

Cation-Electron Interaction in Metal-Ammonia Solutions

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The problem of electron binding in the field of a cation in metal solutions is treated on the basis of an interstitial ion model. The energy levels and charge distribution of the unpaired electron are computed by a self-consistent field treatment for electron binding in a continuous dielectric medium employing one parameter wave function. Comparison with experimental results and with theoretical treatment based on a molecular model is presented. The adequacy of the continuous model is discussed.

INTRODUCTION

IT is fairly well established that in dilute metal-ammonia solutions the ionization of the alkali metal to solvated cations and electrons bound to the solvent is practically complete in the concentration region below $10^{-3}M^{1,2}$. The concentration dependence of the paramagnetic susceptibility^{3,4} and the electrical conductivity⁵⁻⁷ was recently interpreted^{8,9} by assuming that at higher concentration cation-electron interaction occurs. This "ion-pair" is involved in the mechanism of spin pairing, which occurs either by F_2 center⁹ or by dimer formation.⁸ The NMR experiments of McConnell and Holm¹⁰ definitely indicate the existence of charge distribution of the unpaired electron on the alkali cation. Quantum mechanical calculations led to the values of -0.28 eV,⁸ -0.10 eV,¹¹ and -0.61 eV¹¹ for the binding energy of the electron in the ground state of the monomer.

The purpose of this note is to present a treatment of the energy levels and charge distribution of an electron trapped in the field of a cation in solution. The present approach is based on a self-consistent field treatment for electron binding in the field of a positive point charge in a continuous dielectric medium. This formulation of the problem is equivalent to the computation of the energy levels of an electron bound in the field of an interstitial ion in a crystal¹²⁻¹⁴. The present approach involves the application of the static

method.^{15,16} The dynamic interactions between the electron and the nuclear motion of the solvent molecules are not taken into account. The present treatment is based on the assumption that the form of the potential well is solely determined by long-range interactions. Spherical symmetry of the potential is assumed, and one parameter wave functions are employed.

GROUND STATE

In the ground state of the system the potential $V(r)$ is determined by the charge Ze of the cation and the wave function of the electron chosen as

$$\psi_0(r) = (\mu^3/\pi)^{1/2} e^{-\mu r}. \quad (1)$$

The potential is then obtained from the total field acting on the electron,

$$-\text{grad}V(r) = (Ze/D_{0p}r^2) - \{[Z - q(r)]\beta e/r^2\}, \quad (2)$$

where

$$\beta = (1/D_{0p}) - (1/D_s) \quad (3)$$

$$q(r) = \int_0^r |\psi_0(r)|^2 4\pi r^2 dr; \quad (4)$$

D_s and D_{0p} are the static and optical dielectric constants of the medium.

Using Hartree's atomic units the following expression is obtained,

$$V(\mu, r) = -(D_{0p}r)^{-1} + \frac{\beta(1+\mu r)e^{-2\mu r}}{r}. \quad (5)$$

The total energy of the bound electron is computed from the variation integral

$$W_{1s}(\lambda, \mu) = \int \psi_1[-\frac{1}{2}\Delta + V(\mu, r)]\psi_1 4\pi r^2 dr, \quad (6)$$

where

$$\psi_1(r) = (\lambda^3/\pi)^{1/2} e^{-\lambda r}. \quad (7)$$

The reference state is that of a free electron placed at infinity from the cation, while the dielectric medium

¹ M. C. R. Symons, *Quart. Revs. (London)* **13**, 99 (1959).

² J. Jortner, *J. Chem. Phys.* **30**, 839 (1959).

³ S. Freed and N. Sugarman, *J. Chem. Phys.* **11**, 354 (1943).

⁴ C. A. Hutchison and R. C. Pastor, *J. Chem. Phys.* **21**, 1959 (1953).

⁵ C. A. Kraus, *J. Am. Chem. Soc.* **43**, 749 (1921).

⁶ C. A. Kraus, *J. Chem. Ed.* **30**, 83 (1953).

⁷ E. C. Evers and P. W. Frank, *J. Chem. Phys.* **30**, 61 (1959).

⁸ E. Becker, R. A. Lindquist, and B. J. Alder, *J. Chem. Phys.* **25**, 971 (1956).

⁹ M. F. Deigen and Y. A. Tsvirko, *Ukrain Fiz. Zhur.* **1**, 245 (1956).

¹⁰ H. M. McConnell and C. A. Holm, *J. Chem. Phys.* **26**, 1517 (1957).

¹¹ W. E. Blumberg and T. P. Das, *J. Chem. Phys.* **30**, 251 (1959).

¹² N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1948), p. 85.

¹³ R. Kubo, *J. Phys. Soc. Japan* **3**, 254 (1948).

