THE ELECTRONIC STATES OF METAL-AMMONIA CLUSTERS AND SOLUTION

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Abstract A new model $e^- - NH_3$ pseudopotential parameterized to ab initio quantum chemistry calculations on small lithium ammonia clusters is studied in a variety of environments. Results for $Li(NH_3)_n$ ($n = 1, 4$) presented in a previous work are reviewed. Large clusters ($n = 16, 32, 64, 128$) are then studied. The valence electron is found to exist in a surface state far from the lithium ion which is localized at the center of mass of the cluster. Bulk properties of both a single excess electron and the lithium atom in solution are also reported. The solvation energy and spectrum of the excess electron are found to agree well with experiment though the spectrum is somewhat blue shifted. The valence electron of the lithium atom is found to dissociate spontaneously, a property which has not been reproduced in early work. Some preliminary results on the singlet state of two excess electrons in ammonia are presented.

1 Introduction

Metal-ammonia solutions have been extensively studied experimentally for many years [1]. However, detailed theoretical treatments have only recently become possible via the Feynman Path Integral technique and Car-Parrinello type simulations [2-6]. Despite some success, several outstanding problems remain. The spectrum and thermodynamics of a single excess electron in ammonia are not in agreement with experiment and perhaps more seriously, existing models suggest that the lithium atom will not dissociate in ammonia solution [5].

In order to further study metal/ammonia systems and refine the model potentials, small metal ammonia clusters, about the size of the first solvation shell of the metal ion were examined [7]. In particular, a new pseudopotential parameterized to the ground state of $Li(NH_3)_n$, $n = 1, 4$, was constructed. This pseudopotential explicitly treats the polarizability of the ammonia molecule neglected in previous models. Without this term, the ground state of the valence electron of the $Li(NH_3)$ and $Li(NH_3)_4$ cannot be fitted simultaneously [7]. The new potential has been used in conjunction with the Path Integral Monte Carlo (PIMC) method to probe larger clusters ($n = 16, 32, 64, 128$). Here, the valence electron is found to exist in a diffuse surface state far from the lithium ion which is located at the center of mass of the cluster. Furthermore, the electron wave function, rather than having s-like state symmetry, has most of its density associated with one side of the cluster. The excited states of these cluster were also studied. The dipole and ionization spectra were obtained by determining the electronic states of 150 representative

Table I: Parameters for Ammonia-metal ion Potentials

Ion	$r_{M+-N}/\text{\AA}$	$V(r)/K$	C_{12}/au	C_6/au	d^2/au
Li^+	1.9933	-19680	124734.32	0.0	3.58926757

configurations of the PIMC run using the Radial Fast Fourier Lanczos Method [8,7].

In order to further study the model, the bulk properties were calculated again using PIMC. Results for the solvation energy of a single excess electron as well as its average energy are found to be in agreement with experiment. Unfortunately, the dipole spectrum is blue shifted by $0.3eV$ from experiment. This is perhaps due to the neglect of solvent-solvent polarization and manybody polarization effects. The model is found to have the necessary characteristic that the valence electron of a lithium atom dissociates, ie moves away from the lithium ion into a fully solvated state. Preliminary calculations of the singlet state of two excess electrons are also presented. Using Ewald summation techniques to calculate the long range interactions, the bipolaron is found to occupy an elongated cavity with the peaks of the electron density $8\text{\AA}$ apart.

2 Potentials

The ammonia molecule is described by a simple point charge model[9,10]. This rigid model, $r_{N-H} = 1.0124\text{\AA}$ and $r_{H-H} = 1.625\text{\AA}$, has a charge of $q_H = 0.462e$ on each hydrogen and a charge of $q_N = -1.386e$ on a site $0.156\text{\AA}$ down the C_3 axis away from the nitrogen atom. The extra site is denoted r_C . The ammonia molecules interact via electrostatic terms and a Lennard-Jones potential ($\sigma = 3.4\text{\AA}$, $\epsilon = 140K$) between nitrogen sites.

The ammonia-lithium ion (Li^+) potential is written as

$$V_{M+-NH_3}(r) = \frac{eq_N}{r_{M+-C}} + \sum_{i=1}^3 \frac{eq_H}{r_{M+-H_i}} + \frac{C_{12}}{r_{M+-N}^{12}} - \frac{C_6}{r_{M+-N}^6} - \frac{\alpha e^2}{2(r_{M+-N}^2 + d^2)^2} \quad (2.1)$$

The parameters were obtained from a fit to the position and value of the minimum total energy of the $Li^+(NH_3)$ complex determined by quantum chemistry [11,12] (see Table I).

