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# Solvent influence on atomic spectra: The effect of finite size

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Time dependent Hartree theory is used to determine the solvent effect on atomic spectra for a given solvent configuration. Configuration averaging is performed as in the mean spherical approximation, resulting in an upper bound to the polarizability. Comparisons are made with previous, more approximate theories, including path integral treatments. It is found that deviations from previous theories can be significant in certain regimes.

## I. INTRODUCTION

Spectroscopy provides the most direct experimental approach to understanding electronic structure. Because the fundamental spectroscopic study of liquids is not nearly as developed as the spectroscopy of gases and crystalline solids our understanding of the electronic structure of liquids is considerably more rudimentary than our understanding of their other properties. Recent developments in the theoretical treatment of quantum processes in liquids and disordered materials give new life to this area.<sup>1-4</sup>

In this paper we will examine the solvent induced shifts in the electronic absorption spectra of dissolved species. Besides the ubiquitous complex molecular systems, many simple systems have been spectroscopically studied such as noble gas mixtures, solvated electrons, and aromatic molecules in solution. We particularly wish to discuss the relationship between some recent treatments based on path integral techniques<sup>1-5</sup> and more traditional viewpoints from quantum chemistry. A key issue in our discussion is the role of the finite size of the orbitals describing electrons in excited state species. Our discussion of the role of the solvent in modifying the extent of molecular orbitals may be relevant in other contexts. For example, these excited states may be virtual states in the tunneling of electrons between dissolved species. In addition, the extent of the orbitals is important in addressing quantitatively questions of localization in disordered systems that arise in the study of the metal-insulator transition.<sup>6</sup>

The major effects of a solvent on a solute's absorption spectrum are to shift the location of the peak and to broaden the peak. In most systems studied, the shift is to the red but there are, however, cases in which the transition is blue shifted. This variety of behavior suggests a variety of mechanisms for the interaction. Among these are charge polarization interactions, such as those that give rise to the van der Waals attraction in the ground state, and exchange effects that give rise to the repulsive forces in the ground state.

In addition to the variety of mechanisms there have been a variety of theoretical models and methodologies that have been applied to the problem. Among the earliest of these was the continuum electrostatic approach of Jortner and Coulson.<sup>7,8</sup> This theory treated the excited state as a Wannier exciton. The solvent was described as a dielectric continuum and hence ignored exchange effects and the details of the solvent structure. Their theory predicted the possibility of both red and blue shifts. The basic continuum approach has been used in other contexts.

A radically different approach was taken by Saxton and Deutch.<sup>9</sup> They assumed the excited state was fairly well localized, like a Frenkel exciton. In that case, a pairwise additive potential for both ground and excited states would be adequate. The pair potentials were obtained empirically from gas phase data so their treatment includes both exchange and polarization effects. Nevertheless, the pairwise additivity assumption leaves out possible excitation hopping mechanisms that would stabilize the excited state. Their treatment also does not give any direct information about the excited state wave function. Herman and Berne<sup>10</sup> have modernized this approach through their calculations of spectra via molecular dynamics simulation. The simulation technique also gives information about changes in the shape of the spectral lines.

Most recently solution spectra have been analyzed via path integral techniques for a model in which the electronic degrees of freedom are imitated by internal Drude oscillators.<sup>3</sup> Again this model envisions a localized Frenkel excitation but it does allow coherent hopping from site to site. The analysis uses the solution of the mean spherical model in which dipolar couplings between atoms are included. Some of the effects of the finite extent of the orbitals have been taken into account through the inclusion of quadrupolar excitations by Logan.<sup>4</sup> His results are also interesting because of their quantification of collision-induced spectra in these systems. Nevertheless, even this extension, by the nature of the model fails to include the effects of exchange. Also the basic Frenkel-like picture of the excitation is preserved.

In this paper we will show how many of the positive features of each of the above approaches can be combined. Our approach also makes contact with traditional studies of the excited state of small molecules made with Hartree-Fock (HF) and random phase approximation (RPA) ideas. In this sense it has a lot in common with the studies on small clusters that were pioneered in this context by Sun, Rice, and Jortner.<sup>11</sup> Many of our cautionary conclusions are contained in their early presentation. The RPA has been used before in discussing solution spectra<sup>12</sup> but our treatment uses the ideas involved in the MSA theories to take into account the fluid structure. The present paper will focus on the finite orbital size effects but we plan to treat exchange effects later.

## II. REVIEW OF PREVIOUS THEORIES

In this section we shall briefly review the previous theories. The continuum solvent approach was first described by Jortner and Coulson,<sup>8</sup> who treated the solute as an atom



$$E_{\alpha}^{(1)} = \left\langle \Psi_{\alpha} \left| \sum_i V_i \right| \Psi_{\alpha} \right\rangle,$$

$$\Psi_{\alpha} = \psi_{\text{solute}}^{\alpha} \prod_k \phi_{k,\text{solvent}}^{\alpha}.$$

$V_i$  is the interaction between the solute and the  $i$ th solvent molecule and  $\alpha$  refers to the  $\alpha$ th Born–Oppenheimer surface. Thus,

$$\Delta E_{1s-2p} = E_{2p}^{(1)} - E_{1s}^{(1)}.$$

Averaging this over all nuclear configurations, one obtains the expression of Saxton and Deutch:

$$\Delta E = 4\pi\rho \int_0^{\infty} [E_{2p}^{(1)}(r) - E_{1s}^{(1)}(r)]g(r)r^2 dr,$$

where  $\rho$  is the density and  $g(r)$  is the pair distribution function for the system. Rather than calculate the first order correction ( $E_{\alpha}^{(1)}$ ) using electronic wave functions, Saxton and Deutch use a standard Lennard-Jones potential for each surface, choosing the parameters to give correct low density thermodynamics and energy shifts. The radial distribution function is chosen to be its correct low density form for the ground state. Using this form, Saxton and Deutch were able to predict the blue shift of xenon in argon. We can make several comments about this approach. It does not include three-body effects nor does it differentiate between localized and delocalized two-body interactions. It is of interest to know the magnitude of these effects, for the latter may be well represented by a Drude MSA calculation while the former will be completely absent. In addition the Saxton–Deutch theory is a semiempirical model and does not give us any information about the form of the excited state wave function. Also, no information can be obtained about any change in the line shape of the transition, something that should be particularly important when the solute and solvent bands are close to each other.

