

Electronic States in Metal-Ammonia Solutions

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Quantum simulation studies have been performed on metal-ammonia solutions for a wide range of concentrations using a model consisting of excess electrons in a molecular solvent. At low electron concentrations, the electron density is localized, and the electrons pair to form peanut-shaped bipolarons. At higher electron concentrations, the bipolarons exhibit a tendency to cluster. Eventually, at yet higher concentrations, the electron density becomes delocalized and spans the system indicating that the system has become metallic.

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The general behavior of metal-ammonia solutions has been deduced from decades of experimental study [1-3]. At very low metal density, the solutions are characterized by isolated excess electrons [$\rho_e < 0.01$ mole percent electron (MPE)]. At higher concentrations ($\rho_e < 2$ MPE), the solutions are dominated by localized spin paired species (bipolarons). The metal-insulator transition occurs at about 4 MPE, and, for concentrations greater than 9 MPE, the solution behaves like a good liquid metal. Although the available experimental information is extensive, the microscopic understanding of the electronic states of the system is mostly qualitative, especially at concentrations in the metallic regime [4,5].

Previous simulation studies employing path integral Monte Carlo (PIMC) and Car-Parrinello local spin density functional (CP-LSDA) methods have confirmed experimental inferences about the electronic states at low metal concentration [6-11]. At infinite dilution, the excess electrons exist in the separate cavities about 3-4 Å in radius. The surrounding ammonia molecules are ordered with, on average, one N-H bond pointing towards the center of the cavity occupied by the electron [6-9]. At around 1 MPE, the electron density is still localized. However, the electrons spin pair and form peanut-shaped cavities with peaks in the electron density about 7 Å apart [10,11]. These spin paired species are the so-called "bipolarons." This weakly paired state is consistent with many experimental observations [4,10].

In order to obtain a more complete understanding of the metal-ammonia phase diagram at higher metal density and to observe the onset of metallic behavior, CP-LSDA calculations [12-14] have been performed for concentrations that range from the insulating to the metallic regime (1-10 MPE). In particular, three electron densities, 1, 2, and 10 MPE, have been investigated. At 1

MPE, our new calculations confirm that the electron density is a localized bipolaronic structure [10,11]. At 2 MPE, bipolarons are still observed, but have a tendency to cluster. At 10 MPE, the electron density has become extended and spans the entire simulation cell in accord with the experimental data.

In the present calculations, the solvent ammonia molecules are described by a rigid point-charge model [15]. The pseudopotential used to describe electron-ammonia interactions has been discussed in detail elsewhere [16]. It contains the appropriate electrostatic interactions and both polarization and repulsion contributions from the nitrogen. Rather than explicitly including metal cations, a uniform positive charge background is introduced. This is a good approximation because the ions are solvated by the ammonia and isolated from contact with the electron density. Therefore, only small ion effects are expected. Indeed, in test calculations, this was found to be the case [17]. The simulation cell consisted of 256 ammonia molecules and n_e number of excess electrons. We have examined systems of $n_e = 2, 4,$ and 24 which corresponds to roughly 1, 2, and 10 MPE, respectively. The volume of the simulation cell is taken to be [1]

$$V_s = V_{\text{NH}_3} + n_e V_e, \quad (1)$$

where V_{NH_3} is the volume of 256 ammonia molecules at a typical liquid density, $\rho_{\text{NH}_3} = 0.023 \text{ \AA}^{-3}$, and the parameter $V_e = 65 \text{ \AA}^3$ is the excess volume per solvated electron [1]. The temperature of the solution was kept at 260 K, well above the freezing point of the solutions at all concentrations studied, using well-defined canonical dynamics methods [18-20].