The electron-alkali metal ion interaction was taken from the pseudopotential compilation of Bachelet et al. [13]. These potentials are non-local. However, for cluster sizes larger than $Li(NH_3)_4$, non-local effects are small and maybe neglected particularly in the calculation of the ground state energy. Thus, in the Path Integral Monte Carlo calculations $V_{e-M^+}(r)$ is taken to be equal to the s-wave potential. The fully non-local potential was included in the calculation of excited states but its effects were small.

The electron-ammonia potential was taken to be

$$V_{e-NH_3}(r) = -\frac{eq_N}{r_{e-C}} - \sum_{i=1}^3 \frac{eq_H \text{erf}(r_{e-H_i}/r_0)}{r_{e-H_i}} \quad (2.2)$$

$$+ V_0 \exp(-r_{e-N}/r_{N-H}) - \frac{\alpha e^2 [1 - \exp(-r_{e-N}/r_{N-H})]^6}{2r_{e-N}^4}$$

where $r_0 = 0.856\text{\AA}$ [3,14]. The parameter $V_0 = 0.219\text{har}$ was chosen to give the correct binding energy of the valence electron of $Li(NH_3)$ [7,12]. This choice gives the binding

energy of the valence electron of $Li(NH_3)_4$ to within 0.11eV. This model contain the polarization and repulsion contributions on the nitrogen which were neglected in earlier work [2]. As mentioned above neglect of polarization makes it impossible to simultaneously fit the binding energy of the valence electron in of both species, $LiNH_3$ and $Li(NH_3)_4$, to good accuracy.

The dipole polarization energy is treated using the standard formalism. [15,16]. To account for the finite extent of the atom or ion cores an effective coulomb field is used [17,18]

$$E_i^0 = \sum_{j=1}^n \frac{r_{ij} S^{1/2}(r_{ij})}{r_{ij}^3} \quad (2.3)$$

Here, the sum is over all charges j in the system and $S(r)$ is the switching function used to screen the long range polarization interaction. Unless otherwise stated the pair polarization approximation is used and the lithium atom is taken to have zero polarizability.

3 Numerical Methods

Two theoretical techniques Path Integral Monte Carlo and Fast Fourier Projector-Lanczos methods were used in these studies

Path Integral Monte Carlo

The density matrix in the position representation can be expressed as

$$\begin{aligned} \rho(\mathbf{r}, \mathbf{R}; \mathbf{r}, \mathbf{R}; \beta) = & \int d\mathbf{r}_1 \dots \int d\mathbf{r}_{P-1} \int d\mathbf{R}_1 \dots \int d\mathbf{R}_n \\ & \times \exp \left[-\beta \sum_{i>j=1}^n V_{classical}(|\mathbf{R}_i - \mathbf{R}_j|) \right] \\ & \times \prod_{i=1}^P \rho_T(\mathbf{r}_i, \mathbf{r}_{i+1}; \beta/P) \end{aligned} \quad (3.1)$$

in the limit that the ammonia molecules and the alkali ion can be described classically. Here, $\rho_T(\mathbf{r}_i, \mathbf{r}_{i+1}; \beta/P)$ is a high temperature approximation to the density matrix taken to be the primitive short time approximation common to these calculations. In all simulation β/P was taken to be approximately 0.6 so that at 260K, 2000 beads were used and at 150K, 3500 beads were used. Equilibrium properties and imaginary time correlation functions can be calculated by taking the appropriate traces over this density matrix.

The path integral was evaluated using the Metropolis Monte Carlo Method. The classical degrees of freedom were moved according to the conventional algorithm [19,20]. However, the staging method of Ceperley and Pollack[21] was used to move the degrees of freedom associated with the electron. This algorithm which has been described in detail elsewhere [21,22,23] permits many descretizations or beads of the path integral to be sampled simultaneously with high acceptance probability. All systems were equilibrated for 10000 Monte Carlo passes of all degrees of freedom and averaged for at least 30000.