Finally, we mention the Drude model. In this model, the solvent and solute are modeled by fluctuating point dipoles embedded in hard spheres. In the limit of very tightly held charge distributions, this will adequately represent the intermolecular interaction. By design, this approach will not include any effects due to finite size of orbitals or exchange. The quantum version of the Drude model was solved by Thompson, Schweizer, and Chandler<sup>2</sup> as well as Høye and Stell<sup>2</sup> and extended to spectral properties by Schweizer, Chandler, and Wolynes.<sup>3</sup> A further extension to include quadrupolar interactions was made by Logan.<sup>4</sup> The main result of this model is that the solute frequency is shifted away from the solvent band. For the systems studied here, this means the transition will always be red shifted. An important feature is that due to symmetry, terms analogous to  $\Delta E_{1s-2p}^{(1)}$  (the first order shift) are absent since the interaction is dipolar. At large distances, the interactions are dipole–dipole, so we expect the Drude model to be important when the solute and solvent are well separated. If, in addition, at short distances the nondipole interactions are cancelled by exchange, the Drude model should also be a good approximation. Thus, only in these cases do we expect the Drude model may adequately describe the transition.

We shall show how to develop a theory that reduces to each of the above theories in the appropriate limit. First,

though, we shall discuss the use of the time dependent Hartree method at the continuum level as this will illustrate some of the techniques we shall use at the discrete level and give us a limiting expression to which our discrete results must reduce.

### III. CONTINUUM EXCITED STATE

Our excited state calculation will use the time dependent Hartree method, originally suggested by Dirac<sup>15</sup> and modified by Karplus,<sup>16</sup> and Karplus and Kolker<sup>17</sup> particularly to calculate the properties of isolated atoms and molecules. In normal time dependent perturbation theory, details of the perturbed wave function or second order properties such as the polarizability involve infinite summations over virtual states. Such a summation will be slowly convergent, unless the external perturbation is close to resonance with one of the virtual states. Karplus and co-workers suggested a method that by-passed the need to sum over these states. This method creates a functional that satisfies a variational principle and which reduces to the polarizability when the exact function is found. In our problem, the method will be used to develop a functional that includes environmental effects. We shall consider the effect of applying an external field of the form

$$H = H_1 + V_+ e^{i\omega t} + V_- e^{-i\omega t},$$

$$H_1 = -\frac{1}{2} \nabla^2 - \frac{1}{\epsilon(\omega)r} - \frac{1}{2} \left( 1 - \frac{1}{\epsilon(\omega)} \right)$$

$$\times \int \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} |\Psi(\mathbf{r}', t)|^2,$$

$$\Psi(\mathbf{r}', t) = e^{-iE_0 t} [\psi_0 + \psi_+ e^{i\omega t} + \psi_- e^{-i\omega t}].$$

We then form the functional  $L \equiv \langle \Psi | -i\partial/\partial t + H | \Psi \rangle$ , and keep only the time independent terms to second order in the perturbation. We then find

$$L = \langle \psi_+ | \Delta + \omega | \psi_+ \rangle + \langle \psi_- | \Delta - \omega | \psi_- \rangle$$

$$- \alpha_{\omega} \langle (\psi_+ + \psi_-) | P_{\omega} | \psi_0 \rangle$$

$$+ \langle \psi_+ | V_+ | \psi_0 \rangle + \langle \psi_0 | V_+ | \psi_+ \rangle$$

$$+ \langle \psi_- | V_- | \psi_0 \rangle + \langle \psi_0 | V_- | \psi_- \rangle,$$

$$\Delta = H_0 + \alpha_s \left[ \frac{1}{r_{>}} - P_0(r_{>}) \right] - E_0,$$

where

$$\alpha_{\omega} = \left( 1 - \frac{1}{\epsilon(\omega)} \right), \quad P_{\omega} = \int \frac{d\mathbf{r}'}{|\mathbf{r}_{>} - \mathbf{r}'|} (\psi_+ + \psi_-) \psi_0.$$

This functional may be shown to be an upper bound to the polarizability (see the Appendix) and thus, we can minimize  $L$  with respect to  $\psi_+$  and  $\psi_-$ . As variational functions we choose

$$\psi_+ = a_+ \psi_1(\kappa),$$

$$\psi_- = a_- \psi_1(\kappa),$$

$$\psi_1(\kappa) = \sqrt{\frac{\kappa^5}{\pi}} e^{-\kappa r} (\mathbf{r} \cdot \hat{\mathbf{v}}).$$

$\hat{\mathbf{v}}$  is a unit vector in the direction of the applied field. After minimization with respect to  $a_+$  and  $a_-$  and assuming that

$V_+ = V_- = V$ , we find

$$\alpha(\omega) = \frac{2\Delta V_{10}^2}{\Delta^2 - \omega^2 - 2\Delta\alpha_\omega K},$$

$$V_{10} = \langle \psi_1 | V | \psi_0 \rangle,$$

$$\Delta = \langle \psi_1 | H_0 + \alpha_s \left( \frac{1}{r} - P_0 \right) - E_0 | \psi_1 \rangle,$$

$$K = \int d\mathbf{r} K(\mathbf{r}) \psi_0(\mathbf{r}) \psi_1(\mathbf{r}),$$

$$K(\mathbf{r}) = \int \frac{d\mathbf{r}'}{|\mathbf{r}_> - \mathbf{r}'|} \psi_1(\mathbf{r}') \psi_0(\mathbf{r}').$$

We now minimize  $\alpha(\omega)$  with respect to  $\kappa$ , a nonlinear process which must be done numerically. Thus, for a given  $\omega$ , the best  $\kappa$  can be found and the polarizability calculated. In our work, we have only calculated the real part of the polarizability, and, hence, find the anomalous dispersion and indirectly determine the shift in the absorption spectrum.