The electronic states of the system were determined using local spin density functional theory [14]. In this scheme, the energy of an N electron system is written as

$$E[n(\mathbf{r})] = -\frac{\hbar^2}{2m} \int d\mathbf{r} \sum_{i,\sigma} \psi_{i\sigma}(\mathbf{r}) \nabla^2 \psi_{i\sigma}(\mathbf{r}) + \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n_1(\mathbf{r}), n_{-1}(\mathbf{r})], \quad (2)$$

where $n(\mathbf{r}) = n_1(\mathbf{r}) + n_{-1}(\mathbf{r})$, $n_\sigma(\mathbf{r}) = \sum_i^N |\psi_{i\sigma}(\mathbf{r})|^2$, and $N_1 + N_{-1} = N$. The self-consistent equations for the Kohn-Sham (KS) orbitals are then

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}(\mathbf{r})}{\delta n_\sigma(\mathbf{r})} \right] \psi_{i\sigma}(\mathbf{r}) = \epsilon_i \psi_{i\sigma}(\mathbf{r}), \quad (3)$$

where the exchange correlation energy is defined as $E_{xc}(\mathbf{r}) = \int d\mathbf{r} n(\mathbf{r}) [\epsilon_x(\mathbf{r}) + \epsilon_c(\mathbf{r})]$. The form of the spin polarized $\epsilon_x(\mathbf{r})$ and $\epsilon_c(\mathbf{r})$ are taken from Perdew and Zunger [21]. The single-particle orbitals at the Γ point of the Brillouin zone have been expanded in plane waves with a cutoff of $k_{\max} = 6\pi/L$, where L is the size of the simulation cell. It is sufficient to use only the Γ point because of the large size of the unit cell (256 ammonia molecules) and liquid nature of the system. The plane wave cutoff was tested on fixed configurations and was found to give energies to within a few percent of fully converged results.

Local spin density functional theory is a theory for the ground state of the many-electron system [14]. In using this approximation, it has been assumed that the structure and dynamics of the electrons and the nuclei can be adequately modeled by considering the motion on the ground state Born-Oppenheimer surface. Even in the metallic regime, where the electronic excitation energy is comparable to the thermal energy (kT), this approximation has been empirically justified in many calculations [22,23].

The structure and dynamics of the system were determined using the Car-Parrinello method [12,13]. The coefficients of the plane wave basis set are given fictitious momenta and the system propagated according to a Lagrangian consisting of the electronic energy, the solvent potential energy, and the solvent kinetic energy plus the fictitious momenta. The fictitious electronic degrees of freedom are given a small mass ($m_{\text{basis}} = 256$ a.u. for $\rho_e < 2$ MPE and $m_{\text{basis}} = 16$ a.u. for $\rho_e = 10$ MPE) and a very low temperature (0.02 K). This guarantees that in the adiabatic limit the electronic wave function will be in the instantaneous ground state with respect to the nuclear coordinates.

Simulations were run for 30 ps for each state point studied using the velocity Verlet integration algorithm [24]. Time steps of 16 a.u. for $\rho_e \leq 2$ MPE and 4 a.u. for $\rho_e = 10$ MPE were used. The temperature difference between the solvent and the plane wave coefficients was maintained using Nosé thermostats [18–20]. However, we have found that the original Nosé-Hoover constant temperature scheme [18,19] does not maintain good temperature control in the metallic regime (10 MPE) due to the strong coupling of the nuclear dynamics to that of the basis set coefficients. This resulted in large deviations from the Born-Oppenheimer surface. In order to overcome this difficulty, a modified Nosé-Hoover canonical dynamics scheme, the Nosé-Hoover chain method, was used [20]. A set of independent Nosé-Hoover chains is

put on each spin-up and spin-down orbital as well as the translational and rotational degrees of solvent molecules. The Nosé-Hoover chains were found to maintain temperature control very well and as a result deviations from the Born-Oppenheimer surface were observed to be less than 2% during a typical 30 ps trajectory.