Table II: Valence Electron Ground State Energies

Cluster	$r_{M+N}/\text{\AA}$	$ E_0 /\text{eV}$
<i>Li</i>	∞	5.48
<i>Li(NH₃)</i>	2.07	4.18
<i>Li(NH₃)₄</i>	2.05	2.11
<i>Li(NH₃)₄^a</i>	2.09	2.13

a) Manybody polarization

Fast Fourier Projector-Lanczos method

The Radial Fast Fourier Transform Lanczos method [24,8] was used to determine the eigenvalues and eigenfunctions of the valence electron in fixed cluster geometries taken from PIMC runs. This method which permits the use of a non-local pseudopotential, calculates the eigenstates of a short time approximation to $\exp(-\tau\hat{H})$ using a Block Lanczos procedure for successively smaller τ . The eigenvectors of the operator with a preceding larger τ are used as input to the calculation at the smaller value. This process is continued until convergence is obtained. The action of the short time operator $\exp(-\tau\hat{H})$ on a wave function is evaluated on a grid in radial coordinates using Fast-Fourier Transform techniques [18,8]. A grid of 128 points in r , 16 points in ϕ and 16 points in $\cos\theta$ was used. The radial distance measured from the lithium ion, was taken to range from 0 – 100 a_0 . The initial value of the parameter, τ , was taken to be 6.25 au . It was necessary to iterate twice, cutting τ by a factor of 5 au each time to obtain convergence. Ten blocks of 16 states were included in each Block Lanczos procedure. The ground and excited state energies and wave functions of the single excess electron in the bulk ammonia were calculated using the Fast Fourier Transform Lanczos method [24] in the same manner as described above. Here, the grid is in cartesian coordinates, 16x16x16, and is taken to span the simulation box, $\sim 42a_0$. The parameter τ was initially set to 25 au and the procedure iterated three times reducing τ by a factor of 5 au at each step. Six blocks of 7 states were included in each Block Lanczos procedure.

4 Results

Lithium-Ammonia Clusters

In Figure 1, the ground state wave function of the valence electron of *Li*, *LiNH₃* and *Li(NH₃)₄* are presented for the lowest total energy geometries [7]. The corresponding ground state energies can be found in Table II. There is a dramatic shift in both the charge density and the ground state energy as cluster size increases. The electron moves into a large radius Rydberg-like state. The nitrogen atoms which carry a negative charge effectively squeeze the electron out. Thus the solvent atoms successfully compete for “possession” of the stable ion with the electron.

Larger *Li(NH₃)_n*, $n = 16, 32, 64, 128$ with many low frequency degrees of freedom were studied at finite temperature, 150K. At equilibrium, the classical atoms of the cluster are arranged such that the lithium ion is at the center of a roughly spherical cluster.

Figure 1: The probability that the electron is a distance r from the lithium ion in $Li(NH_3)_n$, $n = 0, 1, 4$ ($\int dr P(r) = 1$).

Table III: Average Eigenvalues, $Li(NH_3)_n$

Cluster	E_0/har	E_1/har	E_2/har	E_3/har
$Li(NH_3)_{16}$	-0.053	-0.047	-0.046	-0.043
$Li(NH_3)_{32}$	-0.048	-0.042	-0.040	-0.038
$Li(NH_3)_{64}$	-0.045	-0.038	-0.037	-0.034
$Li(NH_3)_{128}$	-0.042	-0.035	-0.034	-0.030

Comparisons between simulations of the neutral and the charged species indicates that the electron does not cause a significant rearrangement of the classical atoms. The coordination number of the lithium is four in both the charged and uncharged species, a result that is in accord with bulk results.

The properties of the valence electron of the clusters were studied in detail. The electron is in a diffuse state extending far from the cluster. In order to further categorize the electron state, one configuration of each of the clusters is shown in Figure 2. The electron probability distribution function shifts to larger distance as cluster size increases. The model thus seems to favor the dissociation of a lithium atom in the bulk. The electron rather than being in an orbital of s-type symmetry rather prefers one side of the cluster. Thus, a states with enormous dipole moments similar to those observed in $(NH_3)_n^-$ clusters [4] are formed.

The electronic states were examined in detail for 150 representative configurations of each cluster size. In Table III, the average ground state energy and first three excited state energies are reported. A comparison of the energy difference between the ground and first excited state reveals that the electron is in its ground state at equilibrium ($\Delta E_{01} \sim 12kT$).