It should be noticed that our calculated  $\alpha(\omega)$  will not satisfy the Kramers–Kronig<sup>18</sup> relations since  $\kappa$  has a different value at each value of  $\omega$ . We can, however, force  $\alpha(\omega)$  to satisfy the Kramers–Kronig relations by fixing  $\kappa$  to the value that minimizes  $\alpha(\omega)$  at  $\omega = \omega^*$ , the transition frequency. Since we have calculated the real part of the polarizability  $\alpha'(\omega)$ , we can determine the imaginary part  $\alpha''(\omega)$  by using the relation

$$\alpha''(\omega) = \frac{2}{\pi} \int_0^\infty \alpha'(\omega') \frac{\omega d\omega'}{\omega^2 - \omega'^2}.$$

#### IV. DISCRETE MEDIUM

A discrete solvent can be treated by using a combination of the time dependent Hartree (or Hartree–Fock) method and standard liquid state theory. This combination uses the variational properties of the energy and polarizability to derive a density expansion for these quantities that is similar to the mean spherical approximation. In liquid state theory one often resums a density expansion for a quantity by simply Padéing the first two terms in the expansion

$$A(\rho) = A_0 + \rho A_1 - \rho^2 A_2 + \dots$$

$$\sim A_0 + \rho \frac{A_1}{1 + \rho(A_2/A_1)}$$

$$= A_0 + \rho A_1 - \rho^2 A_2 + \rho^3 \frac{A_2^2}{A_1} + \dots$$

This resummation allows the quantity  $A(\rho)$  to be calculated for large values of  $\rho$ . In many types of perturbation theory,<sup>19</sup> it is possible to derive Padé approximates variationally, bounding the desired quantity and giving theoretical justification to this intuitively appealing construction. We shall use the same type of variational ideas to derive expressions for both the ground state energy and the polarizability of the solute.

Consider a system of a solute and  $N$  solvent particles with Hamiltonian:

$$H_0 = h_1(\mathbf{R}_1, \mathbf{r}_1) + \sum_j [h_j(\mathbf{R}_j, \mathbf{r}_j) + V_{1j}(\mathbf{R}_1, \mathbf{R}_j, \mathbf{r}_1, \mathbf{r}_j)] + \sum_{i < j} U_{ij}(\mathbf{R}_i, \mathbf{R}_j, \mathbf{r}_i, \mathbf{r}_j), \quad (4.1)$$

where

$\mathbf{R}_k$  represent the nuclei of the  $k$  th particle,

$\mathbf{r}_k$  represent the electrons of the  $k$  th particle,

$h_k$  is the  $k$  th isolated particle Hamiltonian,

$V_{1j}$  is the total electronic and nuclear interaction between particles 1 and  $j$ , including nucleus–nucleus, electron–electron, and electron–nucleus interactions,

$U_{ij}$  is the total electronic and nuclear interaction between particles  $i$  and  $j$ , including nucleus–nucleus, electron–electron, and electron–nucleus interactions.

We shall make the Born–Oppenheimer approximation and assume the wave function for the system is given by

$$\Psi(\mathbf{r}|\mathbf{R}) = \Psi_1(\mathbf{r}_1|\mathbf{R}_1) \prod_j \frac{\phi_j(\mathbf{r}_j|\mathbf{R}_j) + cc_j(\mathbf{R}_{1j})\delta\phi_j(\mathbf{r}_j|\mathbf{R}_j)}{[1 + c^2c_j^2(\mathbf{R}_{1j})]^{1/2}},$$

$$h_1\psi_1 = \epsilon_1^0\psi_1, \quad h_j\phi_j^0 = \epsilon_j^0\phi_j, \quad h_j\delta\phi_j = \epsilon_j^1\delta\phi_j.$$

Here we are using the tight binding model by assuming that the electrons are localized about nuclear centers. We are also assuming the single excitations of the medium are independent of each other, analogous to the mean spherical and coherent potential approximations. The first order correction to the wave function  $\delta\phi$ , is given to first order, by

$$\delta\phi_j = \sum_{n \neq j} \frac{\langle \delta\phi_j | V | n \rangle}{\epsilon_j^0 - \epsilon_n} | n \rangle,$$

where  $|n\rangle$  are the unperturbed wave functions of the solvent Hamiltonian and  $V$  is the perturbation. As a simple approximation, we choose  $V$  to be due to only the solute and, hence,  $V$  will be directed along  $\hat{R}_{1j}$ . Thus,  $\delta\phi_j$  must be along  $\hat{R}_{1j}$  and will be chosen to include only the lowest eigenfunction that lies along  $\hat{R}_{1j}$ . For a spherically symmetric ground state, this will mean  $\delta\phi_j$  will have  $p$  symmetry.  $c_j(R)$  will be chosen to minimize the energy of the  $j$ th solvent–solute interaction (as in the MSA) and  $c$  will be chosen to minimize the nuclei-averaged energy. To second order in  $c_j(R)$ , the ground state energy is given by

$$E_0 = E_0^{(0)} + \sum_j [c^2c_j^2(\mathbf{R}_{1j})A_j + 2cc_j(\mathbf{R}_{1j})V_{1j}(\mathbf{R}_{1j})] + \sum_{i < j} \{c^2[c_j^2(\mathbf{R}_{1j})U_{20}^i(\mathbf{R}_{1j}) + c_i^2(\mathbf{R}_{1i})U_{20}^i(\mathbf{R}_{1j})] + 4c^2c_i(\mathbf{R}_{1i})c_j(\mathbf{R}_{1j})U_{3j}(\mathbf{R}_{1j})\}, \quad (4.2)$$

$$A_j = \epsilon_j^1 - \epsilon_j^0 + V_2(\mathbf{R}_{1j}) - V_0(\mathbf{R}_{1j}), \quad \epsilon_j^1 = \langle \delta\phi_j | h_j | \delta\phi_j \rangle, \quad \epsilon_j^0 = \langle \phi_j | h_j | \phi_j \rangle,$$