The electronic structure of metal-ammonia solutions at densities of 1, 2, and 10 MPE is very different. At low electron density, the electrons are localized in bipolaronic structures in which the weakly paired electrons form a peanut-shaped cavity [10]. At the slightly higher electron density, the bipolarons begin to associate and form clusters. Two types of clusters were observed. In Fig. 1(a), the first cluster type, a weakly associated dimer of bipolarons, is shown. This state occurs in 80% of the configurations. In Fig. 1(b), the second cluster type which accounts for 20% of the configurations is shown. Here, the electron density has connected to form an amoeba or tubelike structure which almost spans the simulation cell. This delocalization of the electron density occurs concomitantly with a decrease of the energy gap [the difference between the energies of the lowest unoccupied and highest occupied KS states; cf. Eq. (3)] to a value close to that observed at 10 MPE. At this highest electron density studied, the electronic structure of the system is radically different (see Fig. 2), although the solution remains a good liquid. The electrons are delocalized in a multitunnel-like structure which spans the entire simulation cell. Individual orbitals are also delocalized. For example, in an attempt to characterize the nature of the electronic states, random walkers are placed on a real grid of the electron points and allowed to hop to the nearest-neighbor sites if the electron density is greater than a small threshold defined to be one-tenth of the maximum value on the grid. The mean square displacement of such walkers on an extended (localized) state always increases (plateaus) [22]. No localized bipolaronic structures are observed at this concentration.

The single-particle electronic density of states $N(E)$, calculated by averaging over KS eigenvalues [cf. Eq. (3)] of 40 configurations well separated in time, is presented in Fig. 3. As there are only a few states below Fermi level, there is likely a large error in the detailed shape of the computed density of states. However, the major difference in the density of states for the three concentrations studied is in the behavior at the Fermi level $N(E_F)$. For both 1 and 2 MPE, $N(E_F)$ is equal to zero within our numerical error. This indicates that the system is not metallic at these densities. However, at 10 MPE, the lower and upper bands cross and $N(E_F)$ becomes nonzero. Detailed analysis shows the states at the Fermi level are extended (see above), which suggests that the system is metallic at this concentration as in experiment [25,26].

The appearance of delocalized KS states has important consequences for the dc conductivity. The frequency-dependent conductivity obtained from the Kubo-Greenwood (KG) relation is [27,28]

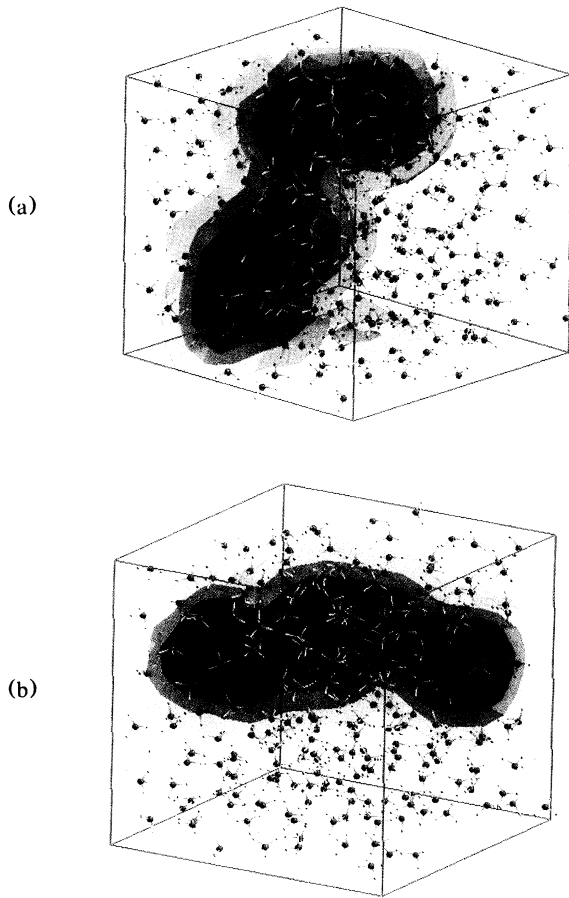


FIG. 1. The electron density of representative configurations at 2 MPE taken from the present LSDA calculations. The simulation system consists of 4 excess electrons in 256 ammonia molecules. (a) Dimerized bipolaronic structure. (b) Amoeba-like extended structure.