Figure 2: Instantaneous configurations of $Li(NH_3)_n$ cluster; the small balls represent electron density

Therefore, the ionization spectra pictured in Figure 3 is simply a histogram of the ground state energies. The peak of the spectrum red shifts and the half width increases with cluster size indicating that the electron is becoming more weakly bound. In Figure 4, the dipole spectra of the clusters are presented. The spectra are surprisingly similar though there is a slight decrease in the intensity and broadening of the "p-band" and an increase in intensity of the higher energy transitions. Interestingly, the weak second peak does not arise from a "d-state" but rather from the ninth excited state or the first "f-state". This may be due to some symmetry induced in the surface ammonia molecules by the electron or may, in fact, be caused by some remnant of the octopolar symmetry of the tetrahedral $Li^+(NH_3)_4$ complex at the center of the cluster.

The solvated electron and Lithium ammonia solutions

A single excess electron in fluid ammonia ($T=260K$, $\rho = 0.227\text{\AA}^3$, $N_{mol} = 256$) has been studied using PIMC and the new model pseudopotential. Ewald summation was used to calculate the long range interactions. The ammonia-ammonia potential energy was found to agree within the error bar $0.3eV$ with the isolated solvent. This is consistent with the analysis of Schindewolf [25] who found a small contribution to ΔH from the solvent. The structure of the electron is shown in Figure 5, where the electron-center of mass-Nitrogen and the electron-center of mass-Hydrogen $g(r)$ are presented. Here, the electron-center of mass is average position of the electron for a given PIMC configuration. From this figure it can be seen that electron is localized a cavity formed by the solvent molecules. The estimate of the radius of this soft cavity is difficult to obtain quantitatively. Based on the zero of the $g(r)$'s the cavity radius is between $2.5\text{\AA}$ and $3\text{\AA}$ however, based on the value at half maximum the cavity radius is about $4\text{\AA}$.

Figure 3: Normalized ionization spectra for $Li(NH_3)_n$ clusters.

Figure 4: Normalized dipole spectra for $Li(NH_3)_n$ clusters.

Figure 5: a) Electron c.o.m.-nitrogen $g(r)$ and b) Electron c.o.m.-hydrogen $g(r)$ for the solvated electron in liquid ammonia

The electronic states of each model were studied by again examining 150 configuration taken from the PIMC runs. In Figure 6a, the density of states (ground state only) is presented (the system is again ground state dominated). The peak is consistent with the data of Schindewolf [25] ($E_0 \sim -1.1\text{eV}$) and the data of Bowen ($E_0 \sim -1.3 \pm 0.3\text{eV}$) [26]. The dipole spectrum however, is not in agreement with experiment (Figure 6b). This may be due the neglect of polarization in the solvent-solvent interaction or might indicate the need for a non-local pseudopotential.

Lithium in fluid ammonia was studied next at the same state point. At equilibrium, the most probable separation for the electron is greater than half the box length indicating that the electron has spontaneously dissociated. This is another desirable property of the model whose major problem seems to be its inability to reproduce the electronic absorption spectra, a result that may have more to do with solvent force field than with the electron-solvent pseudopotential.

Two excess electrons

The singlet state of two excess electrons has been studied using PIMC and Ewald summation. The electron-electron (spin up-spin down) probability distribution function is shown Figure 7 peaks at around $8\text{\AA}$ indicating the elongated cavity state which is pictured in Figure 8. The total energy of the bipolar state is slightly less than twice the energy of an isolated electron indicating that the state is indeed "bound". Of course, in analogy with classical ions in solution, potential of mean force calculations must be performed to more precisely determine this binding.

Figure 6: a)Ground density of states and b)Dipole spectra for the solvated electron in liquid ammonia

Figure 7: The electron-electron probability distribution for two electrons in liquid ammonia

Figure 8: Instantaneous configuration of the bipolaron in liquid ammonia; the small balls represent electron density

5 Discussion

Small and large $Li(NH_3)_n$ clusters have been examined using a new model pseudopotential. The valence electron of the metal atom is found to exist in a surface state far from the metal cation which is buried inside the cluster. When transferred to the bulk, the thermodynamic properties of an excess electron are in agreement with the experiment however, the dipole spectrum is blue shifted approximately 0.3eV . This could possibly be corrected by incorporating a fully polarizable solvent into the model. As is, the model predicts the ionization of a lithium atom in fluid ammonia, a result not properly reproduced by earlier work. Study of the singlet state of the bipolaron predicts that the two electrons occupy an elongated cavity with the spin-up spin-down distribution peaked at about $8\text{\AA}$. In future work we plan to study the Li/NH_3 system at finite lithium concentration.

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