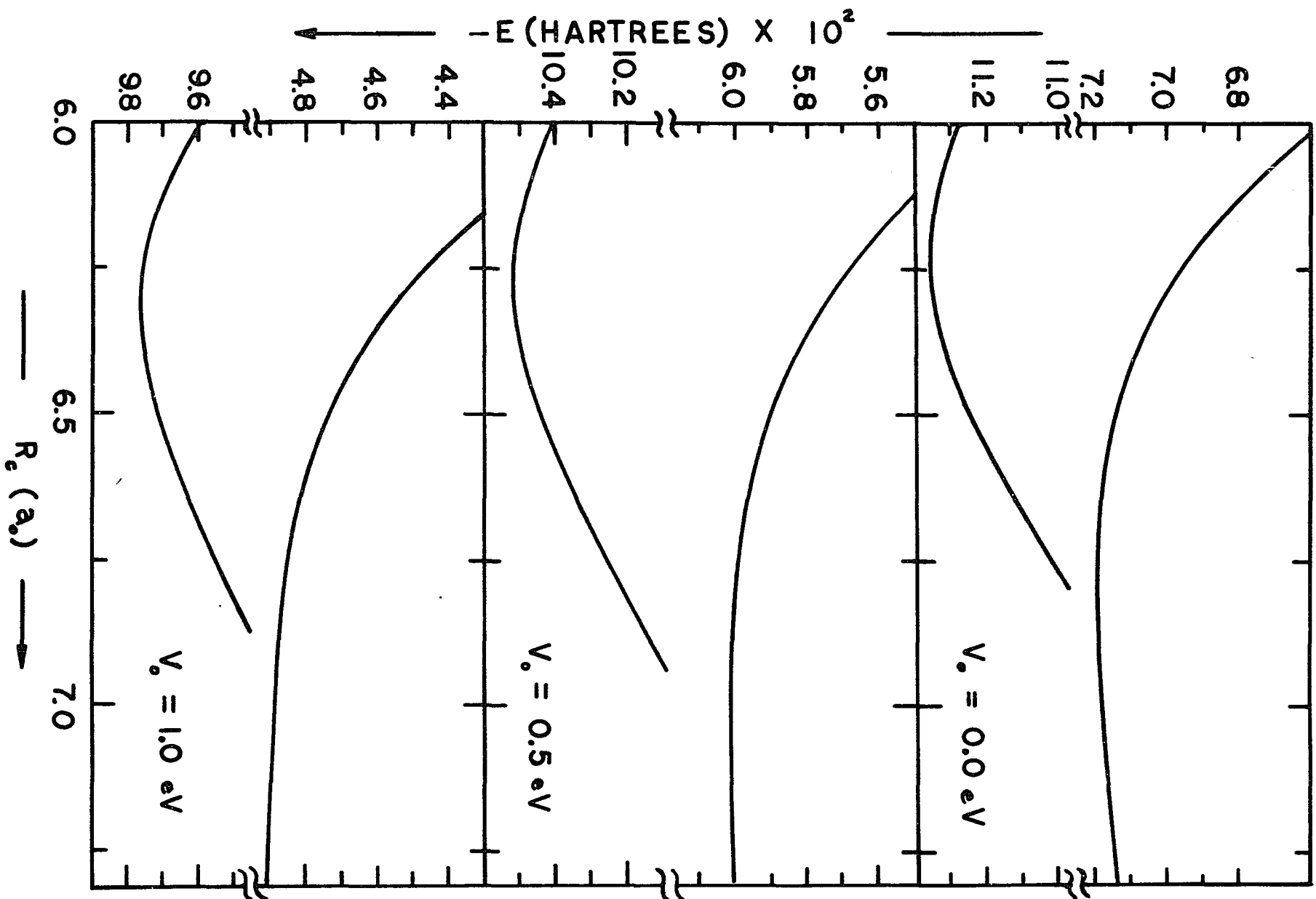
With this assumption band widths can be predicted. For the one-electron twelve-molecule cavity (V_o = 0.0 eV), a band width of 0.0057 Hartrees (0.16 eV) is predicted at $240^{\circ}K$ and is found to be asymmetric toward higher energies (Figure V). In the energy diagrams given in Figure V, several features should be noted. These are also characteristic of the other species considered. As the energy V_o is increased from 0.0 to 1.0 ev the position of the minimum moves to higher values of R_c because the increased amount of charge in the void region increases the induced dipole-induced dipole repulsions. This is found to be true for the ground and excited p states. The energy E_T also flattens out with increasing value of V_o. It should also be noted that the minimum values of E_T for the excited states are at larger R_c than in the ground state. This would predict an emission band at a lower energy than the absorption band. Such an experiment has not been conducted.

Since the most important temperature dependence is in the calculation of μ_{eff}, the effect of temperature on the absorption band can be noted. Since the charge-dipole interaction is greater for the ground states which have a greater charge density inside the void region, the ground state energies will increase to a greater extent than the excited state energies and thus give lower transition energies with increased temperatures. A similar trend is predicted based simply on the asymmetry of the energy plots. This trend agrees with experimental observations.

Because the density of the molecules on the surface of the
cavity is lower than the density of the molecules in the bulk liquid,
several factors must be taken into account before the cavity sizes
can be compared with experimental estimates. Since the experimental
values are obtained from volume expansion data, we must determine the
actual volume of the cavity plus the increased volume arising from
the lower molecular density of the surface molecules. The cavity
radius R_o ($= R_c - 1.81 \, a_o = R_m - R_{NH_3}$) must be used in determining
the volume of the actual cavity since this radius takes into account
the average volume of the surface molecules when the cavity is not
present, i.e., this takes into account the volume of the liquid
before the metal is added to the ammonia. By considering the volume
change for the one-electron twelve-molecule cavity ($V_o = 0.0$ eV),
a cavity with an effective $R_o = 7.2 \, a_o$ would be predicted by these
calculations. Such a value is not very different from the
experimental estimates of 5.67 to 6.50 a_o. A larger value for V_o
would predict even larger values for the effective R_o. The
predicted cavity sizes for the eighteen-molecule species are
extremely large and therefore unrealistic.

Extending the one-electron calculation to the two-electron
species has yielded several interesting results. Several investigators
have speculated that the two-electron cavities would be larger than
the one-electron cavities.[13,24,26] We have not found this prediction
to be true. All of the two-electron cavities that we have considered

were found to be smaller than their one-electron counterpart. The two-electron transition energy given in Table I-B is based on the assumed larger cavity. If the cavities were larger for the two-electron species, the transition energies would be smaller since both the ground state and ^1P energies are converging as the cavity size is increased. The larger cavities are not justified by the results of this calculation. If at all, a two-electron transition energy larger than the one-electron one should be expected. The main factors which result in a smaller two-electron cavity are the decrease in the charge-dipole interaction energy as the size of the cavity increases and the increase in the electron-electron interaction. As the size of the cavity increases, the effective dipole moment μ_{eff} decreases by a factor proportional to R_m^2 and the charge-dipole interaction decreases as $1/R_m^2$. A larger cavity also puts a greater electron density inside the void region where the Coulomb repulsion of the electrons is increased. Thus the Coulomb repulsion can be lowered at the expense of increased kinetic energy by reducing the size of the cavity. Greater stabilization is thus obtained by reducing the cavity size.

The lack of any major concentration dependence of the observed spectra as well as the lack of any major pressure shifts of many properties of metal-ammonia solutions as a function of concentration as found in the recent unpublished work of Schinderwolf[58] also suggest that the two-electron species is not

stable. Possibly a species consisting of a metal ion bound to a
two-electron cavity is stable, but its properties would have to be
investigated before it can be justified. The models reported here
should be extendable to such species.

Because of the two-electron polarizations and the screened
Coulomb interactions for the case where one or both of the electrons
are outside the void region, the two-electron electronic energies are
not extremely different from twice the one-electron energies. This is
not the case for the total energy E_T since the induced dipole-induced
dipole repulsions between the surface molecules is almost doubled
(not doubled since the percent charge in the void region is decreased
by the effect of the Coulomb repulsions). On combining the energy
Π with the total energy E_T and the surface energy E_{st}, we have
obtained the heats of solution for the species considered (Tables XII
and XIII). The energy ΔH_{21} (Table XIII) indicates that the two-electron
cavities are not stable relative to two one-electron cavities. The
calculations of Land and O'Reilly[23,26] also found positive ΔH_{21}
values but their results were biased in favor of such an answer
because of their arbitrary choice of a large cavity and the method
employed to calculate Σ.

Since the molecules on the surface of the cavities are
loosely packed, a conduction mechanism which involves cavities that
are easily deformed would be possible. This could involve a cavity
that elongates in an electric field and then forms another cavity.

This mechanism would involve very little energy in forming the "new" cavity. The loose packing also predicts a decrease in the viscosity of metal-ammonia solutions with increasing concentrations of the electrons. This is consistent with experimental viscosity data.[59] The short "lifetime" measured by NMR and ESR methods also is nicely consistent with our model.

The large dipole moment and the high polarizability of the ammonia molecules are the most important factors that lead to the stability of the one-electron cavities while the hydrogen-hydrogen repulsions are the most important factor for determining the sizes of the cavities. Additional calculations should be carried out for cavities with fewer molecules on the surface to see if better agreement with volume expansion and spectroscopic data can be found. In such calculations an accurate hydrogen-hydrogen repulsion potential for the ammonia molecules is one very important factor that must be included.

The short-range electron-molecule exchange interactions have indicated that NH_3^- is not stable, but the calculations reported here indicate that there is a high charge density very close to the surface layer. This result indicates that a species of the form $(NH_3)_n^-$ might be stable because of the electron-multipole and other strong interactions. We expect n to be an integer from four to fourteen. Experiments are currently underway to check such a proposal.[60] In some calculations not reported here continuum effects

were eliminated and a stable species was found. Thus we suspect that at reasonable gas densities the ammonia molecules cluster around an electron. Evidence is available for a cavity model in super heated water at temperatures above the critical point and densities as low as one-third the critical density.[61]

A calculation similar to the one reported here might be carried out for other media. Water is the obvious medium for such a calculation, but hydrogen bonding is one factor that would be difficult to take into account. On comparing the characteristics of ammonia and water several analogies can be made. Because the water molecule has only two hydrogens as compared to three for ammonia, the hydrogen-hydrogen repulsions would not be as important and would give a smaller cavity. A smaller cavity would also be favored since the optical polarizability is smaller than ammonia's which makes the induced dipole-induced dipole repulsions of less importance.[46] Since water has a larger dipole moment and a smaller quadrupole moment,[46] a greater charge density would be in the void region if V_o for water is zero or somewhat positive. These comparisons indicate that a cavity in water would probably have four or six molecules on the surface of a cavity. Alcohols and other hydrocarbons could also be considered, but only the smaller molecules could be considered using a spherical molecule approximation. Methanol is one alcohol for which these methods could yield reasonable results.