$$\sigma(\omega) = \frac{\pi e^2}{3m^2 \Omega \omega} \sum_{\sigma} \sum_i \sum_j (f_i^{\sigma} - f_j^{\sigma}) |M_{i,j}^{\sigma}|^2 \times \delta(\epsilon_i^{\sigma} - \epsilon_j^{\sigma} - \hbar \omega), \quad (4)$$

where σ is the spin state, f_i^{σ} is the occupation number of the spin state (σ, i) , Ω is the volume of the simulation cell, and $M_{i,j}^{\sigma} = \langle \Psi_i^{\sigma} | \hat{p} | \Psi_j^{\sigma} \rangle$ is the momentum-operator matrix element between states (σ, i) and (σ, j) . The spin-up and spin-down single-particle KS states and eigenvalues are used instead of the true many-body eigenfunctions and eigenvalues. Also, only the Γ point was used in the calculation due to the large size of the cell (256 molecules) and the liquid nature of the solutions. For low concentration (1 and 2 MPE), $\sigma(0) = 0$ within our numerical uncertainty. This is consistent with a system that has a zero density of states at the Fermi level as discussed above [25,26]. However, for 10 MPE, a dc conductivity of about $700 \Omega^{-1} \text{cm}^{-1}$ is obtained by ex-

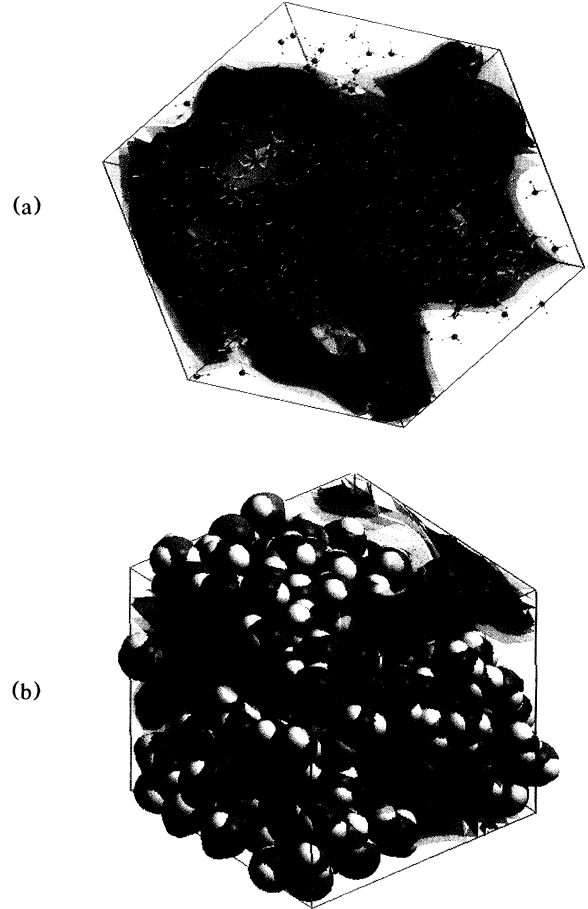


FIG. 2. The electron density of representative configurations of metal-ammonia solution at high electron concentration (10 MPE). The system consists of 24 excess electrons in 256 ammonia molecules. (a) Ball and stick representation of ammonia molecules using covalent bond lengths. (b) Space filling ammonia molecules using the van der Waals radii of the atoms.

trapolating our results to zero frequency. This is in reasonable agreement with the experimental value, $1500 \Omega^{-1} \text{cm}^{-1}$ [1]. Test calculations reveal only small changes are induced by the addition of the ions [17].

In summary, the results of a study of the electronic structure of metal-ammonia solutions has been presented. As the electron concentration increases, the character of the electron density changes from localized to extended. At very low metal concentration, the excess electrons localize in the separate cavities. At higher concentration, the electrons spin pair and form peanut-shaped bipolarons. Next, the bipolarons start to cluster and form elongated structures. At high metal concentration (10 MPE), the electron density becomes completely delocalized. The delocalization of the electron density is accompanied by a decrease in the energy gap and an increase of the density of states at the Fermi level. This in turn

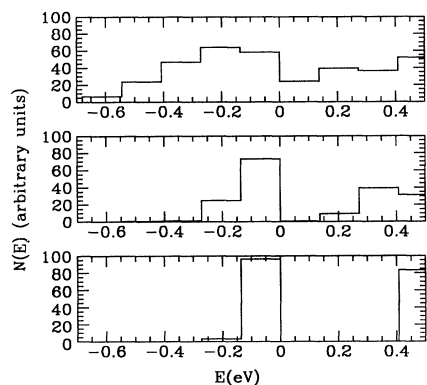


FIG. 3. The single-particle electronic density of states $N(E)$, calculated by averaging over Kohn-Sham eigenvalues of 40 configurations well separated in time. The Fermi energy defined as the eigenenergy of the highest occupied orbital has been set to zero for each configuration. From the top to the bottom: $\rho_e = 10$ MPE, $\rho_e = 2$ MPE, and $\rho_e = 1$ MPE.

yields a nonzero dc conductivity indicating that the system is a good liquid metal, in agreement with experiment.