¹⁴ J. H. Simpson, *Proc. Roy. Soc. (London)* **A197**, 269 (1949).

¹⁵ H. Frohlich, *Phil. Mag. Suppl.* **3**, 325 (1954).

¹⁶ J. H. Simpson, *Proc. Roy. Soc. (London)* **231**, 308 (1955).

has attained the nuclear configuration forming the potential well presented by Eq. (5).

The best wave function of this form is obtained by solving for λ the equation

$$[\delta W(\lambda, \mu)/\delta \lambda]_{\mu} = 0, \quad (8)$$

and for self-consistency of the field then setting $\lambda = \mu$. Hence

$$\lambda = \frac{1}{18}[(5/D_{0p}) + (11/D_s)] \quad (9)$$

$$W_{1s} = -\frac{1}{518}[(5/D_{0p}) + (11/D_s)][(15/D_{0p}) + (1/D_s)]. \quad (10)$$

The Bohr radius of the bound electron is $r_B = 1/\lambda$.

In order to check the validity of the variational treatment, the calculation was repeated using the wave function

$$\psi_0 = (\mu^3/7\pi)^{1/2}(1 + \mu r)e^{-\mu r}. \quad (11)$$

By applying Eqs. (2) and (6),

$$V(\mu, r) = -(D_{0p}r)^{-1} + \beta(r^{-1} + \frac{1}{4}\mu + \frac{5}{7}\mu^2r + \frac{1}{7}\mu^3r^2)e^{-2\mu r}. \quad (12)$$

And by the solution of the variational integral (8) with $\psi_1(\lambda)$ of the form (11) we readily obtain

$$\lambda = \frac{7}{8}[(0.2170/D_{0p}) + (0.4259/D_s)] \quad (13)$$

$$W_{1s} = (3\lambda^2/14) - (9\lambda/14D_{0p}) + 0.2145\beta\lambda. \quad (14)$$

The Bohr radius of the bound electron presented by a wave function (11) is given by $r_B = [(5)^{1/2} + 1]/2\lambda$.

For liquid ammonia at -33°C we set

$$D_s = 22 \quad D_{0p} = n^2 = 1.76 \quad \text{and} \quad \beta = 0.523.$$

The results of the calculations using the wave function of the type (1) and (11) are presented in Table I. No significant lowering of the energy is observed by applying the wave function (11). This result indicates the adequacy of the variational treatment using the potential function defined by Eq. (2).

It is interesting to consider the period of the bound electron in the ground state which can be approximately presented by

$$\tau = 512\pi\hbar^3/[(5/D_{0p}) + (11/D_s)]^2 \quad (15)$$

for liquid ammonia at -33°C $\tau \sim 3.10^{-13}$ sec. The comparison of this value with the relaxation time of liquid ammonia 1, 3.10^{-12} sec at -40°C ,¹⁷ yields a justification for the static approximation employed in the present treatment.

OPTICAL EXCITATION ENERGY

The energy of the first excited state ($2p$ state in our approximation) was calculated by using the wave

TABLE I. Calculations for the electron binding in the ground state.

Wave function	λ a.u.	W_{1s} ev	r_B a.u.
(1)	0.209	-1.52	4.79
(11)	0.334	-1.65	4.85

functions

$$\psi_{2p} = (\alpha^5/\pi)^{1/2}r e^{-\alpha r} Y_{2m}(\theta, \phi). \quad (16)$$

The vertical electronic transition is subjected to the restrictions of the Franck-Condon principle. Thus we have computed the energy of the excited state in the nuclear configuration of the ground state. In this approximation Eqs. (2) and (4) remain unchanged; the potential corresponds to the ground state, while the charge distribution is given by Eq. (16).

As the energy of the excited state is not very susceptible to the behavior of the potential function at small distances, the calculation was carried out by using only the potential $V(\mu, r)$ presented by Eq. (5). The energy of the excited state W_{2p} is given by

$$W_{2p} = \frac{1}{2}\alpha^2 - (\alpha/2D_{0p}) + \frac{1}{2}\beta\alpha(1+X)^{-4} + \beta\mu(1+X)^{-5}, \quad (17)$$

where $X = \mu/\alpha$; X was then obtained from

$$\delta W/\delta \alpha = \alpha - (2D_{0p})^{-1} + \frac{1}{2}\beta(15X^2 + 6X + 1)(1+X)^{-6} = 0. \quad (18)$$

Thus we calculate for the excited state

$$\alpha = 0.200 \text{ a.u.} \quad r_B = 5.24 \text{ \AA} \quad W_{2p} = -0.51 \text{ ev.}$$

The first electronic transition in the monomer is expected to occur at

$$h\nu = W_{2p} - W_{1s}, \quad (19)$$

thus the calculated value for $h\nu$ is about 1.1 ev.