II. ACCURATE "EFFECTIVE" INTERMOLECULAR PAIR POTENTIALS
IN GASEOUS ARGON

A. DISCUSSION

Statistical mechanical calculations for the macroscopic

properties of media require an accurate knowledge of the inter-

molecular forces between the atoms (or molecules) in the media.

At low densities pair potentials are adequate, but for higher

densities of gases and liquids many-body interactions must be

considered. Many-body interactions arise because the electrons

in each atom or molecule readjust their motions in response to

every new atom or molecule entering within its force range.[62]

We have examined in detail one specific case, namely

the argon-argon interaction. Using presently proposed two-body

potentials we have evaluated effective two-body potentials as a

function of temperature and density where the nonadditive correction

to the two-body potentials is taken as the induced dipole effects

of three-body interactions. The results and details of this

calculation are given in Appendix IV.

APPENDIX I

THE ONE- AND TWO-ELECTRON SPHERICAL
BOX PROBLEM

The spherical box problem with one electron in an infinite well has been used extensively as a pedagogic example,[63-66] but the two-electron problem has been investigated almost exclusively within the Hartree-Fock approximation.[67] To aid in our understanding of the cavity species discussed in the Introduction and to help in the formulation of the model that we have considered, we undertook an extensive investigation of the two-electrons-in-a-spherical-box problem with an infinite potential outside the box.

Before we consider the two-electron problem we shall review some of the results of the one-electron case. The acceptable solutions to the Schroedinger equation,

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\psi}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} = E\psi \qquad (I\text{-}1)$$

for the one-electron problem are found (in unnormalized form) to be

$$\psi_{n\ell m} = j_\ell(Kr)\, Y_{\ell m}(\theta,\phi) \qquad (I\text{-}2)$$

where $Y_{\ell m}(\theta,\phi)$ is a spherical harmonic, $j_\ell(Kr)$ is a spherical Bessel function, and (r, θ, ϕ) are the spherical coordinates of the electron relative to the center of the cavity. The value of K

is found from the boundary condition

$$j_\ell(KR_b) = 0 \qquad\qquad (I-3)$$

In solving equation (I-1) the substitution $K = \sqrt{2E}$ was made; therefore, we have $E = \frac{K^2}{2}$. Thus we can obtain the energy levels of this one-electron system from a table of the zeros of the spherical Bessel function.[68] Because of the infinite number of roots that can be found for equation (I-1), the quantum number n is introduced to denote which root is being considered for a given ℓ(e.g., n = 1 denotes the smallest root for a given ℓ). The quantum numbers ℓ and m are apparent from equation (I-2). The radial part of the wavefunctions for the three lowest energy levels with their respective energies are given in Table I-1. The nomenclature used in Table I-1 to denote the energy states is used because of the similarity of the angular dependence of this problem to the hydrogen

Table I-1. The (unnormalized) radial wavefunctions and energies of the three lowest energy levels of the one-electron-in-a-spherical-box problem with an infinite well.

ℓ	State	$E_{1\ell m} \cdot R_b^2$ [b]	$R'_{1\ell}$
0	(1s)	$.5\pi^2$	$\dfrac{\sin(\pi r)}{\pi r}$
1	(2p)	$1.023\pi^2$	$\dfrac{\sin(Kr)}{(Kr)^2} - \dfrac{\cos(Kr)}{Kr}$
2	(3d)	$1.683\pi^2$	$\left[\dfrac{3}{(Kr)^3} - \dfrac{1}{Kr}\right]\sin(Kr) - \dfrac{3}{(Kr)^2}\cos(Kr)$

[a] n = 1

[b] Energy in Hartrees$\cdot a_o^2$.

atom problem. Unlike the situation in atoms, the radial nodes in the wavefunctions increase the energy more than angular nodes.

If the energy of the helium atom is calculated by assuming that the two electrons occupy a 1s orbital with opposite spins, an error of approximately 0.056 a.u. is obtained in the resulting energy.[69] The essential weakness of such a calculation is in the assumption that each electron sees only the average field of the other electron. In fact, the electronic motions are _correlated_ in some detailed fashion. This error in the Hartree-Fock energy has thus become known as the _correlation_ _energy_. Since the total electron correlation problem has not been investigated for the two-electrons-in-a-spherical-box problem, we have carried out such an investigation.

Since the method of Hylleraas gives the non-relativistic ground state energy in almost exact agreement with experiment for the helium atom,[70] we have carried out a similar calculation for the two-electron-box problem. The explicit inclusion of the inter-electron distance r_{12} in the variational function in the Hylleraas method would make this method of obtaining the energy of a cavity system most unwieldy if extended to include the various medium interactions. We have thus repeated our calculations with a configuration interaction method that could easily be extended to include the medium interactions. With the Hylleraas type calculation

assumed to give the exact correlation δE_2 for the system, we can

judge the accuracy obtained from the configuration interaction.

The Hamiltonian for the two-electron-box problem can be

written (in atomic units) as

$$\mathcal{H}_2 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{r_{12}} \tag{I-4}$$

For the Hylleraas type calculation we have assumed the wavefunction

$$\psi_H = \psi_{1s}(1)\psi_{1s}(2)(1 + \alpha_H r_{12}) \tag{I-5}$$

where $\psi_{1s}(i)$ is a normalized 1s wavefunction (unnormalized is given

in Table (I-1)) and α_H is a variational parameter to be used in

minimizing the energy. We obtain the energy of the system from the

integral relation

$$E_H = \frac{\langle \psi_H | \mathcal{H}_2 | \psi_H \rangle}{\langle \psi_H | \psi_H \rangle} = \frac{\langle \psi_H | T_2 + \frac{1}{r_{12}} | \psi_H \rangle}{\langle \psi_H | \psi_H \rangle} \tag{I-6}$$

where T_2 is the kinetic energy operator of the Hamiltonian. The

problems encountered by using the Laplacian operator as the kinetic

energy operator are easily eliminated by using the $\nabla\varphi \cdot \nabla\varphi$ form of

the operator which yields the integral relation[70,71]

$$\int \varphi_1 T_2 \varphi_2 d\tau = \int \{ \frac{1}{2}(\frac{\partial\varphi_1}{\partial r_1})(\frac{\partial\varphi_2}{\partial r_1}) + \frac{1}{2}(\frac{\partial\varphi_1}{\partial r_2})(\frac{\partial\varphi_2}{\partial r_2}) + (\frac{\partial\varphi_1}{\partial r_{12}})(\frac{\partial\varphi_2}{\partial r_{12}})$$
$$+ \frac{1}{4}\frac{(r_1^2+r_{12}^2-r_2^2)}{r_1 r_{12}}[(\frac{\partial\varphi_1}{\partial r_1})(\frac{\partial\varphi_2}{\partial r_{12}}) + (\frac{\partial\varphi_2}{\partial r_1})(\frac{\partial\varphi_1}{\partial r_{12}})]$$
$$+ \frac{1}{4}\frac{(r_2^2+r_{12}^2-r_1^2)}{r_2 r_{12}}[(\frac{\partial\varphi_1}{\partial r_2})(\frac{\partial\varphi_2}{\partial r_{12}}) + (\frac{\partial\varphi_2}{\partial r_2})(\frac{\partial\varphi_1}{\partial r_{12}})]\}d\tau \tag{I-7}$$

After taking the partial derivatives and simplifying the expressions, we left with several integrals of the form

$$\int \psi_{1s}(1)\psi_{1s}(2)\ r_1^p\ r_2^q\ r_{12}^s\ dv_1 dv_2 \tag{I-8}$$

with p, q, s taking integer values. Since $\psi_{1s}(1)$ and $\psi_{1s}(2)$ are both spherically symmetric, these integrals can be evaluated by using the integral identity[72]

$$8\pi^2\{\int_o^\infty \psi_{1s}(1)r_1^{p+1}dr_1\int_o^{r_1}\psi_{1s}(2)r_2^{q+1}dr_2\int_{r_1-r_2}^{r_1+r_2} r_{12}^{s+1}\ dr_{12}$$

$$+ \int_o^\infty \psi_{1s}(2)r_2^{q+1}dr_2\int_o^{r_2}\psi_{1s}(1)r_1^{p+1}dr_1\int_{r_2-r_1}^{r_1+r_2} r_{12}^{s+1}\ dr_{12}\}$$

The first two integrations in each of the triple integrals can be performed with relative ease, but the third integration is very involved. Consequently, the third integration was carried out numerically with a Gaussian quadrature. The resulting energy of the system was found to be given as a function of R_b by

$$E_H = \frac{A_1 + \alpha_H A_2 + \alpha_H^2 A_3}{B_1 + \alpha_H B_2 + \alpha_H^2 B_3} \tag{I-9}$$

where

$$A_1 = \frac{19.7392}{R_b^2} + \frac{3.3721}{R_b}$$

$$A_2 = \frac{27.6081}{R_b} + 4.0000$$

$$A_3 = 13.1595 + (1.3986)R_b$$

$$B_1 = 2.0000$$

$$B_2 = (2.7974)R_b$$

and

$$B_3 = (1.1307)R_b^2$$

Upon differentiating E_H with respect to α_H and setting the result equal to zero, in accordance with the variational method, we obtained the minimum energy. Since the minimum energy is a function of R_b, it is tabulated in Table I-2 and illustrated in Figure I-1. The values of α_H and the correlation energy for the minimum energy are also tabulated in Table I-2.

TABLE I - 2

RESULTS FOR HYLLERAAS TYPE CALCULATION OF THE GROUND STATE ENERGY

OF A TWO-ELECTRON SPHERICAL, INFINITE WELL

$R_b(a_0)$	E_H^a	$-\delta E_2$	α_H	E_{100}
0.5	42.98953	0.06102	0.26743	19.73907
1.0	11.59606	0.05961	0.28708	4.93477
1.5	5.51899	0.05822	0.30931	2.19323
2.0	3.30365	0.05679	0.33449	1.23369
2.5	2.23821	0.05536	0.36325	0.78956
3.0	1.63805	0.05393	0.39645	0.54831
3.5	1.26348	0.05251	0.43527	0.40234
4.0	1.01226	0.05111	0.48133	0.30842
4.5	0.83456	0.04974	0.53701	0.24369
5.0	0.70360	0.04840	0.60573	0.19739
5.5	0.60391	0.04710	0.69288	0.16313
6.0	0.52600	0.04584	0.80721	0.13708
6.5	0.46376	0.04462	0.96398	0.11680
7.0	0.41313	0.04345	1.19253	0.10071
7.5	0.37129	0.04231	1.55740	0.08773
8.0	0.33624	0.04123	2.23347	0.07711
8.5	0.30655	0.04018	3.91729	0.06830
9.0	0.28112	0.03918	15.48499	0.06092
9.5	0.25915	0.03821	-8.02780	0.05468
10.0	0.24002	0.03729	-3.20185	0.04935
10.5	0.22323	0.03640	-2.00497	0.04476

[a] Energies are in Hartree units.

Figure I-1. Energies as a function of the radius of an infinite
well cavity for two-electrons.