$$U_{20}^i(\mathbf{R}_{ij}) = U_2^i(\mathbf{R}_{ij}) - U_0(\mathbf{R}_{ij}),$$

$$V_0(\mathbf{R}) = \langle \psi_1\phi | V(\mathbf{R}) | \psi_1\phi \rangle,$$

$$V_1(\mathbf{R}) = \langle \psi_1\phi | V(\mathbf{R}) | \psi_1\delta\phi \rangle,$$

$$V_2(\mathbf{R}) = \langle \psi_1\delta\phi | V(\mathbf{R}) | \psi_1\delta\phi \rangle,$$

$$\begin{aligned}
 U_0(\mathbf{R}_{ij}) &= \langle \phi_i \phi_j | U_{ij}(\mathbf{R}_{ij}) | \phi_i \phi_j \rangle, \\
 U_2^i(\mathbf{R}_{ij}) &= \langle \delta \phi_i \phi_j | U_{ij}(\mathbf{R}_{ij}) | \delta \phi_i \phi_j \rangle, \\
 U_3(\mathbf{R}_{ij}) &= \langle \delta \phi_i \phi_j | U_{ij}(\mathbf{R}_{ij}) | \phi_i \delta \phi_j \rangle, \\
 E_0^0 &= \epsilon_1^0 + \sum_j [\epsilon_j^0 + V_0(\mathbf{R}_{1j})] + \sum_{i < j} U_0(\mathbf{R}_{ij}), \\
 \epsilon_1^0 &= \langle \psi_1 | h_1 | \psi_1 \rangle, \\
 \mathbf{R}_{ij} &= \mathbf{R}_i - \mathbf{R}_j.
 \end{aligned}$$

We choose  $c_j(R_{1j})$  by assuming that the solute interacts with just one solvent molecule at a time and  $c$  is then used to incorporate higher order effects. Thus,  $c_j$  can be obtained from the two body variational equation

$$\begin{aligned}
 \frac{\partial E_0}{\partial c_j} &= 2c_j \Delta_j + 2V_1 = 0, \\
 c_j &= -V_1 / \Delta_j.
 \end{aligned}$$

Inserting  $c_j$  into Eq. (4.2) and averaging over nuclear positions, we obtain

$$\begin{aligned}
 \langle E_0(\mathbf{R}) \rangle_{\mathbf{R}} &= \bar{E}_0 = E_0^0 + c^2 A - 2cA + c^2 A' + c^2 D, \\
 A &= \left\langle \sum_j \frac{V_1^2(\mathbf{R}_{1j})}{\Delta_j(\mathbf{R}_{1j})} \right\rangle_{\mathbf{R}}, \\
 A' &= \left\langle \sum_{i < j} \left[ \frac{V_1^2(\mathbf{R}_{1j}) U_{20}^j(\mathbf{R}_{ij})}{\Delta_j^2(\mathbf{R}_{1j})} + \frac{V_1^2(\mathbf{R}_{1i}) U_{20}^i(\mathbf{R}_{ij})}{\Delta_i^2(\mathbf{R}_{1i})} \right] \right\rangle_{\mathbf{R}}, \\
 D &= \left\langle 4 \sum_{i < j} \frac{V_1(\mathbf{R}_{1j}) U_3(\mathbf{R}_{ij}) V_1(\mathbf{R}_{1i})}{\Delta_i(\mathbf{R}_{1i}) \Delta_j(\mathbf{R}_{1j})} \right\rangle_{\mathbf{R}}.
 \end{aligned}$$

We now choose  $c$  as a variational parameter to minimize  $\bar{E}_0$ , thus finding the variational equation

$$\partial \bar{E}_0 / \partial c = 2cA - 2A + 2c(A' + D) = 0$$

or

$$c = \frac{A}{A + A' + D}$$

and

$$\bar{E}_0 = E_0^0 - \frac{A}{1 + (A' + D)/A}. \quad (4.3)$$

Thus, the MSA style Pade appears naturally as a result of the minimization process.

The excited state is treated, as a first approximation, by time dependent Hartree theory. We consider the effect of turning on an electric field of the form  $U_{\text{ext}} = U_0(r_1)e^{-i\omega t}$ ; i.e., a field that interacts only with the solute. If the solute and solvent absorption frequencies are well separated, this approximation will be valid. However, for treating pure solvents or solutes with nearly resonant frequencies, it may be necessary to self-consistently determine all the polarizabilities in the problem. As a simple first application, we shall consider the system of atomic hydrogen dissolved in rare gas liquids, ignore the self-consistency problem and assume the solvent polarizabilities are not renormalized. With the above assumptions, the Hamiltonian becomes

$$H = H_0 + U_0(e^{-i\omega t} + e^{i\omega t}),$$

where  $H_0$  is given in Eq. (4.1). To first order in the perturbation, it can be shown that the wave function must be the form

$$\begin{aligned}
 \psi_0 &= e^{-iE_0 t} \frac{\psi_1 + d_1^- \delta \psi_1 e^{-i\omega t} + d_1^+ \delta \psi_1 e^{+i\omega t}}{(1 + (d_1^-)^2 + (d_1^+)^2)^{1/2}} \\
 &\times \prod_j \frac{\phi_j^{(0)} + d_j^- \delta \phi_j^{(1)} e^{-i\omega t} + d_j^+ e^{i\omega t} \delta \phi_j^{(1)}}{[1 + (d_j^-)^2 + (d_j^+)^2]^{1/2}}, \\
 \phi_j^{(0)} &= \frac{\phi_j + c c_j \delta \phi_j}{(1 + c^2 c_j^2)^{1/2}},
 \end{aligned}$$

where  $E_0$  is the ground state energy determined from Eq. (4.3),  $d_j$  are constants that will be chosen variationally,  $\delta \psi_1$  is an orbital polarized in the direction of the applied electric field, and  $\delta \phi_j^{(1)}$  is an orbital orthogonal to  $\phi_j^{(0)}$ . As previously mentioned, the functional  $L = \langle \Psi | H - i\partial/\partial t | \Psi \rangle$  is an upper bound to the polarizability. Minimizing  $L$  in a way analogous to Sec. III, we obtain