THERMAL AND OPTICAL DISSOCIATION ENERGIES

The binding energy $-W_{1s}$ of the electron in the ground state represents the optical dissociation energy corresponding to a vertical ionization process. The thermal dissociation energy of the monomer involves the formation of an unbound electron and a normally solvated cation. The thermal and optical dissociation energies are related by

$$-H = W_{1s} + \chi, \quad (20)$$

where χ is the electrostatic energy required to transform the configuration of the dielectric medium which is in equilibrium with the alkali cation to the configuration which forms the potential well $V(\mu, r)$. For the calculation of χ we applied the theory of Marcus¹⁸ for the electrostatic free energy of nonequilibrium states. This

¹⁷ K. Fish, C. Miller, and C. P. Smyth, J. Chem. Phys. **29**, 745 (1958).

¹⁸ R. A. Marcus, J. Chem. Phys. **24**, 979 (1956).

TABLE II. Density of unpaired electron spin on Na⁺ nucleus.*

Wave function	$ \psi_{1s} ^2$	$\langle 1s \psi_{1s} \rangle$	$\langle 2s \psi_{1s} \rangle$	$ \psi_{1s} ^2$
(1)	0.00202	0.0212	0.160	0.107
(11)	0.00170	0.0161	0.137	0.096

* Charge density expressed in a.u. units (Bohr radius)⁻³.

theory leads to the general result¹⁹ for the work required to transform a system which is in equilibrium in respect of a charge distribution ρ^0 to a nonequilibrium state where the permanent orientation polarization¹ is in equilibrium with the charge distribution ρ ,

$$\chi = \frac{\beta}{8\pi} \int (E_c - E_c^0)^2 dv, \quad (21)$$

where

$$\begin{aligned} \operatorname{div} E_c &= 4\pi\rho \\ \operatorname{div} E_c^0 &= 4\pi\rho^0. \end{aligned} \quad (22)$$

For the present case

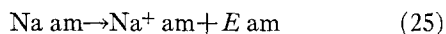
$$\begin{aligned} E_c^0 &= e/r^2. \\ E_c &= e[1 - q(r)]/r^2. \end{aligned} \quad (23)$$

Hence

$$\chi = \frac{\beta e^2}{2} \int_{R_0}^{\infty} \frac{|q(r)|^2}{r^2} dr. \quad (24)$$

Assuming that the configuration of the primary solvation layer of the cation M^+ is not affected by the introduction of the electron we set $R_0 = r_{M^+} + 2r_{NH_3}$. Hence R_0 and thus χ will be slightly dependent on the nature of the cation. For Na⁺ ion $R_0 = 3.80$ Å. Using the wave function (1) we obtained $\chi = 0.72$ eV and $H = 0.80$ eV.

It is interesting to compare this result with the value of the thermal dissociation energy of the bound electron in infinitely dilute metal ammonia solutions. A self-consistent field treatment using one parameter wave function of the form (1) yielded the result of 0.845 eV for the thermal dissociation energy of the electron bound to the polarized dielectric medium. Thus the calculated energy change accompanying the thermal process



is 0.045 eV.

HYPERFINE INTERACTIONS WITH THE Na NUCLEI

It is interesting to compare the charge distribution predicted on the basis of the simple variational wave functions (1) and (11) with the experimental results obtained from NMR Knight shifts in this system.¹⁰ The calculation method is based on the general treat-

ment of Gourary and Andrian.^{20,11} The wave function ψ_{1s} of the unpaired electron is orthogonalized with respect to all the other electrons ψ_i of the system using Schmidt's orthogonalization process. Neglecting overlap between adjacent molecules and the ion the orthogonalized wave function ϕ_{1s} of the unpaired electron is presented by

$$\phi_{1s} = \frac{\psi_{1s} - \langle \psi_{1s} | \psi_i \rangle \psi_i}{(1 - \sum_i \langle \psi_{1s} | \psi_i \rangle^2)^{1/2}} \quad (26)$$

ϕ_{1s} admixes into its components the orbital wave functions of all the electrons of the system with the same spin.

The Na⁺ atomic orbitals were represented by Tubis' wave functions²¹

$$\begin{aligned} (1s) &= 19.95e^{-10.66r} \\ (2s) &= 6.52e^{-3.36r} - 4.31e^{-9.64r}. \end{aligned} \quad (27)$$

For NH₃ molecule central field wave functions were employed.²² However their effect on the unpaired electron density on the sodium ion nucleus is negligible. The results of these calculations employing for ψ_{1s} the wave function (1) and (11) used for energy calculations are summarized in Table II.