▲ ^{1}P energy from 2 term CI calculation

o ^{3}P energy from 2 term CI calculation

x ^{1}S energy from 3 term CI calculation

+ ^{1}S energy from Hylleraas type calculation

—·— ^{1}S → ^{1}P transition energy

--- Correlation energy for ^{1}S Hylleraas type calculation

... Correlation energy for ^{1}S 3 term CI calculation
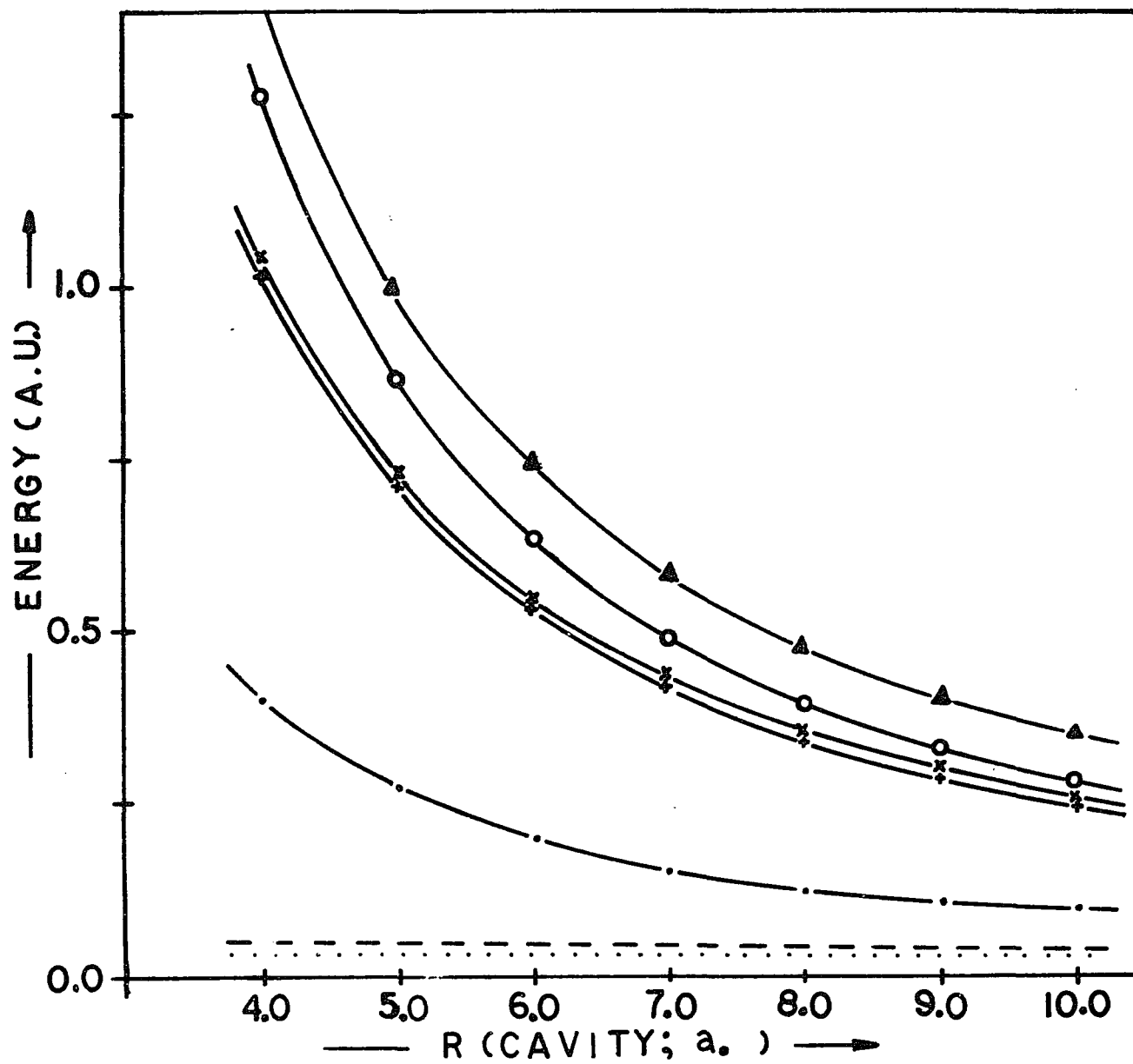
The similarity between the angular dependence of the wavefunctions of the one-electron-box and the hydrogen atom implies that the techniques used in configuration interaction (CI) calculations for atomic systems are appropriate for the two-electron-box calculations.[52,53] From the LS coupling scheme we have that the wavefunction of a given symmetry can be formed as a linear super-position of state functions that have been combined to be of the same symmetry. Thus we have

$$\Psi_{(sy)} = \sum_i c_i \, \psi_{i(sy)}; \quad sy = {}^1s, \, {}^1p, \cdots; \quad i = 1, 2, \cdots; \quad (I\text{-}10)$$

where $\Psi_{(sy)}$ is the wavefunction to be determined by minimizing the energy, $\psi_{i(sy)}$ is an appropriate combination of state functions, and c_i is a coefficient to be determined by minimizing the energy. The energy of a given symmetry of the two-electron-box system is found by using the Hamiltonian given in equation (I-4) in conjunction with a wavefunction similar to the one given in equation (I-10). The coefficients for the minimum energy satisfy the equations

$$\sum c_i (H_{ij} - S_{ij}E) = 0 \qquad (I\text{-}11)$$

and the corresponding minimum energy is the lowest root of the secular equation

$$|H_{ij} - S_{ij}E| = 0 \qquad (I\text{-}12)$$

where

$$H_{ij} = \int \psi_{i(sy)} \mathcal{H}_2 \psi_{j(sy)} d\tau \text{ and } S_{ij} = \int \psi_{i(sy)} \psi_{j(sy)} d\tau \qquad \text{(I-13)}$$

Since the wavefunctions that we have used satisfy the relation

$$\delta_{ij} = \int \psi_{i(sy)} \psi_{j(sy)} d\tau = S_{ij} \qquad \text{(I-14)}$$

where δ_{ij} is the Kronecker symbol defined by

$$\delta_{ij} = 1 \qquad \text{if } i = j$$
$$= 0 \qquad \text{if } i \neq j \qquad \text{(I-15)}$$

we are left with the secular equation

$$|H_{ij} - \delta_{ij} E| = 0 \qquad \text{(I-16)}$$

which is equivalent to an eigenvalue problem. Thus we can determine the minimum energy by diagonalizing the matrix

$$||H_{ij}|| \qquad \text{(I-17)}$$

and extracting the smallest diagonal element.

We have carried out the above procedure to determine the correlation energies of the three two-electron states ^1S, ^1P, and ^3P. Approximate radial wavefunctions were used in the CI calculation to alleviate the very tedious integrations encountered when the radial wavefunctions given in Table I-1 are used. The one-electron wave-functions that were used in this CI calculation are given in Table I-3

Table I-3. The radial one-electron wavefunctions used in the CI calculations for the two-electron-box problem. The angular dependence is the same as for the wavefunctions given in Table III.[a]

ℓ	State[b]	$E_{1\ell m} \cdot R_b^2$	$R_{1\ell}(r)$ [c]
0	(1s)	5.0000	$\sqrt{\dfrac{30}{R_b^5}}(R_b - r)$
1	(2p)	10.5000	$\sqrt{\dfrac{105}{R_b^7}}\, r(R_b - r)$
2	(3d)	16.8950	$\dfrac{17.2163}{R_b^{15/2}}\, r^2(R_b^4 - 1.9R_b^2 r^2 + .9r^4)$

[a] Energy is in Hartrees$\cdot a_o^2$.

[b] $n = 1$

[c] normalized

and the two-electron state functions are given in Table I-4. All of the integrals involving $1/r_{12}$ were evaluated by converting the integrals to the F and G integrals that are common to atomic calculations.[52,53] The ground state energy was obtained by mixing the three ^{1}S states of $(1s)^2$, $(2p)^2$ and $(3d)^2$ where the term within the brackets denotes the one-electron wavefunction (or functions) used and the superscript denotes that both of the electrons are in similar spatial orbitals. We obtained

Table I-4

The normalized antisymmetrized spin wavefunctions for the various

configurations used in the CI calculations

Symmetry	Configuration	$\psi_{i(sy)}$ [a]
^1S	$(1s)^2$	$1s_0(1)1s_0(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
	$(2p)^2$	$\frac{1}{\sqrt{3}}\{2p_1(1)2p_{-1}(2)+2p_{-1}(1)2p_1(2)-2p_0(1)2p_0(2)\}\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)]$
	$(3d)^2$	$\frac{1}{\sqrt{5}}\{3d_2(1)3d_{-2}(2)+3d_{-2}(1)3d_2(2)-3d_1(1)3d_{-1}(2)-3d_{-1}(1)3d_1(2)$
		$+\ 3d_0(1)3d_0(2)\}\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
^1P	$(1s2p)$	$\frac{1}{\sqrt{2}}\{1s_0(1)2p_0(2)+1s_0(2)2p_0(1)\}\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)]$
	$(2p3d)$	$\frac{1}{\sqrt{60}}\{3[2p_1(1)3d_{-1}(2)+2p_{-1}(1)3d_1(2)+2p_1(2)3d_{-1}(1)+2p_{-1}(2)3d_1(1)]$
		$-\ 2\sqrt{3}[2p_0(1)3d_0(2)+2p_0(2)3d_0(1)]\}\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)]$
^3P	$(1s2p)$	$\frac{1}{\sqrt{2}}\{1s_0(1)2p_0(2)-1s_0(2)2p_0(1)\}\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\alpha(2)\beta(1)]$
	$(2p3d)$	$\frac{1}{\sqrt{60}}\{3[2p_1(1)3d_{-1}(2)+2p_{-1}(1)3d_1(2)-2p_1(2)3d_{-1}(1)-2p_{-1}(2)3d_1(1)]$
		$-\ 2\sqrt{3}[2p_0(1)3d_0(1)-2p_0(2)3d_0(1)]\}\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\alpha(2)\beta(1)]$

[a] $1s_0(1) \equiv R_{10}(r_1)Y_{00}(\theta_1,\phi_1)$; $2p_m(1) \equiv R_{21}(r_1)Y_{1m}(\theta_1,\phi_1)$; $3d_m(2) \equiv R_{12}(r_2)Y_{2m}(\theta_2,\phi_2)$.

the following matrix elements for the ^1S ground state:

$$H_{11} = \frac{10.0000}{R_b^2} + \frac{1.7857}{R_b}$$

$$H_{22} = \frac{21.0000}{R_b^2} + \frac{1.7908}{R_b}$$

$$H_{33} = \frac{33.7900}{R_b^2} + \frac{1.9649}{R_b}$$

$$H_{12} = -\frac{0.5694}{R_b}$$

$$H_{13} = \frac{0.5136}{R_b}$$

$$H_{23} = -\frac{0.8092}{R_b} \tag{I-18}$$

where we have taken Ψ_{1_S} to be given by

$$\Psi_{1_S} = C_1 (1s)_{1_S}^2 + C_2 (1p)_{1_S}^2 + C_3 (3d)_{1_S}^2 \tag{I-19}$$

and we have only given the diagonal elements and the elements to the right of the main diagonal since the matrix is Hermitian. The coefficients for equation (I-19) and the correlation energy are given in Table I-5 for several values of R_b. A ^1S mixing was also carried out with Ψ_{1_S} given by

$$\Psi_{1_S} = C_1 (1s)_{1_S}^2 + C_2 (2p)_{1_S}^2 \tag{I-20}$$

to determine the additional correlation energy obtained by the mixing represented in equation (I-19). The results obtained by the two term ^1S mixing are given in Table I-6.