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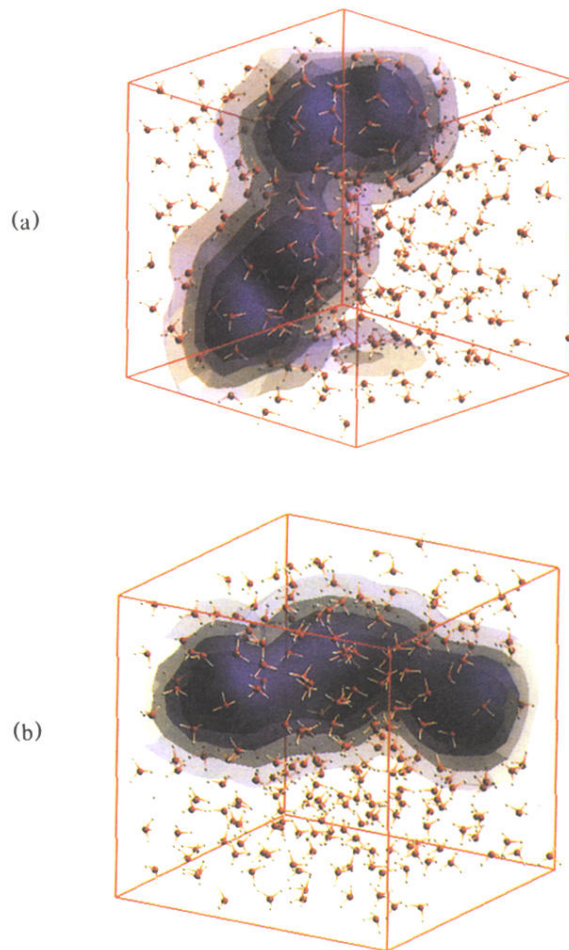


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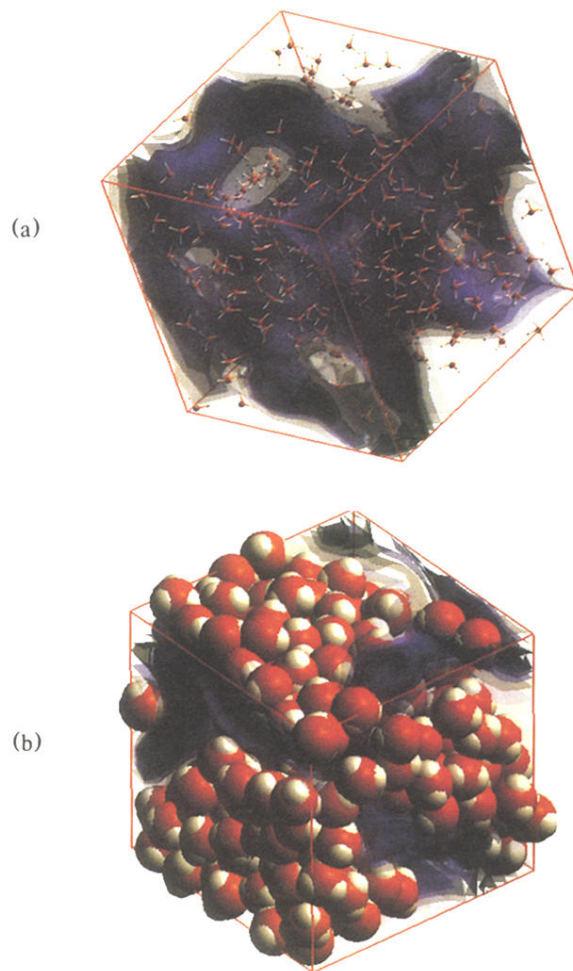


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