$$\begin{aligned}
 \delta \psi_1 &= \sqrt{\frac{\kappa_s}{\pi}} e^{-\kappa r} \cos \theta, \\
 U_0 &= E_0 \hat{z}, \\
 L_{\text{min}} = \alpha(\omega) &= \frac{2[\bar{U}_0(\kappa)]^2 [\Delta \epsilon_1(\kappa) + J(\kappa)]}{[\Delta \epsilon_1(\kappa) + J(\kappa)]^2 - \omega^2 - 2E(\kappa, \omega, \alpha_{\text{solvent}})}, \quad (4.4)
 \end{aligned}$$

$$E(\kappa, \omega, \alpha_{\text{solvent}}) = \frac{\bar{A}(\kappa, \omega)}{1 + \{[\bar{A}'(\kappa, \omega) + \bar{D}'(\kappa, \omega)]/\bar{A}(\kappa, \omega)\}},$$

$$\bar{U}_0 = \langle \delta \psi_1 | U_0 | \psi_1 \rangle,$$

$$\Delta \epsilon_1 = \langle \delta \psi_1 | h_1 | \delta \psi_1 \rangle - \epsilon_1,$$

$$J = \left\langle \sum_j [\langle \delta \psi_1 \phi_j^0 | V_j | \delta \psi_1 \phi_j^0 \rangle - \langle \psi_1 \phi_j^0 | V_j | \psi_1 \phi_j^0 \rangle] \right\rangle_{\mathbf{R}},$$

$$\bar{A} = \left\langle \sum_j \Delta_j \frac{(\bar{V}_j^{(3)})^2}{\Delta_j^2 - \omega^2} \right\rangle_{\mathbf{R}} \cdot 2(\Delta \epsilon_1 + J),$$

$$\bar{A}' = \left\langle 4 \sum_{i < j} \frac{(\Delta_i^2 + \omega^2)}{(\Delta_i^2 - \omega^2)^2} (\bar{V}_i^{(3)})^2 \bar{U}_i^{(20)} \right\rangle_{\mathbf{R}},$$

$$\bar{D} = \left\langle 4 \sum_{i < j} \Delta_i \Delta_j \frac{\bar{V}_i^{(3)} \bar{U}_j^{(3)} \bar{V}_j^{(3)}}{(\Delta_i^2 - \omega^2)(\Delta_j^2 - \omega^2)} \right\rangle_{\mathbf{R}} \cdot (\Delta \epsilon_1 + J),$$

$$\Delta_i = \langle \delta \phi_i^{(1)} | h_i | \delta \phi_i^{(1)} \rangle - \epsilon_i + \langle \delta \phi_i^{(1)} \psi_1 | V_i | \delta \phi_i^{(1)} \psi_1 \rangle - \langle \phi_i^0 \psi_1 | V_i | \phi_i^0 \psi_1 \rangle,$$

$$\bar{V}_j^{(3)} = \langle \delta \phi_j^{(1)} \psi_1 | V_j | \phi_j^0 \delta \psi_1 \rangle,$$

$$\bar{U}_i^{(20)} = \langle \delta \phi_i^{(1)} \phi_j^0 | U_{ij} | \delta \phi_i^{(1)} \phi_j^0 \rangle - \langle \phi_i^0 \phi_j^0 | U_{ij} | \phi_i^0 \phi_j^0 \rangle,$$

$$\bar{U}_j^{(3)} = \langle \delta \phi_i^{(1)} \phi_j^0 | U_{ij} | \phi_i^0 \delta \phi_j^{(1)} \rangle.$$

$L$  must then be minimized with respect to  $\kappa$  at each value of  $\omega$ . To evaluate  $L$  at a given value of  $\omega$  and  $\kappa$  typically took 5 min of VAX 11/780 time, so this was not a difficult calculation.

## V. LIMITING FORMS

In this section, we shall show how our formulation reduces to the Drude limit, the continuum limit, and the Saxton-Deutch limit. It is educational to do this because the limiting process allows the explicit demonstration of the assumptions made in each case.

The Drude limit is obtained when the electronic charge distributions on the solute and solvent molecules become tightly held relative to the size of the molecules. In this case, the overlap of the molecular wave functions will be negli-

ble and we can replace the intermolecular Coulomb interactions by their long range limit, i.e., dipole-dipole. Thus, we replace all the intermolecular interactions by dipole-dipole interactions. Then by symmetry the ground state energy does not change and  $J(\kappa) \rightarrow 0$ . In addition, one can show that

$$E(\kappa, \omega, \alpha_{\text{solvent}}) \rightarrow E(\alpha_{\text{solvent}}),$$

where  $E(\alpha_{\text{solvent}})$  would be the Drude result described in Ref. 3 if the Padé approximante to  $E(\alpha)$  was derived by differentiating the results of Rushbrooke, Stell, and Høye<sup>20</sup> rather than differentiating and re-Padéing. Thus,  $\alpha(\omega)$  can be written

$$\alpha(\omega) = \frac{1}{\alpha_0^{-1}(\omega) - 2E(\alpha_{\text{solvent}})},$$

which is the Drude form of Ref. 3.