TABLE I - 5

RESULTS OF A THREE TERM CONFIGURATION INTERACTION FOR THE
GROUND STATE ENERGY OF A TWO-ELECTRON SPHERICAL, INFINITE WELL

$R_b(a_0)$	E_{1s}^a	$-\delta E_2$	C_3	C_2	C_1
0.5	43.53179	0.03961	0.01031	-0.02546	-0.99962
1.0	11.74704	0.03866	0.01968	-0.05004	-0.99955
1.5	5.59720	0.03771	0.02811	-0.07368	-0.99689
2.0	3.35607	0.03678	0.03564	-0.09636	-0.99471
2.5	2.27841	0.03587	0.04231	-0.11806	-0.99210
3.0	1.67137	0.03497	0.04817	-0.13881	-0.98915
3.5	1.29242	0.03410	0.05327	-0.15862	-0.98590
4.0	1.03817	0.03326	0.05766	-0.17753	-0.98242
4.5	0.85821	0.03244	0.06137	-0.19558	-0.97876
5.0	0.72549	0.03165	0.06447	-0.21282	-0.97496
5.5	0.62436	0.03089	0.06700	-0.22929	-0.97105
6.0	0.54524	0.03015	0.06899	-0.24504	-0.96706
6.5	0.48196	0.02944	0.07049	-0.26011	-0.96300
7.0	0.43042	0.02876	0.07153	-0.27455	-0.95891
7.5	0.38776	0.02811	0.07215	-0.28841	-0.95478
8.0	0.35198	0.02748	0.07237	-0.30172	-0.95064
8.5	0.32162	0.02687	0.07223	-0.31453	-0.94650
9.0	0.29558	0.02629	0.07175	-0.32687	-0.94234
9.5	0.27304	0.02573	0.07094	-0.33877	-0.93819
10.0	0.25338	0.02519	0.06985	-0.35027	-0.93404

^{a}Energies are in Hartree units.

TABLE I - 6

RESULTS OF A TWO TERMS CONFIGURATION INTERACTION FOR
GROUND STATE ENERGY OF A SPHERICAL TWO-ELECTRON INFINITE WELL

$R_b(a_o)$	$E_{1_S}^a$	$-\delta E_2$	C_2	C_1
0.5	43.54195	0.02945	0.02585	-0.99967
1.0	11.75632	0.02938	0.05153	-0.99867
1.5	5.60563	0.02928	0.07690	-0.99704
2.0	3.36371	0.02914	0.10182	-0.99480
2.5	2.28532	0.02896	0.12615	-0.99201
3.0	1.67759	0.02876	0.14981	-0.98872
3.5	1.29800	0.02852	0.17269	-0.98498
4.0	1.04316	0.02826	0.19473	-0.98086
4.5	0.86267	0.02798	0.21588	-0.97642
5.0	0.72947	0.02767	0.23611	-0.97173
5.5	0.62790	0.02735	0.25540	-0.96684
6.0	0.54838	0.02701	0.27376	-0.96180
6.5	0.48475	0.02666	0.29119	-0.95667
7.0	0.43288	0.02631	0.30771	-0.95148
7.5	0.38993	0.02594	0.32335	-0.94628
8.0	0.35389	0.02557	0.33815	-0.94109
8.5	0.32329	0.02520	0.35213	-0.93595
9.0	0.29704	0.02483	0.36534	-0.93087
9.5	0.27431	0.02446	0.37782	-0.92588
10.0	0.25448	0.02409	0.38961	-0.92098

[a] Energies are in Hartree units.

The ^1P energy was obtained by mixing the ^1P states of (1s2p) and (2p3d), and the ^3P energy was obtained by mixing the ^3P states of (1s2p) and (2p3d). We have taken Ψ_{1_P} to be given by

$$\Psi_{1_P} = C_1(1s2p)_{1_P} + C_2(2p3d)_{1_P} \qquad (I-21)$$

and we have taken Ψ_{3_P} to be given by

$$\Psi_{3_P} = C_1(1s2p)_{3_P} + C_2(2p3d)_{3_P} \qquad (I-22)$$

The results of the ^1P calculation are given in Table I-7 and the results of the ^3P calculation are given in Table I-8. The matrix elements used in the ^1P calculation are as follows:

$$H_{11} = \frac{15.5000}{R_b^2} + \frac{1.8861}{R_b}$$

$$H_{22} = \frac{37.3950}{R_b^2} + \frac{4.6189}{R_b}$$

$$H_{12} = -\frac{0.3732}{R_b} \qquad (I-23)$$

The matrix elements used in the ^3P calculation are as follows:

$$H_{11} = \frac{15.5000}{R_b^2} + \frac{1.2295}{R_b}$$

$$H_{22} = \frac{37.3950}{R_b^2} + \frac{4.0924}{R_b}$$

$$H_{12} = -\frac{0.3219}{R_b} \qquad (I-24)$$

TABLE I - 7

RESULTS OF A TWO TERM CONFIGURATION INTERACTION FOR THE

^{1}p ENERGY OF A SPHERICAL TWO-ELECTRON INFINITE WELL

$R_b(a_0)$	$E_{^1p}^a$	$-\delta E_2$	C_2	C_1
0.5	65.76621	0.00599	0.00802	-0.99997
1.0	17.38045	0.00565	0.01515	-0.99989
2.0	4.81296	0.00509	0.02725	-0.99963
2.5	3.22960	0.00484	0.03242	-0.99947
3.0	2.34630	0.00462	0.03712	-0.99931
3.5	1.79977	0.00442	0.04141	-0.99914
4.0	1.43604	0.00423	0.04533	-0.99897
4.5	1.18050	0.00406	0.04894	-0.99880
5.0	0.99331	0.00391	0.05226	-0.99863
5.5	0.85156	0.00376	0.05533	-0.99847
6.0	0.74128	0.00362	0.05818	-0.99831
6.5	0.65353	0.00350	0.06082	-0.99815
7.0	0.58239	0.00338	0.06329	-0.99800
7.5	0.52376	0.00327	0.06560	-0.99785
8.0	0.47478	0.00317	0.06775	-0.99770
8.5	0.43336	0.00307	0.06978	-0.99756
9.0	0.39794	0.00298	0.07168	-0.99743
9.5	0.36739	0.00289	0.07348	-0.99730
10.0	0.34080	0.00281	0.07517	-0.99717

[a]Energies are in Hartree units.

TABLE I - 8

RESULTS OF A TWO TERM CONFIGURATION INTERACTION FOR THE

^3p ENERGY OF A SPHERICAL TWO-ELECTRON INFINITE WELL

$R_b(a_o)$	E_{3p}^a	$-\delta E_2$	C_2	C_1
0.5	64.45456	0.00444	0.00690	-0.99998
1.0	16.72531	0.00419	0.01300	-0.99992
1.5	7.70460	0.00396	0.01843	-0.99983
2.0	4.48600	0.00375	0.02329	-0.99973
2.5	2.96824	0.00356	0.02767	-0.99962
3.0	2.12866	0.00340	0.03163	-0.99950
3.5	1.61335	0.00324	0.03524	-0.99938
4.0	1.27302	0.00310	0.03853	-0.99926
4.5	1.03568	0.00297	0.04155	-0.99914
5.0	0.86304	0.00286	0.04432	-0.99902
5.5	0.73319	0.00275	0.04688	-0.99890
6.0	0.63283	0.00265	0.04925	-0.99879
6.5	0.55347	0.00255	0.05146	-0.99868
7.0	0.48951	0.00246	0.05351	-0.99857
7.5	0.43711	0.00238	0.05542	-0.99846
8.0	0.39357	0.00231	0.05721	-0.99836
8.5	0.35695	0.00223	0.05888	-0.99826
9.0	0.32580	0.00217	0.06046	-0.99817
9.5	0.29906	0.00210	0.06194	-0.99808
10.0	0.27591	0.00204	0.06333	-0.99799

^{a}Energies are in Hartree units.

The energies of the three states considered and the correlation
energy (of the three term mixing) of the ground state are illustrated
in Figure I-1.

APPENDIX II

TWO-ELECTRON MOLECULAR POLARIZATION POTENTIAL

From equation (56) of Chapter I, Section B we have that the two-electron polarization interaction with a molecule is

$$V_{2pol}^{i} = - \frac{\alpha_o \cos\theta_b}{\rho_1^2 \rho_2^2} \tag{II-1}$$

where the coordinates are defined as given in Figure II. Using the law of cosines to remove the θ_b angular dependence of equation (II-1) yields

$$V_{2pol}^{i} = - \frac{\alpha_o}{2} \{ \frac{1}{\rho_1 \rho_2^3} + \frac{1}{\rho_1^3 \rho_2} - \frac{r_{12}^2}{\rho_1^3 \rho_2^3} \} \tag{II-2}$$

The law of cosines is again used to put the ρ_1 and ρ_2 coordinates of the electrons in terms of the coordinates of the center of the cavity. Thus we have

$$\rho_1^2 = R_m^2 + r_1^2 - 2r_1 R_m \cos\theta_1 \tag{II-3}$$

and

$$\rho_2^2 = R_m^2 + r_2^2 - 2r_2 R_m \cos\theta_2 \tag{II-4}$$

where these coordinates are as given in Figure II. By expanding $1/\rho_1$ and $1/\rho_1^3$ in terms of Legendre polynomials we obtain the relations[73]

$$\frac{1}{\rho_1} = \sum_{n=o}^{\infty} \frac{r_1^n}{R_m^{n+1}} \ P_n(\cos\theta_1) \tag{II-5}$$

and

$$\frac{1}{\rho_1^3} = \sum_{m=o}^{\infty} \frac{r_1^m(2m+1)}{R_m^{m+1}(R_m^2-r_1^2)} \, P_m(\cos\theta_1) \qquad \text{(II-6)}$$