DISCUSSION

The direct comparison of the results obtained on the basis of the interstitial ion model with experimental data is rather difficult because of the relative low concentration of this species. The application of the equilibrium constants⁸ derived from conductivity and magnetic data indicates that the concentration of the monomer unit does not exceed 10% of the total metal concentration.²³

The comparison of our results with previous treatment¹¹ based on a molecular model indicates that the present approach yields higher values for the binding energy of the electron in the ground state. The optical dissociation energy is comparable with the energy corresponding to the photoelectric threshold which is about 1.5 eV.²⁴ However this comparison should be accepted with reservation as the inner potential of liquid ammonia is unknown, and the role of other species e.g., e centers and dimers in this process has to be considered. For the energy change accompanying the thermal process²¹ inspection of the equilibrium constants⁸ for K solutions yields $\Delta H = 0$, $\Delta G = -0.09$ eV. The agreement with the theoretical value 0.045 eV is fair.

The present treatment indicates that the absorption band of the system, arising from a $1s \rightarrow 2p$ transition,

²⁰ B. S. Gourary and F. J. Andrian, Phys. Rev. **105**, 1180 (1957).

²¹ A. Tubis, Phys. Rev. **102**, 1049 (1956).

²² K. S. Pitzer, J. Chem. Phys. **29**, 453 (1958).

²³ H. C. Clark, A. Horsfield, and M. C. R. Symons, J. Chem. Soc. **1959**, 2478.

²⁴ G. K. Teal, Phys. Rev. **71**, 138 (1947).

¹⁹ J. Jortner (unpublished).

should lie at 1.1 eV. Thus this band should be placed at higher energy than that corresponding to the first transition of the bound electron in infinitely dilute solution ($h\nu=0.8$ eV).^{1,2}

Recently Clark, Horsfield and Symons²³ have demonstrated that addition of 0.1M sodium iodide to sodium ammonia solutions results in the formation of a new absorption band at 1.55 eV. This band was tentatively ascribed to the monomer unit. The results of the theoretical calculation support this assignment. However it should be pointed out that in liquid ammonia solutions ion-pair formation is rather extensive. The dissociation constants of some alkali halides in liquid NH₃ are of the order of 10⁻³.²⁵ Thus under the experimental conditions of Symons *et al.* the role of the centers involving Na⁺I⁻ ion pairs has to be considered. Electron binding in the field of a Na⁺I⁻ ion pair may be analogous to that of a *D* center²⁶ (an *F* center whose nearest-neighbor cation is missing). The absorption band recorded in NaI solution²³ shows a fine structure and one of these bands may be due to electron binding in the field of an ion pair. More experimental work is needed to establish this point.

The charge distribution obtained on the basis of the present treatment indicates that the maximum probability for the location of the bound electron is in the region of 2.5 Å. This result is similar to that obtained by Blumberg and Das¹¹ on the basis of a molecular model. The result obtained for the electron spin density on the Na⁺ nucleus is of the same order of magnitude as the values of 0.014 and 0.066 a.u. obtained by application of the molecular model in agreement with experimental data.¹¹ Direct comparison is still impossible as the equilibrium constants for Na ammonia solutions at room temperature are unknown. However

²⁵ V. F. Hindza and C. A. Kraus, *J. Am. Chem. Soc.* **71**, 1565 (1949).

²⁶ L. Pincherle, *Proc. Roy. Soc. (London)* **A64**, 648 (1951).

it appears that the present treatment overestimates the charge distribution on the Na nucleus.

We wish to compare the charge distribution of the unpaired electron in the interstitial ion with the 3s sodium atom orbital. This alkali atom wave function is an example of spatially diffuse charge distribution. Within the ionic radius of Na⁺ ion (1.85 a.u.) there is included only 4.3% of the total charge.²⁷ For the wave functions employed in our treatment 5% of the total electronic charge is included within the ionic radius of the sodium ion. This comparison yields a certain justification for the employment of a point charge model for the alkali cation. In the present treatment the basic difficulty rises because of the application of the static and optical dielectric constants inside the sodium ion core. The closed electronic shells of the cation will tend to repel the unpaired electron from the origin of the binding center. The application of high-dielectric constant in the potential function in that region is qualitatively similar to the effect of interelectronic repulsion.

All the previous models employed for the study of metal solutions were static. Experimental data indicate the existence of a rapid exchange between solvent molecules in the vicinity of the binding center of the electron (the *e* centers or the monomer) and the solvent molecules in the bulk. These include the absence of NMR lines at unshifted position¹⁰ and the extreme narrowness of the ESR band.²⁸ The present static model is however suitable for the calculation of the optical absorption spectrum and of the mean charge distribution of the center.

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²⁷ L. Dexter, *Phys. Rev.* **108**, 707 (1957).

²⁸ J. Kaplan and C. Kittel, *J. Chem. Phys.* **21**, 1429 (1953).