To obtain the continuum limit, we must make two more assumptions. Since the continuum limit implies that the solvent molecules are much smaller than the solute molecule, we should expect the density of solvent atoms to be uniform outside a sphere corresponding to the solute's hard core. Hence, we replace the solute-solvent radial distribution function by a step function  $g(r) = \theta(r - R_0)$ , where  $R_0$  is a measure of the free volume available to the solute. If we also ignore local field effects on the solvent molecules, which amounts to ignoring the screening of solvent-solute interactions, we can obtain the continuum limit. The lack of local field effects allows us to ignore three body interactions. The shift in the ground state energy becomes

$$\Delta E = -A.$$

For  $\psi$  chosen as in the continuum Sec. II and  $\phi$  and  $\delta\phi$  of the form described in Sec. IV and shown here explicitly:

$$\phi_j = \frac{\beta^{3/2}}{\pi^{3/4}} e^{-\beta^2 r^2/2},$$

$$\delta\phi_j = \frac{\sqrt{2}\beta^{5/2}}{\pi^{3/4}} e^{-\beta^2 r^2/2} (\mathbf{r} \cdot \hat{\mathbf{E}}_j),$$

$$\beta^2 = m\omega_0,$$

it is easily shown that

$$\begin{aligned} \Delta E = & -4\pi\rho\alpha \frac{1}{2R_0} (1 + \frac{2}{3}X + \frac{1}{2}X^2 + X^3)e^{-4X} \\ & - \frac{\alpha_s}{2R_0} (1 + \frac{2}{3}X + \frac{1}{2}X^2 + X^3)e^{-4X} \end{aligned} \quad (5.1)$$

with

$$\begin{aligned} 4\pi\rho\alpha &= 3(\epsilon - 1)/(\epsilon + 2) \sim \epsilon - 1 \\ &= \epsilon(1 - 1/\epsilon) \sim 1 - 1/\epsilon = \alpha_s, \end{aligned}$$

for  $\epsilon \sim 1$ . We note that, apart from an additive constant, Eq. (5.1) is the expression derived earlier in the continuum limit. The polarizability is obtained by choosing the solvent excited orbital to be directed along the local electric field at that point (the first order perturbation guess to the wave function) and ignoring any overlap effects with  $\delta\phi_j$ :

$$\delta\phi_j^{(1)} = \frac{\sqrt{2}\beta^{5/2}}{\pi^{3/4}} e^{-\beta^2 r^2/2} (\mathbf{r} \cdot \hat{\mathbf{E}}_j),$$

$$\hat{\mathbf{E}}_j = N_j \left[ -\nabla_{\mathbf{R}_j} \int d\mathbf{r}' \psi(\mathbf{r}') \delta\psi(\mathbf{r}') V(\mathbf{r}, \mathbf{r}', \mathbf{R}_j) \right],$$

where  $R_j$  is the distance between the centers of the solute and

the  $j$ th solvent, and  $N_j$  is a normalization constant. From Eq. (4.4), one can show that the continuum limit of the polarizability is

$$U_0 \rightarrow V_{10},$$

$$J(\kappa) \rightarrow \alpha_s \left[ \langle \delta\psi | \frac{1}{r} - P_0 | \delta\psi \rangle - \langle \psi | \frac{1}{r} - P_0 | \psi \rangle \right],$$

$$\Delta\epsilon_1 + J \rightarrow \Delta,$$

$$E(\kappa, \omega, \alpha_{\text{solvent}}) \rightarrow \alpha_\omega K \Delta,$$

and

$$L \rightarrow \frac{2V_{10}^2}{\Delta^2 - \omega^2 - 2\Delta\alpha_\omega K}.$$

Thus, our result for the polarizability reduces to the continuum result.

To obtain the Saxton-Deutch-like result, we note that the absorption frequency is given by the roots of the following equation:

$$[\Delta E_1(\kappa) + J(\kappa)]^2 - \omega^2 - 2E(\kappa, \omega, \alpha_{\text{solvent}}) = 0$$

or

$$\omega \cong \Delta E_1(\kappa) + J(\kappa) - \frac{E(\kappa, \omega, \alpha_{\text{solvent}})}{\Delta\epsilon_1(\kappa) + J(\kappa)}.$$

Thus, the form of the Saxton-Deutch result is obtained by combining

$$J(\kappa) - \frac{E(\kappa, \omega, \alpha_{\text{solvent}})}{\Delta\epsilon_1(\kappa) + J(\kappa)}$$

into one two-body integral and ignoring all higher order terms. Thus

$$\omega \cong \Delta E_1(\kappa) - \frac{1A(\kappa, \omega)}{\Delta\epsilon_1(\kappa) + J(\kappa)} + J(\kappa).$$

## VI. CALCULATIONS

We begin by discussing the form of the solute and solvent wave functions. As a simple application, we shall assume the solute is a hydrogen atom with ground and excited state wave functions corresponding to  $1s$  and  $2p$  orbitals:

$$\psi_1 = \sqrt{\frac{\lambda^3}{\pi}} e^{-\lambda r} \quad \delta\psi_1 = \sqrt{\frac{\kappa^5}{\pi}} e^{-\kappa r} r \cos \theta,$$

where  $\lambda$  and  $\kappa$  are variational parameters. For our current study, we are interested in rare gas solvents so that we can compare our results with the MSA calculations. Since MSA calculations assume the solvent atoms can be described by one electron models (Drude oscillators), we use a single electron model for our solvents developed by McGinnies and Jansen.<sup>21</sup> The function is assumed to be of the form

$$\phi_j = \frac{\beta^{3/2}}{\pi^{3/4}} e^{-\beta^2 r^2/2},$$

where  $\beta^2 = m\omega_0$  and  $\omega_0$  is the first electronic transition in the solvent. The polarizability is given by  $\alpha_0 = e^2/m\omega_0^2$ . For simplicity we assume that  $m = 1$ , and, hence choose  $e$  to give the correct polarizability. This model has the advantage that, for fixed  $\omega_0$  and  $\alpha_0$ , increasing  $\beta$  (and  $m$ ) will give the Drude oscillator result for the solvent. While there are certainly more realistic models for the solvent involving more electrons, we choose a simple form in the hope that the ma-

jority of the physics is not overly sensitive to this choice. The modeling of many electron atoms by a single electron is not as arbitrary as it may seem. Indeed, the van der Waals interaction between rare gas atoms has been adequately represented by models of this form. Using a variant of the procedure described in Ref. 21, we vary the effective electron charge until the polarizability of the atom is correct. Thus, we are in a sense renormalizing the interaction. More detailed calculations can use the correct number of electrons in a manner described by Buckingham.<sup>22</sup> All interactions are then assumed to be Coulombic, with the form

$$V_j = \frac{e}{R_{1j}} + \frac{e}{r_{1j}} - \frac{e}{|\mathbf{r}_1 - \mathbf{R}_j|} - \frac{e}{|\mathbf{r}_j - \mathbf{R}_1|},$$

$$U_{ij} = \frac{e^2}{R_{ij}} + \frac{e^2}{r_{ij}} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_j|} - \frac{e^2}{|\mathbf{r}_j - \mathbf{R}_i|},$$

$$R_{ij} = |\mathbf{R}_i - \mathbf{R}_j| \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|.$$