Similar relations are also obtained for ρ_2. Substituting these relations into equation (II-2) yields the desired result

$$V_{2po\ell}^i = -\frac{\alpha_o}{2} \sum_{n=o}^{\infty} \sum_{m=o}^{\infty} \frac{r_1^n r_2^m}{R_m^{n+m+2}} \left\{ \frac{(2m+1)}{(R_m^2-r_2^2)} + \frac{(2n+1)}{(R_m^2-r_1^2)} - \frac{r_{12}^2(2m+1)(2n+1)}{(R_m^2-r_1^2)(R_m^2-r_2^2)} \right\}$$

$$P_n(\cos\theta_1)P_m(\cos\theta_2) \qquad \text{(II-7)}$$

APPENDIX III

TWO-ELECTRON CONTINUUM POLARIZATION POTENTIAL

The two-electron polarization potential for the continuum region with the electrons not in the continuum can be expressed in the form

$$V^c_{2po\ell} = -\alpha_o \bar{\rho}_d \int \frac{g(r)L(r)\cos\theta_b}{s_1^2\, s_2^2}\, d\tau \qquad (III-1)$$

where $g(r)$ and $L(r)$ are taken as defined in equations (46) and (47) of Chapter I, Section B. The coordinates S_1 and S_2 are similar to ρ_1 and ρ_2, but are the distances from the electrons to a point in the continuum (e.g., the coordinate s in Figure II). The angle θ_b is the angle between S_1 and S_2 at the point in the medium (see Figure II). Substituting the relations for $g(r)$ and $L(r)$ into equation (III-1) yields

$$V^c_{2po\ell} = - \frac{\alpha_o \bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \int_{R_d}^{\infty} \frac{\cos\theta_b}{s_1^2\, s_2^2}\, d\tau \qquad (III-2)$$

where the integration is taken over the region R_d to infinity. By analogy with the two-electron molecule polarization potential, this equation can be written as follows:

$$V^c_{2po\ell} = - \frac{\alpha_o\, \bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \sum_{n=o}^{\infty} \sum_{m=o}^{\infty} \int_{R_d}^{\infty} \int_o^{\pi} \int_o^{2\pi} \frac{r_1^n\, r_2^m}{r^{n+m+2}}$$

$$\{\frac{(2m+1)}{(r^2-r_2^2)} + \frac{(2n+1)}{(r^2-r_1^2)} - \frac{r_{12}^2(2n+1)(2m+1)}{(r^2-r_1^2)(r^2-r_2^2)}\}P_n(\cos\theta_1)P_m(\cos\theta_2)r^2\sin\theta$$

$$drd\theta d\phi \quad (III-3)$$

which is to be integrated. For a spherical cavity in a uniform

continuum medium, the two-electron polarization potential of the

continuum is only dependent on the relative positions of the two

electrons to each other. Thus we can choose arbitrary axes for

measuring the angular dependence of θ and ϕ of the potential.

For simplicity we have assumed that the angular dependence can be

expressed in terms of θ_1 and ϕ_1, the angular coordinates of electron

one. The angular dependence of θ_2 can be expressed in terms of

θ_1, ϕ_1 and θ_{12} by the addition theorem of Legendre polynomials which

is[73]

$$P_m(\cos\theta_2) = P_m(\cos\theta_1)P_m(\cos\theta_{12})$$

$$+2\sum_{k=1}^{m} \frac{(m-k)!}{(m+k)!} P_m^k(\cos\theta_1)P_m^k(\cos\theta_{12})\cos(k\phi_1) \quad \text{(III-4)}$$

where $P_m^k(\cos\theta)$ is an associated Legendre function. The angle ϕ_{12}

which usually appears in equation (III-4) was taken as zero to

yield an expression which is only dependent on the angle θ_{12}. This

does not affect the final results and gives an expression that is

easily handled. After making this substitution in equation (III-3),

the final result is

$$V_{2po\ell}^c = - \frac{4\pi\alpha_o\bar{\rho}_d}{(1+\frac{8\pi}{3}\alpha_o\bar{\rho}_d)} \sum_{n=o}^{\infty} \frac{(n+1)}{(2n+1)} \frac{r_1^n r_2^n}{R_d^{2n+1}} P_n(\cos\theta_{12}) \quad \text{(III-5)}$$

which is the two-electron polarization potential of the continuum

arising from an additional electron being in the cavity. It should

be noted that if θ_{12} is zero and $r_1 = r_2$, i.e., both charges are at

the same position in the cavity, the resulting potential is twice the one-electron potential. This result is what would be expected since the factor of two arises from the cross terms as shown in equation (55) of Chapter I, Section B.

APPENDIX IV

REPRINT FOR CHAPTER II

ACCURATE "EFFECTIVE" INTERMOLECULAR PAIR
POTENTIALS IN GASEOUS ARGON
David A. Copeland and Neil R. Kestner,
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Accurate "Effective" Intermolecular Pair Potentials in Gaseous Argon

David A. Copeland and Neil R. Kestner

Accurate "Effective" Intermolecular Pair Potentials in Gaseous Argon*

DAVID A. COPELAND AND NEIL R. KESTNER†

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana

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The "effective" intermolecular potential in gaseous argon has been determined, accurate through first order in density, for various assumed argon–argon potentials and the triple-dipole interaction. This potential should lead to the correct radial-distribution function. The calculations do not agree with the 1965 analysis of experimental data by Mikolaj and Pings [Phys. Rev. Letters 15, 849 (1965)]. Our results suggest a density dependence of the minimum of the effective potential of only about 17 $\bar{\rho}$ (in degrees Kelvin), where $\bar{\rho}$ is the density in grams per cubic centimeter. This constant has a sizeable temperature dependence but only a small variation proportional to density. The contribution of other nonadditive effects is briefly examined as is the small contribution of nonadditive effects to the x-ray structure factor of the liquid.

I. INTRODUCTION

In recent years there have been many calculations of the effect of many-body interactions on the properties of gases and liquids.[1–15] In all cases, approximations had to be made in order to arrive at a result, and in no case is it proven that the many-body interaction is important. Its presence is always inferred by comparing calculated and observed quantities, or often simply two calculated quantities.

Recently we have seen two developments, one experimental and one theoretical, which could lead to a direct observation of the many-body contribution. First has been the experimental work by Mikolaj and Pings[16] which, if increased in accuracy, should enable one to determine accurate "effective" two-body interactions between atoms in low-density gases. Second has been the work of Rushbrooke and Silbert[17] and Rowlinson[18] who have been able to show in a straightforward way

how the three-body potential should affect the two-body radial-distribution function, or conversely, what effective two-body interaction would yield the correct radial-distribution function.

Many-body interactions arise because the electrons in each molecule readjust their motions in response to every new molecule entering within its force range.[19] This force range in quantum-mechanical calculations can be broken into two parts, obviously coupled with one another in general. There are Coulombic interactions, and there are exchange interactions. If the molecules are far apart, the latter has little influence on the system, and one can use ordinary perturbation theory to derive the nonadditive effects. It is found[19] that only in third order do such effects occur. They are of two major types: The interaction of three induced dipoles[9] and the interaction of two induced dipoles and one induced quadrupole.[15] At low densities the latter is unimportant and will be neglected until later.

The triple-dipole effect, as it is usually called, can be written as

$$\phi(123) = \nu(1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3)/r_{12}{}^3 r_{23}{}^3 r_{13}{}^3, \quad (1)$$

where θ_i are the interior angles of a triangle of sides r_{12}, r_{13}, and r_{23}. ν is a coefficient which is found to be given accurately[20] (to within a few percent) by

$$\nu = \tfrac{3}{4}\alpha C_6, \quad (2)$$

where α is the polarizability and C_6 is the theoretical coefficient of the London interaction between two atoms $(-C_6/R^6)$. Using any other source for C_6 introduces large errors.

Using the formulas of Rushbrooke and Silbert[17] and the triple-dipole potential we can, in fact, accurately predict the density dependence of the effective intermolecular pair potential found by the procedure of Mikolaj and Pings.[16] We can then compare the results with more approximate calculational methods and judge their accuracy and limitations. Since the original

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¹⁹ H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces* (Pergamon Press, Inc., New York, 1968), Chap. 5.
²⁰ A. Dalgarno and W. D. Davison, Advan. At. Mol. Phys. **2**, 1 (1966).

experimental work was on argon gas, we shall restrict our calculations to this one species and then evaluate only the low-order density corrections.

II. EFFECTIVE PAIR POTENTIAL

A. Definition and Density Expansion

The total energy of a system can be written as the sum of two- and many-body interactions

$$E= \sum_{i>j}\sum \phi(ij)+ \sum_{i>j>k}\sum\sum \phi(ijk)$$
$$+ \sum_{i>j>k>l}\sum\sum\sum \phi(ijkl)+\cdots, \quad (3)$$

where $\phi(ij)$ is the actual two-body interaction, $\phi(ijk)$ the three-body interaction, etc.

We could also write this as

$$E= \sum_{i>j}\sum V^{\text{eff}}(ij). \quad (4)$$

In a pure liquid or solid we would find therefore that

$$V^{\text{eff}}(ij)=\phi(ij)+\tfrac{1}{3}\sum_k \phi(ijk)+\cdots \quad (5)$$

would yield the *correct total energy*. However, in deriving the density expansion for a radial-distribution function, it is found that the effective potential which yields the correct first-order density correction is *not* Eq. (5). The reasons are related to the discussion by Sinanoğlu[2] concerning solvent effects on the interaction of two unlike molecules placed in a medium. In considering the radial distribution, $g(1\,2)$, molecules 1 and 2 are considered different and unique from the rest of the liquid.

To first order in density the effective potential *which yields the correct radial-distribution function* is[17]

$$\phi^{\text{eff}}(12)$$
$$=\phi(12)-\rho kT \int \left[\exp\left(\frac{-\phi(123)}{kT}\right) -1\right] e(13)e(23)d\tau_3,$$
$$(6)$$

where ρ is the number density and e.g.,

$$e(13)= \exp[-\phi(13)/kT]. \quad (7)$$

Numerical computations (our calculations as well as others; see, for example, Ref. 12) confirm that the integral is given with an error of less than three percent if the exponential in Eq. (6) is expanded and only the first term retained. Thus in this work we shall use

$$\phi^{\text{eff}}(12)=\phi(12)+\rho \int \phi(123)e(13)e(23)d\tau_3. \quad (8)$$

This is in accord with our belief that $\phi(123)$ is a small perturbation. In the remainder of the paper "effective" potential will mean ϕ^{eff}, Eq. (8), unless statements are made to the contrary.

We cannot emphasize strongly enough, however, that using Eq. (8) to determine the *energy* of the gas will lead to a gross overestimate of the nonpairwise additive effects. To find an effective potential which when summed yields the correct energy, we would have to divide the second term by three. This emphasizes a fact discussed in our earlier work,[1] and recently carefully elaborated by Sinanoğlu,[2] that an effective potential is not only density dependent but can, in fact, be different in different applications. The problems of thermodynamics when density-dependent potentials are used is also elaborated in Sinanoğlu's work.[2] The effect of these triple-dipole contributions and effective potentials on the law of corresponding states is discussed by Donth.[21]

B. Numerical Evaluation

Using, at low densities, the triple-dipole formula for the three-body potential we can rewrite the effective potential as

$$\phi^{\text{eff}}(12) =\phi(12)+\tfrac{3}{4}\alpha\rho(C_6/r_{12}{}^6)K_{AB}, \quad (9)$$

where

$$K_{AB}= \int \frac{r_{12}{}^3(1+3\Theta_{123})}{(r_{23}r_{13})^3} e(13)e(23)d\tau_3 \quad (10)$$

and $\Theta_{123}= \cos\theta_1 \cos\theta_2 \cos\theta_3$.

Following Sinanoğlu[2] we evaluate K_{AB} using "bicentric" coordinates:

$$K_{AB}=2\pi \int_0^\infty \int_{|R-r|}^{R+r} \frac{R^2(1+3\Theta_{123})}{r^2s^2} e(s)e(r)drds, \quad (11)$$

with

$$\Theta_{123}=[(s^2-r^2+R^2)(r^2-s^2+R^2)(r^2+s^2-R^2)]/8r^2s^2R^2, \quad (12)$$

using $R=r_{12}$ for simplicity. Measuring all distances in units of R we can evaluate the integrals numerically. As upper limits for the integrals we have used $5R$, which has proved adequate. The double integral was evaluated by Gaussian integration on our IBM 7040 computer. This procedure was arrived at after encountering many problems in obtaining the necessary accuracy.

Four different pair potentials were used: a hard-sphere potential, a Lennard-Jones 6–12 potential, a Kihara potential, and Kingston's composite potential. The results will be analyzed in Sec. VI.

1. Hard-Sphere Potential

The hard-sphere potential is

$$\phi(ij)=\infty, \quad \text{if } r_{ij}<\sigma$$
$$=0, \quad \text{if } r_{ij}>\sigma, \quad (13)$$

[21] E. Donth, Physica 32, 913 (1966).

TABLE I. Constants and predicted change in the potential for argon interactions represented by a Lennard-Jones potential.

R		4ε/kT					
		2.6		3.0		3.4	
R/σ	R (Å)	K_{AB}	$\frac{3}{4}\alpha K_{AB}$	K_{AB}	$\frac{3}{4}\alpha K_{AB}$	K_{AB}	$\frac{3}{4}\alpha K_{AB}$
0.90	3.064	2.237	2.754	2.525	3.108	2.863	3.525
1.00	3.405	3.169	3.901	3.561	4.383	4.019	4.948
1.10	3.745	4.303	5.296	4.815	5.927	5.415	6.665
1.14	3.882	4.804	5.914	5.369	6.609	6.030	7.423
1.17	3.984	5.200	6.401	5.803	7.144	6.510	8.013
1.20	4.086	5.616	6.914	6.260	7.706	7.017	8.637
1.23	4.188	6.048	7.446	6.736	8.291	7.537	9.278
1.28	4.358	6.787	8.355	7.550	9.294	8.438	10.388
1.32	4.495	7.392	9.100	8.210	10.107	9.165	11.282
1.37	4.665	8.173	10.060	9.059	11.152	10.091	12.422
1.40	4.767	8.652	10.651	9.581	11.794	10.658	13.120
1.42	4.835	8.973	11.046	9.931	12.225	11.043	13.594
1.48	5.039	9.912	12.202	10.955	13.486	12.164	14.974
1.60	5.448	11.657	14.350	12.824	15.786	14.170	17.443

where σ is the hard-sphere radius. With this potential

$$e(ij) = 0, \qquad \text{if } r_{ij} < \sigma$$
$$= 1, \qquad \text{if } r_{ij} > \sigma, \qquad (14)$$

analytic solutions for K_{AB} can be obtained easily. They are a special case of the more general results of Sinan-oğlu,[2] and they are given by (see Fig. 1)

$$K_{AB} = 8\pi/3, \qquad R > 2\sigma$$
$$= (\pi R^6/12\sigma^6)[(6\sigma^2/R^2) - 1], \qquad R < 2\sigma. \quad (15)$$

2. Lennard-Jones 6–12 Potential

The integral was also evaluated using a Lennard-Jones 6–12 potential:

$$\phi(ij) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6], \qquad (16)$$

with ϵ the depth of the potential well and σ the zero. Various attempts to fit this potential to argon data yield values of ϵ/k from 115° to 120°K. In this work we will use the latest values determined from virial data by Weir, Jones, Rowlinson, and Saville[22]: $\epsilon/k = 116°$K and $\sigma = 3.41$ Å. The values of K_{AB} for values of $4\epsilon/kT =$

2.6, 3.0, and 3.4 are given in Table I and Fig. 2. These values were chosen since they correspond to the range in which some of the experimental work of Pings and others is being done. In Table I we also list the contribution of these nonadditive effects to the potential at various distances.

3. Kihara Potential

The hard-core pair potential of Kihara can be written in the form

$$\phi(ij) = 4\epsilon\left[\left(\frac{1-\gamma}{(r_{ij}/\sigma)-\gamma}\right)^{12} - \left(\frac{1-\gamma}{(r_{ij}/\sigma)-\gamma}\right)^6\right], \quad (17)$$

where ϵ is the depth of the potential, σ the zero, and γ an effective hard-core parameter. The parameters we shall use are those determined by Weir et al.[22]: $\epsilon/k = 163.7$ and $\sigma = 3.15$ Å, and $\gamma = 0.164$. It can easily be shown that if the second term in Eq. (12) is expanded in powers of r_{ij}^{-1}, the coefficient of r_{ij}^{-6} is very close to
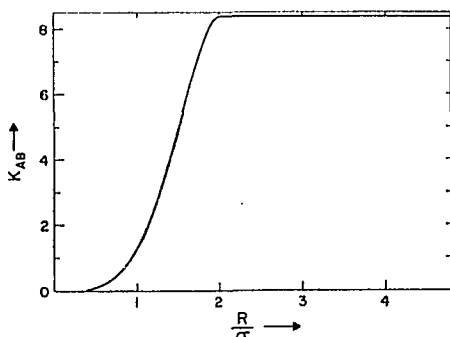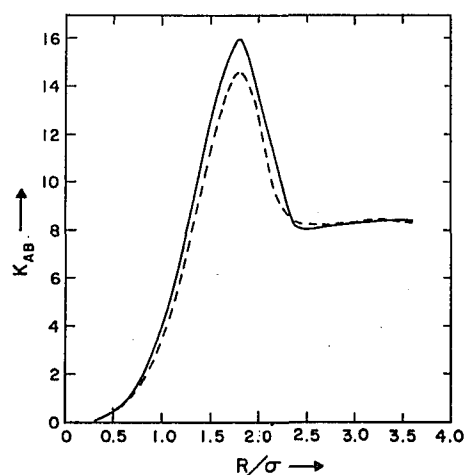

FIG. 1. The constant K_{AB} for a hard-sphere interaction.

[22] R. D. Weir, I. W. Jones, J. S. Rowlinson, and G. Saville, Trans. Faraday Soc. **63**, 1320 (1967).

FIG. 2. The constant K_{AB} as a function of R/σ for a Lennard-Jones potential between argon atoms. ——, $4\epsilon/kT = 3.4$, - - -, $4\epsilon/kT = 3.0$.

TABLE II. Constants and predicted change in the potential for argon interactions represented by a Kihara potential.

R		$4\epsilon/KT$					
		3.4		4.0		4.8	
R/σ	R (Å)	K_{AB}	$\frac{3}{4}\alpha K_{AB}$	K_{AB}	$\frac{3}{4}\alpha K_{AB}$	K_{AB}	$\frac{3}{4}\alpha K_{AB}$
0.900	2.835	2.589	3.188	3.117	3.837	4.040	4.973
1.000	3.150	3.636	4.476	4.347	5.351	5.584	6.874
1.100	3.465	4.900	6.032	5.821	7.166	7.418	9.131
1.140	3.591	5.460	6.721	6.473	7.969	8.226	10.126
1.170	3.685	5.898	7.260	6.980	8.592	8.850	10.894
1.200	3.780	6.356	7.824	7.509	9.243	9.499	11.693
1.230	3.875	6.829	8.407	8.056	9.917	10.171	12.521
1.280	4.032	7.636	9.400	8.983	11.059	11.303	13.915
1.320	4.158	8.312	10.232	9.750	12.002	12.218	15.041
1.370	4.316	9.174	11.294	10.748	13.231	13.439	16.543
1.400	4.410	9.666	11.899	11.308	13.920	14.124	17.386
1.420	4.473	9.996	12.305	11.671	14.368	14.545	17.905
1.480	4.662	11.033	13.582	12.827	15.790	15.876	19.544
1.600	5.040	12.857	15.827	14.841	18.269	18.198	22.401

the correct theoretical value. This therefore lends some validity to this potential. The depth is in part understood for, whenever the correct R^{-6} interactions are introduced and allowance made for higher-order effects (R^{-8}, R^{-10}), the potential usually deepens significantly.[23-25] For reasonable comparisons with the Lennard-Jones and experimental results we have used $4\epsilon/kT = 3.4$, 4.0, 4.8. These results are listed in Table II and illustrated in Fig. 3. Also in Table II we list the contribution of these nonadditive effects to the potential at various distances.

4. Kingston Potential

Kingston[24] has attempted to derive the best composite potential consistent with theory as far as possible.
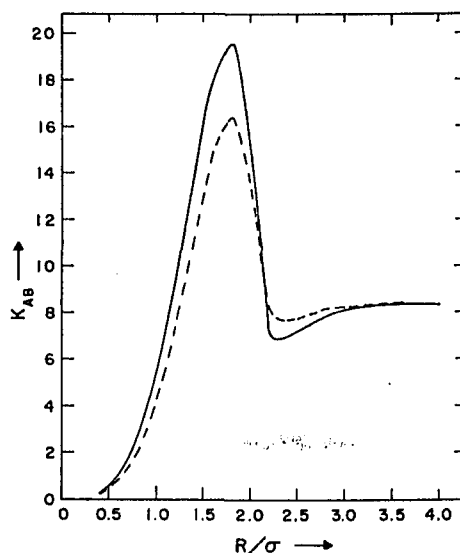

FIG. 3. The constant K_{AB} as a function of R/σ for a Kihara potential between argon atoms. ——, $4\epsilon/kT = 4.8$; — — —, $4\epsilon/kT = 4.0$.

His potential is shown in Fig. 4. It has the correct R^{-6} behavior at large R and fits virial data very well. It is similar to potentials constructed by Munn.[23] The results from this potential are intermediate between the Lennard-Jones and the Kihara results. They will be tabulated later and compared in Sec. VI.

III. OTHER CONTRIBUTIONS TO THE NONADDITIVE POTENTIAL

Thus far we have assumed that the only nonpairwise additive contribution to the intermolecular interaction was the triple-dipole effect. We shall now consider other contributions and show that at low densities the triple-dipole effect is the only major contribution. At higher densities, especially in the liquid or solid, we shall show that while that effect is still dominant, there are many other interactions which cannot be neglected. Our calculations are only semiquantitative, and thus some of the contributions either alone or in concert with one another could be even larger. We shall consider dispersion-overlap, triple-overlap, many-body dispersion, and dipole–dipole–quadrupole contributions.

FIG. 4. Argon–argon interactions. Curve 1, Lennard-Jones 6–12 potential. Curve 2, Kingston composite potential. Among its other features it contains the correct R^{-6} interaction. Curve 3, Kihara potential.