$\mathbf{R}_i$  is the nuclear position and  $\mathbf{r}_i$  is the electron position. The evaluation of the electronic integrals is accomplished most easily by Fourier transforming the integrals:

$$\int d\mathbf{r} d\mathbf{r}' \rho_1(\mathbf{r}) \rho_2(\mathbf{r}') W_{ij}(\mathbf{r}, \mathbf{r}')$$

$$= \frac{4\pi}{(2\pi)^3} \int \frac{d\mathbf{K}}{K^2} e^{-i\mathbf{K} \cdot \mathbf{R}_{ij}} [1 - \rho_1(\mathbf{K})] [1 - \rho_2(-\mathbf{K})],$$

$$\rho_i(\mathbf{K}) = \int d\mathbf{r} \rho_i(\mathbf{r}) e^{i\mathbf{K} \cdot \mathbf{r}},$$

$$W_{ij} = U_{ij} \quad \text{or} \quad V_j,$$

$$\rho_i(\mathbf{r}) = |\psi_i(\mathbf{r})|^2.$$

In our calculations, the averages over  $R$  were performed by assuming that the configurational probabilities are determined primarily by hard core interactions. Thus we assume that the two- and three-body radial distribution functions are determined by those of a system of hard spheres with radii determined from liquid state measurements.

As a test, we can evaluate the shift in the  $1s-2p$  transition for a system in which the solvent-solvent and solute-solvent hard core radii are the same. In atomic units, we choose the polarizability and the bare solvent frequency to be  $\alpha_0^* = \alpha_0/\sigma_{bb}^3 = 0.01$  and  $\omega_0 = 0.5$  ( $\sigma_{bb}$  is the solvent-solvent hard core diameter). In atomic hydrogen, the excitation frequency is 0.375, thus choosing  $\omega_0 = 0.5$  should ensure that the solvent atoms' bare polarizability is not dramatically altered. We choose a density of  $\rho^* = \rho\sigma_{bb}^3 = 0.8$ , a high enough density so that three-body interactions should be important. Given  $\alpha_0^*$ , we can calculate  $\epsilon_s$  (for use in the continuum calculation) from the Clausius-Mossotti equation

$$\alpha_0^* = \frac{3}{4\pi\rho^*} \cdot \frac{\epsilon_s - 1}{\epsilon_s + 2} \sim \frac{1 - 1/\epsilon_s}{4\pi\rho^*}.$$

Further, since the hard core diameters are the same, we can compare our results with those of Chandler, Schweizer, and Wolynes,<sup>3</sup> who studied a system of Drude oscillators. In the Drude oscillator study, the solvent polarizability was renormalized, so we have performed two Drude calculations, one with and one without a renormalized polarizability. The effect of renormalizing the solvent polarizability on the solute

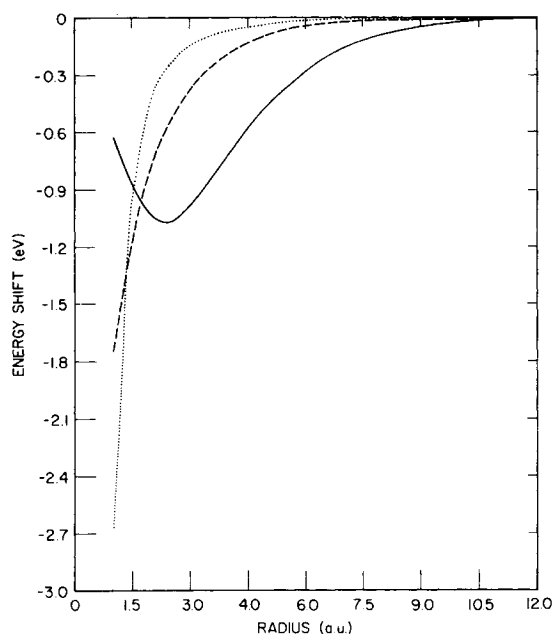


FIG. 1. The shift in the solute frequency as a function of hard sphere radius. The dotted line is the MSA result, the dashed line the continuum result, and the solid line our result. Energies are measured relative to the atomic transition.

shift is minor. In Fig. 1 we present the results of the different methods of calculating the spectral shift: the continuum medium, our discrete solvent, and the two MSA calculations. We see that only at large hard core diameters do any of the more approximate models come close to our Hartree RPA result.

The largest contribution to the frequency shift is  $J(\kappa)$ , the first order shift in energy. Since this term is absent (due to symmetry) from the MSA calculation, we expect the MSA result to be adequate only when the first order term is cancelled by exchange effects. If this were so, we would expect the MSA to be accurate if  $E(\kappa, \omega, \alpha_{\text{solvent}})$  approaches the  $E(\alpha)$  calculated by the MSA. In Fig. 2, we display the ratio of our  $E(\alpha)$  to the MSA  $E(\alpha)$ . As can be seen even if the first order term is negligible, there are major differences between our result and the MSA result.

Without renormalizing the solvent frequency, we do not expect the solvent line to be broadened unless it has some intrinsic line shape. This is due to the fact that the absorption then involves the mixing of delta functions, which can only result in delta functions. However, if the solvent frequency is renormalized, the solvent band can overlap the solute frequency and add shape to the line. This would involve either using the MSA result for the solvent (as an approximation) or developing an equation for the solvent polarizability that is analogous to Eq. (4.4) and solving for the solute and solvent polarizabilities self-consistently.