[23] R. J. Munn, J. Chem. Phys. 40, 1439 (1964).
[24] A. E. Kingston, J. Chem. Phys. 42, 719 (1965).
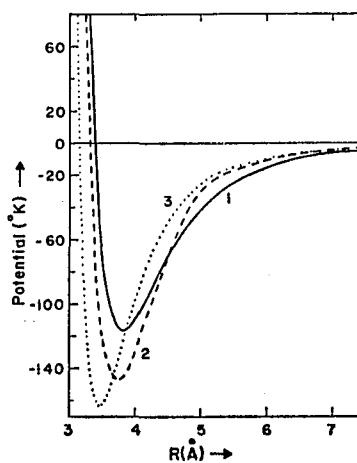[25] L. W. Bruch and I. J. McGee, J. Chem. Phys. 46, 2959 (1967).

TABLE III. Various three-body interactions relative to the two-body interaction calculated for the equilateral-triangle configuration of the three particles.

R Å	Two body[a,b] E_2 $-C_6/R^6$	Three-body effects (relative to E_2)[b]			
		Triple overlap	Dispersion overlap	Triple dipole	Dipole–dipole–quadrupole
$2.65E\ 00$	$-4.16E-03$	$3.95E-01$	$-6.25E-02$	$-9.17E-02$	$-2.60E-02$
$3.18E\ 00$	$-1.39E-03$	$3.46E-02$	$-8.27E-03$	$-5.31E-02$	$-1.05E-02$
$3.70E\ 00$	$-5.52E-04$	$2.63E-03$	$-1.02E-03$	$-3.34E-02$	$-4.84E-03$
$4.23E\ 00$	$-2.48E-04$	$1.80E-04$	$-1.15E-04$	$-2.24E-02$	$-2.48E-03$
$4.76E\ 00$	$-1.22E-04$	$1.14E-05$	$-1.24E-05$	$-1.57E-02$	$-1.38E-03$
$5.29E\ 00$	$-6.50E-05$	$6.77E-07$	$-1.34E-06$	$-1.15E-02$	$-8.13E-04$
$5.82E\ 00$	$-3.67E-05$	$3.83E-08$	$-1.48E-07$	$-8.61E-03$	$-5.05E-04$
$6.35E\ 00$	$-2.18E-05$	$2.08E-09$	$-1.69E-08$	$-6.63E-03$	$-3.27E-04$
$7.41E\ 00$	$-8.63E-06$	$5.55E-12$	$-2.38E-10$	$-4.18E-03$	$-1.51E-04$
$8.47E\ 00$	$-3.87E-06$	$1.33E-14$	$-3.47E-12$	$-2.80E-03$	$-7.76E-05$

[a] In atomic units.

[b] $1.0E-01$ means 1.0×10^{-1}.

A. Dispersion–Overlap Contributions

McGinnies and Jansen[26,27] have shown that there are overlap corrections to the simple perturbation results. The lowest-order effects involve three molecules and are overlap corrections to the simple two-body dispersion interaction. In Table III we compare these effects with the triple-dipole contribution for an equilateral triangle of atoms for various internuclear separations. These were evaluated by taking McGinnies and Jansen's helium result and considering that the only important electron exchanges for two adjacent argon atoms would be between the $3p_z$ orbitals, where we have taken the z axis as the axis connecting the centers of the adjacent atoms. The final result is easily obtained by a rotation and a transformation to elliptic coordinates. For overlap integrals at separations greater than $6a_0$ (3.17 Å), we have found that the overlap of $3p_z$ orbitals accounts for most of the total overlap as listed in Table IV. The effective nuclear charge of our $3p_z$ orbitals is taken as $Z=6.75$ from Clementi tables. It should be noted that these overlap values are much smaller than those of McGinnies and Jansen,[27] who used Gaussian type wavefunctions.

B. Triple-Overlap Contributions

Jansen[26] has discussed the role of three-body contributions involving the overlap of three atoms. Since overlap is small for the separations of interest to us here, we use the approximate form suggested by Sherwood, DeRocco, and Mason.[6] Using overlap integrals calculated from Hartree–Fock orbitals for argon (Table IV) we find the energy contributions for an equilateral triangle configuration as listed in Table III. The contribution is quite small, although not negligible even at the potential minimum. Similar conclusions have been reached by Williams, Schaad, and Murrell.[28]

C. Higher-Order Perturbation Contributions

The convergence of the perturbation expansion of dispersion forces is well documented. The early work of Bade[10] showed that four-body effects contributed little to crystal stability even at normal solid densities for most substances. We also know that the higher-order interactions (in terms of perturbation theory) are mainly three-body effects.[10] Doniach[29] and, more recently, Lucas[30] have evaluated the higher-order effects in closed form. Lucas also presents a perturbation analysis of his result. For the argon solid, the fourth-order contribution is about a fourth of the third-order result (and opposite in sign), the fifth is about a fourth of the fourth-order result, etc. Thus it appears that, as regards both perturbational order and number of molecules involved, there are no convergence problems even in the argon solid with the induced dipole contribution.

D. Dipole–Dipole–Quadrupole Interactions

Recently we have begun to appreciate again that induced dipole–quadrupole interactions can be a significant part of long-range two-body interactions (see Ref. 19 for a typical discussion). It is therefore of

TABLE IV. Overlap of two argon atoms.[a]

R		Overlap S_{12}
a_0	Å	
4.00	2.116	0.5353
5.00	2.646	0.2521
6.00	3.175	0.1009
7.00	3.704	0.0357
8.00	4.233	0.0115
10.00	5.292	0.00095

[a] Calculated using Hartree–Fock atomic orbitals.

[26] R. T. McGinnies and L. Jansen, Phys. Rev. 101, 1301 (1956).

[27] L. Jansen and R. T. McGinnies, Phys. Rev. 104, 961 (1956).

[28] D. R. Williams, L. J. Schaad, and J. N. Murrell, J. Chem. Phys. 47, 4916 (1967).

[29] S. Doniach, Phil. Mag. 8, 129 (1963).

[30] A. Lucas, Physica 35, 353 (1967).

interest to consider three-body effects involving induced quadrupoles. The most important term is the induced dipole–dipole–quadrupole contribution. This was derived by Ayres and Tredgold.[15] Using their formulas and matrix elements appropriate to the argon system, one finds the results presented in Table III. It is obvious that this effect is not completely negligible at ordinary liquid densities.

E. Contributions to the Effective Pair Potential

In Table III we have represented the major contributions to the three-body potential. All are significantly less than the triple-dipole term evaluated in this and other papers. Considering these contributions, as well as the higher-order many-body effects discussed in Sec. C above and noting the signs of the terms, we discover that the total of all contributions at small separations such as the solid separation of about $7a_0$ (3.7 Å) is only 5%–10% of the triple-dipole contribution. At larger separations the cancellations would involve the dipole–dipole–quadrupole and the higher-order three-body contributions, both of which should die off slowly but with comparable magnitudes and opposite signs.

Although these estimates are based on consideration of only one configuration of the three particles, the general ideas should extend to the effective potential as well. All three-body effects appear to have rather similar angular dependences. The more complex the term, the more reason there is to expect and to find a reduction in these contributions when they are averaged over all angles. This was found by Bade,[10] for example, in evaluating fourth-order four-body induced dipole contributions.

Thus we believe that the use of the triple-dipole term alone is a very accurate representation of the many-body effects for two atom separations near and beyond the minimum of the two-body potential, at least in the gas and low-density liquid phases.

IV. EFFECT OF NONADDITIVE POTENTIALS ON $g(R)$

In this section we shall briefly discuss the contributions of the triple-dipole potential to the radial-distribution function. We shall not explore this in detail since Rowlinson and co-workers plan to examine this more fully in some of their papers.

If we expand the radial-distribution function in powers of the density

$$g(R) = e(R)[1 + \rho g_1{}^T(R) + \rho^2 g_2{}^T(R) + \cdots],$$

we find that $g_1{}^T(R)$ has two components, an additive $g_1{}^A$, and a nonadditive part. The latter is (with $\beta = 1/kT$)

$$g_1{}^{NA}(r_{12}) = -\beta \int \phi(1, 2, 3)e(13)e(23)d\mathbf{r}_3,$$

which except for a constant, is the same as our K_{AB}

FIG. 5. Typical first-order density corrections to $g(R)$, based on an assumed Lennard-Jones potential. $g_1{}^A$ (– – –) contains only pairwise additive contributions, while $g_1{}^{NA}$ (···) is the first correction due to the triple-dipole interaction. $g_1{}^T$ (——) is the sum of the two contributions. $4\epsilon/kT = 3.4$.
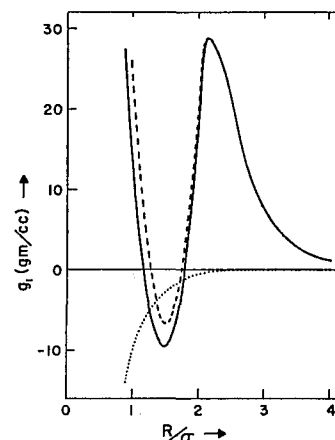
($\rho g_1{}^{NA}$ is referred to as d_1 by Rowlinson[18] and as x_1 by Rushbrooke and Silbert[17]). Thus we can easily obtain $g_1{}^{NA}(R)$. We find that it is small compared with $g_1{}^A(R)$ when $R/\sigma < 1$ for all three potentials and all temperatures considered in Sec. II. In the region $1 < R/\sigma < 3$, both contributions are important with $g_1{}^{NA}$ decreasing the value of g_1. Typical results are illustrated in Fig. 5. A decrease in g_1 due to $g_1{}^{NA}$ at about $R/\sigma = 1.3$ is found to be quite general; a greater decrease is found at the lower temperatures. In the region $R/\sigma > 3$, $g_1{}^A$ is the dominant contribution to g_1. Thus the nonadditive effects imply a slightly more decreased density in the immediate vicinity of one molecule than a strictly pairwise additive potential would predict.

Using $g_1{}^{NA}$ we have evaluated its contribution to the x-ray structure factor for the liquid. In Fig. 6 we compare $S(K)$ using the additive parts of $g(R)$ correct through first order in density and the first-order nonadditive part. It is seen that even at $\bar{\rho} = 0.54$ g/cc, a density at which our results concerning linear density corrections are probably barely adequate, the nonadditive corrections to $S(K)$ are minor. Furthermore, their K dependence is inadequate to explain the discrepancy recently noted by Levesque and Verlet[31]: Pings' data[16] do not agree with the $g(R)$ calculated by molecular dynamics for several potentials. It is difficult to understand why Pings' $S(K)$ is higher for $K\sigma$ less than about 12 and smaller beyond this. Based on our calculations the evidence suggests that nonadditive effects are not the reason.

V. SECOND-ORDER DENSITY CORRECTIONS TO THE EFFECTIVE INTERACTION

Rowlinson[18] has pointed out that the Percus–Yevick equation actually not only predicts linear terms in density for the effective potential but also higher-order terms. The structure of the higher terms, at least the ρ^2 term, is relatively simple. Following Eq. (20) in

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[31] D. Levesque and L. Verlet, Phys. Rev. Letters 20, 905 (1968).

TABLE V. Predicted change in the effective potential due to triple-dipole contributions for various assumed argon interactions.

		C [Predicted decrease (°K) for $\bar{\rho}=1$][a]								
		Lennard–Jones			Kihara			Kingston	
R Å	Hard sphere $\sigma=3.15$ Å	178°K	155°K	136°K	193°K	164°K	136°K	178°K	136°K
3.18	10.95	19.5	23.2	26.5	30.5	36.5	46.8		
3.44	9.08	16.5	18.6	21.0	24.3	28.9	36.8		
3.71[b]	7.42	13.5	15.1	17.0	19.4	23.0	29.1	16.5	22.7
3.97	6.24	10.9	12.15	13.63	15.6	18.4	23.2		
4.24	5.20	9.1	10.1	11.3	12.7	15.7	19.8	11.0	14.8
4.50	4.34	7.50	8.34	9.31	10.2	12.0	14.9		
4.77	3.66	6.17	6.83	7.60	8.35	9.66	11.9	7.3	9.7
5.03	3.02	5.60	5.60	6.22	6.57	7.59	9.30		

[a] Actual decrease $=\bar{\rho}C$, where $\bar{\rho}$ is the density in grams per cubic centimeter.

[b] Approximately the potential minimum. (Experiments suggest a value of about 54 at this point.)

Rowlinson's paper we find

$$\phi^{\text{eff}}=\phi-kT\rho g_1^{NA}+kT\rho^2 g_1^{NA}\left[\tfrac{1}{2}g_1^{NA}+g_1^{A}\right]+\cdots$$

$$=\phi-kT\rho g_1^{NA}(1-\tfrac{1}{2}\rho g_1^{NA}-\rho g_1^{A})+\cdots.$$

We have evaluated the correction terms. Although they appear large, the number density of argon atoms is sufficiently small that coupled with the cancellations between g_1^{A} and g_1^{NA} the ρ^2 contributions amount to only something of the order of 10% of the ρ contributions for $\bar{\rho}=1$ g/cc at the potential minimum. Using the Lennard-Jones potential, the change is -8% for 137°K, -3% for 155°K, and $+5\%$ for 179°K at the potential minimum. At larger separations the corrections are somewhat larger and positive.

It thus appears that one can include many-body effects to first order and account for most of their importance at moderate densities. At a density of $\bar{\rho}=1$ g/cc, the expansion in density is probably poor, and one expects large higher-order corrections. Some very sketchy evidence suggests that the linear density correction may over estimate the effects at very high densities.
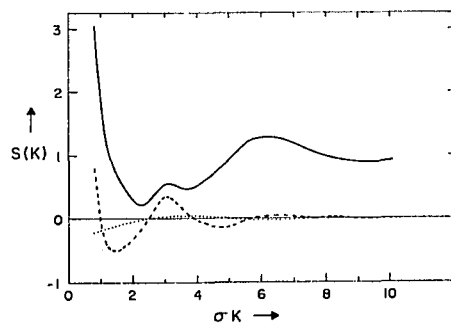

FIG. 6. X-ray structure factor calculated using $g(R)$ correct to first order in density. $S(K)$ is the total pairwise additive contribution with $S_1^{A}(K)$ (– – –) being the first-order density contribution. [——, $S(K)$ with $S_1^{A}(K)$ included.] $S_1^{NA}(K)$ (···) is the first correction to $S(K)$ due to the triple-dipole interaction. A Lennard-Jones potential was used. $4\epsilon/kT=3.0$; $\bar{\rho}=0.54$ g/cc.

VI. SUMMARY; COMPARISON WITH EXPERIMENT; PREDICTIONS

This work was begun in order to make detailed comparisons with experiments, in particular, the x-ray diffraction studies at low densities. Pings and co-workers have now published some data at low densities. This early data is compared with our predictions in Fig. 7. In that figure we plot the depth of the potential needed to make the observed x-ray data agree with the Percus-Yevick equation as a function of density.[16] At low density this should be a very accurate procedure. It is apparent that the potentials used in our treatment and the experimental results as interpreted above are not consistent. The experimental potentials are too shallow. Also some of the dependence of depth on density must be a temperature dependence and higher order in density (see Sec. V). These effects, however, are small at low density. The Kihara results do not even approximate the experimental data. The slope is closer to the experimental data but this depends in
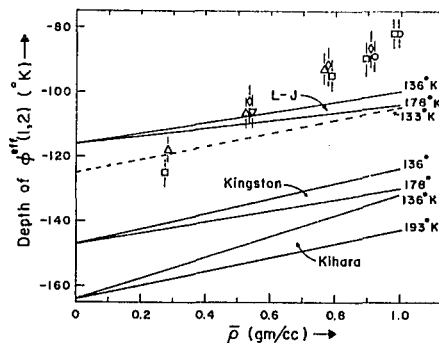

FIG. 7. Predictions for the density dependence of the depth of the minimum of the effective intermolecular potential using the Kihara, Kingston, and Lennard-Jones potentials for argon. The points with error bars are based on the analysis of x-ray data by Mikolaj and Pings [Ref. 16(a) in text]. O, 130°C; □, 125°C; ◇, 120°C; ▽, 115°C; △, 110°C. The dotted line is an attempt to find a Lennard-Jones potential which agrees with the experimental data.

large part also on depth; the deeper the potential, the larger the slope. The Kingston potential, one of the best potentials available, is also in conflict with the experimental data.

A deeper minimum for the Lennard-Jones potential gives slightly better agreement with the work of Pings as shown by the dashed line in Fig. 7, but this depth is not in accord with virial data of Weir et al.[22]

In Table V we have presented the changes predicted in the potential for various values of R. This result is actually better known than values previously presented since the minimum of the potential and σ are not known exactly. They are not needed to obtain Table V; so numbers in Table V are precise. They should be directly compared with experiments carried out at low densities. At small separations (3.1–3.6 Å) these values are but one of the many contributions to the effective intermolecular potential (see Sec. III), but beyond about 3.7 Å all other contributions should be no more than about 10% of these. Hence the listed values should accurately reflect experimental data on the change in the potential as a function of density for low densities. Experimentalists should compare the potentials at these points rather than simply at the potential minimum. For comparison Pings' data[16a] yields a constant of 14.7 at 5 Å and 28 at 4.5 Å, both much larger than predicted. At the minimum his value is closer to 54.

The other aspect of Table V is the temperature dependence: a 30% variation in temperature can lead to a 20% change in the potential. Consider a typical case of density 0.25 g/cc and assume that the Lennard-Jones potential is reasonable. At 178°K we would expect the potential to change by 2.7°K; at 136°K the change should be 3.4°K. Near the potential minimum such differences are much larger so that such temperature dependences might be experimentally verified. Obviously such effects are greater at greater densities, but at high densities one fights the problem of the validity of our first-order density expansion, and thus we can make no exact predictions. The magnitude of the experimental temperature dependence at any separation should also verify the best values for the depth of the potential. However, the experimental problems involved in such accurate determinations are immense and may not be soluble.

At higher densities such as those characteristic of liquids at low temperatures, it is suspected that our results are subject to sizeable errors. In that case the first-order expansion in density is not sufficient. Higher-density dependence in the effective potential can come from two sources, statistical and the other many-body potentials. As to the potential, we have seen that four- and higher-body effects are even smaller. Thus we have reason to suppose that the major density dependence of the effective potential will be given by statistical effects. Sinanoğlu[2] has proposed that we can get a good estimate for these effects by using the super-

position approximation on the three-body radial-distribution function which means replacing $e(R)$ in the effective potential [Eq. (8)] by $g(R)$. This $g(R)$ should be the true distribution function if no nonpairwise additive effects were present. However, it should be a good approximation to simply use the experimental $g(R)$ if the corrections are small in the regions around the potential minimum. Otherwise iterative schemes can be developed.

We have evaluated these integrals for the Lennard-Jones liquid using $g(R)$ from the molecular dynamics results of Verlet.[32] The predicted density dependence of the potential is then about 30% less than Table V suggests near the potential minimum.

The effect of the density dependence of $g(R)$ on the effective potential can be understood in a qualitative way. The major contribution to the necessary integrals are the large portions of $g(R)$ near the potential minimum. These peaks decrease at a given temperature with density, and thus we should expect the earlier predictions to be high in the region of higher densities.

At high densities there is also evidence that the effective potential is density dependent. Johnson and March[33] have used the YBG equation to analyze several x-ray and neutron diffraction results and to find a significant variation in the effective potential with temperature and density. The two effects cannot be separated in their data. Rice and Gray[34] have used the PY equation on the same data and again find similar changes in the effective potential. It is interesting that their data for the density dependence of the potential is in reasonable agreement with all of the above statements and calculations.

In this paper we have examined in detail one specific case, namely the argon–argon interaction. Using presently proposed two-body potentials we have evaluated effective two-body potentials as a function of density and temperature. Should accurate effective potentials become available soon, using the techniques of Mikolaj and Pings[16] these predictions can be completely tested. At present our results yield very accurate *predictions* for the results expected. They do not, however, agree with the experimental facts. Many problems remain. The large density dependence of the effective potential found by Pings and Mikolaj cannot be explained by three-body interactions. The Kihara potential is in some ways the simplest representation of molecular interactions, and yet in this case it seems to yield predictions for the depth and density dependence at variance with known facts. The same is true for the even more accurate Kingston potential, which

[32] L. Verlet, Phys. Rev. 159, 98 (1967); 165, 201 (1968).

[33] M. D. Johnson and N. H. March, Phys. Letters 3, 313 (1963).

[34] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience Publishers, Inc., New York, 1965), pp. 125–128. Note, however, that in the important Fig. 2.7.7 the 84° and 149°K curves are interchanged.

should be very close to the true potential. Further cooperation between theory and experiment is needed before all of our results can be understood. Apparently something basic is not being considered in either the theory or the experiments. We suggest that most of the difficulty is not due to three-body interactions.

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VITA

David A. (Anthony) Copeland was born in Jasper, Alabama, on December 4, 1942. He attended Thomas W. Martin High School, Gorgas, Alabama, and graduated in May, 1961. He received his B.S. in Chemistry from the University of Alabama in May, 1965, and his M.A. in Mathematics from the University of Alabama in August, 1966. He entered the Graduate School of the Louisiana State University in September, 1966, where he is presently a candidate for the Doctor of Philosophy Degree.

He is married to the former Helen Grace Stalcup.

EXAMINATION AND THESIS REPORT

Candidate: David A. Copeland

Major Field: Chemical Physics

Title of Thesis:
I. Studies of Cavities Containing One and Two Electrons in Metal-Ammonia Solutions.
II. Accurate "Effective" Intermolecular Pair Potentials in Gaseous Argon.

Approved:

Neil R. Kestner
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Paul Varlashkin

_____

R. G. Goodrich

James G. Traynham

_____

_____

Date of Examination:

August 4, 1969