## VII. CONCLUSION

We have developed an expression for the polarizability of a solute molecule in a solvent. It includes the effects of the finite size charge distributions of the molecules and shows



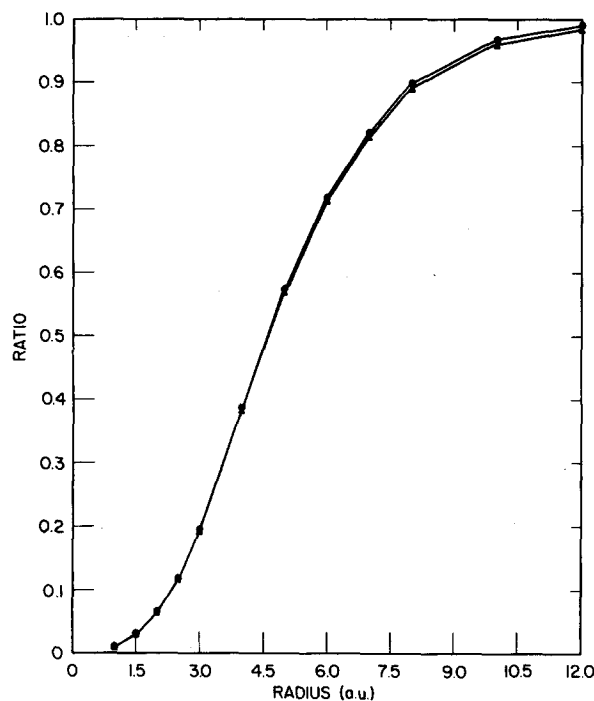


FIG. 2. The ratio of  $E(\alpha)$  as determined here and  $E(\alpha)$  from the MSA. Triangles are for the MSA with renormalized solvent polarizabilities and circles are for the MSA without renormalized solvent polarizabilities.

the details of the solute wave function, both significant advances over previous work. In addition, we have shown how our result reduces to the more approximate theories in certain limits, which should enable one to decide when the more approximate theories are applicable. We have studied a simple model system using our method and have seen that significant differences do occur between our theory and previous theories. Although we have so far ignored exchange, future work will show how to include this effect.<sup>23</sup>

## APPENDIX

Here we show that the functions used in sections III and IV are upper bounds to the polarizabilities following the ideas of Karplus<sup>16</sup> and Karplus and Kolker.<sup>17</sup> We assume a many-body Hamiltonian of the form

$$H = H_0 + V_+ e^{i\omega t} + V_- e^{-i\omega t} \quad (\text{A1})$$

with wave functions

$$\Psi = (\Psi_0 + \delta\Psi_+ e^{i\omega t} + \delta\Psi_- e^{-i\omega t}) e^{-iE_0 t} \quad (\text{A2})$$

with

$$H_0\Psi_0 = E_0\Psi_0. \quad (\text{A3})$$

Consider the functional

$$L = \langle \Psi | H | \Psi \rangle + \langle \Psi | -i(d/dt) | \Psi \rangle. \quad (\text{A4})$$

In the long time limit, we need only consider the time independent part of  $L$ , as the time dependent part will average to zero. Thus, we find

$$\begin{aligned} L = & \langle \delta\Psi_+ | H - E_0 + \omega | \delta\Psi_+ \rangle \\ & + \langle \delta\Psi_- | H - E_0 - \omega | \delta\Psi_- \rangle \\ & + \langle \delta\Psi_+ | V_+ | \Psi_0 \rangle + \langle \delta\Psi_- | V_- | \Psi_0 \rangle \\ & + \langle \Psi_0 | V_- | \delta\Psi_+ \rangle + \langle \Psi_0 | V_+ | \delta\Psi_- \rangle. \end{aligned} \quad (\text{A5})$$

If we minimize  $L$  with respect to  $\delta\Psi_+$  and  $\delta\Psi_-$ , we find

$$(H - E_0 + \omega) | \delta\Psi_+ \rangle + V_+ | \Psi_0 \rangle = 0, \quad (\text{A6a})$$

$$(H - E_0 - \omega) | \delta\Psi_- \rangle + V_- | \Psi_0 \rangle = 0, \quad (\text{A6b})$$

and

$$L_{\min} = \langle \Psi_0 | V_+ | \delta\Psi_+ \rangle + \langle \Psi_0 | V_- | \delta\Psi_- \rangle = \alpha, \quad (\text{A7})$$

which is the polarizability. Hence, if we could solve Eqs. (A6) exactly, we would find the polarizability. If, however, we cannot find an exact pair of  $\delta\Psi_+$  and  $\delta\Psi_-$ , we still have a bound on  $\alpha$ . We can show this by considering

$$\frac{\delta^2 L}{\delta(\delta\Psi_+)^2} = \langle \delta(\delta\Psi_+) | H - E_0 + \omega | \delta(\delta\Psi_+) \rangle, \quad (\text{A8a})$$

$$\frac{\delta^2 L}{\delta(\delta\Psi_-)^2} = \langle \delta(\delta\Psi_-) | H - E_0 - \omega | \delta(\delta\Psi_-) \rangle, \quad (\text{A8b})$$

Expanding  $\delta(\delta\Psi_+)$  and  $\delta(\delta\Psi_-)$  in terms of the eigenfunctions of  $H$ ,

$$\delta(\delta\Psi_+) = \sum_j a_j^+ \phi_k \quad \delta(\delta\Psi_-) = \sum_j a_j^- \phi_j, \quad (\text{A9})$$

we find Eqs. (A8) become

$$\frac{\delta^2 L}{\delta(\delta\Psi_+)^2} = \sum_j a_j^{+2} (E_j - E_0 + \omega) \geq 0 \text{ for all } \omega, \quad (\text{A10a})$$

$$\frac{\delta^2 L}{\delta(\delta\Psi_-)^2} = \sum_j a_j^{-2} (E_j - E_0 - \omega) \geq 0 \text{ for } \omega < E_j - E_0. \quad (\text{A10b})$$

Thus,  $L$  is an upper bound to  $\alpha$  for  $\omega$  less than the first excitation frequency of  $H$ .

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