

## QMCF-MD Simulation and NBO Analysis of K(I) Ion in Liquid Ammonia

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### ABSTRACT

Ab initio of Quantum Mechanics Charge Field Molecular Dynamic (QMCF-MD) of K(I) ion in liquid ammonia has been studied. A Hartree-Fock level of theory was coupled with LANL2DZ ECP basis set for K(I) ion and DZP (Dunning) for ammonia. Two regions as first and second solvation shell were observed. In the first solvation shell at distance 3.7 Å, K(I) ion was coordinated by four to eight ammonia molecules dominated by  $K(NH_3)_6^+$  species. Second shell of solvation was ranging between 3.7 Å to 7.3 Å. Within simulation time of 20 ps, the frequent exchange processes of ligands indicating for a very labile solvation structure. Four mechanism types of ligand exchange between first and second solvation shell were observed. Mean residence time of ligand is less than 2 ps confirming weak in ion-ligand interaction. Evaluation of  $K(NH_3)_6^+$  using natural bond orbital analysis shows that the Wiberg bond Index is less than 0.05 indicating weak electrostatic interaction of K-N.

**Keywords:** potassium; ammonia; simulation; ligand exchange; QMCF; NBO

### ABSTRAK

Simulasi dinamika molekuler ion K(I) dalam amoniak cair menggunakan perhitungan Ab initio Quantum Mechanics Charge Field Molecular Dynamic (QMCF-MD) telah dikaji. Perhitungan dilakukan pada teori level Hartree-Fock dengan menggunakan basis set LANL2DZ ECP untuk ion K(I) dan DZP (Dunning) untuk amoniak. Dua daerah solvasi teramati sebagai kulit solvasi pertama dan kedua. Pada kulit solvasi pertama, jarak ion-ligand maksimum adalah 3,7 Å dan ion K(I) terkoordinasi dari empat sampai delapan amoniak dengan spesies paling dominan adalah  $K(NH_3)_6^+$ . Daerah kulit solvasi kedua berada diantara jarak 3,7 Å hingga 7,3 Å. Dalam waktu simulasi 20 ps, proses pertukaran ligan yang sering terjadi mengindikasikan bahwa struktur solvasi sangat labil. Terdapat empat tipe mekanisme pertukaran ligan antara kulit solvasi pertama dan kedua yang teramati. Waktu tinggal rata-rata ligand kurang dari 2 ps menunjukkan interaksi ion-ligan yang lemah. Evaluasi spesies  $K(NH_3)_6^+$  menggunakan analisis natural bond orbital menunjukkan bahwa indeks Wiberg kurang dari 0,05, hal ini mengindikasikan bahwa interaksi K-N adalah tipe interaksi electrostatic lemah.

**Kata Kunci:** kalium; amoniak simulasi; pertukaran ligan; QMCF; NBO

### INTRODUCTION

Numerous methodologies have been used to study solvation of alkali metals. Quantum mechanics and molecular mechanics (QM/MM) was used to generate dynamical data of a molecular dynamic (MD) simulation with some modification in potential parameter such reconstructing pair potential of ion-ligand [1-2], implementing polarizable force field [3], or applying flexible-boundary with partial charge transfer between QM and MM region [4].

An MD simulation using QM/MM with pair potential construction by Tongrar et al. [5] for K(I) in liquid ammonia had predicted that K(I) was surrounded by 8.7 ammonia. It is overestimated compared to the experimental data that coordinated by 6 ammonia [6]. A MD simulation with better prediction using drude polarizable model produced coordination number of 6.1 by Orabi et al. [3]. But, Orabi's work seemed to overestimate in determination of coordination number of the second solvation shell where the K(I) ion is surrounded by 39.6 ammonia.

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Modified QM/MM with the enlarged size of QM region and electrostatic force implementation have been constructed in QMCF method. The QM region is twice larger than regular QM/MM, which will cover up to second layer of solvation shell. The non-coulombic interaction forces are calculated in both QM region and MM region, then the electrostatic interactions of atoms in both region are incorporated through perturbation term in the Hamilton operator [7]. Electrostatic force constructions in both regions are replaced by any interatomic potential function for ion-ligand in the system. This methodology promises to overcome the overestimation of previous calculation in first and second solvation shell. The QMCF-MD has been proven to successfully produce the dynamical data that meet with experiment result in exploring solvation of heavy metal ions, highly charged ions and light ion [8-13].

In the other side, natural bond orbital (NBO) analysis has been used widely to evaluate structure, bonding, and electronic donor-acceptor properties of molecules [14-19]. It has been investigated using NBO that a cluster of Li ion containing four to six ammonia. Interaction that will stabilize the complexes involving delocalization of atomic charge of N ammonia to Rydberg orbital of metal. Backward donation of the charge was observed for singly occupied NBO of metal to Rydberg orbital and to  $\sigma^*$  bond of N-H. Wiberg bond index shows that interaction of Li-NH<sub>3</sub> was non covalent character, but strong van der Waals interaction [20]. Backward donation of a singly occupied molecular orbital from metal to ligand was influenced by geometry and coordination number [21].

Our work shows the QMCF-MD simulation to investigate light ion such K(I) in liquid ammonia and produce satisfactory data of structural and dynamical properties. We also performed the NBO analysis after simulation to analyze ion-ligand bond character in first solvation shell.

## EXPERIMENTAL SECTION

### Materials

The software that was used in this research were Gaussian (version. 09) [21], Turbomole (version. 5.9) [22], QMCF package (version. 1.3.1) [23] VMD (Virtual Molecular Dynamic) [24] and a parser script program to generate trajectories. While the hardware is a parallel computing with each unit consisting of processor Dual-Core AMD Opteron 2400 MHz.

### Methods

The two principles of QMCF-MD are enlarged QM region and embedding coulombic charge calculation in a

whole system. In the first principles, the system is divided into three regions that consist of a core, solvation shell and classical region. The core and solvation shell region are treated by an *ab initio* QM method, while the classical region is calculated by MM. In the second principle, electrostatic fluctuation is embedded for all atoms in both QM and MM region [7,10]. The force field of molecular interaction in the MM part of the system was treated by pairwise interatomic potential functions. It is composed of Coulombic and non-Coulombic contributions and employed corrections in association with the cutoff of electrostatic long-range interactions. Detail equations in each region have been described by Rode in his paper [7]. The Hartree-Fock (HF) level of theory has been preferable used since the Density Functional Theory (DFT) has issues of underestimating of excitation, charge-transfer excitation energies and poor reproducibility of van der Waals (vdW) bondings [25-26].

The difference between QM and MM region was resulted to a discontinuity of the forces of the moving particles. Here the smoothing function is implemented to make the force of moving particles from MM zone to QM zone correct according to eq. 1-2 [27]:

$$F_J^{\text{Smooth}} = S(r) \cdot (F_J^{\text{layer}} - F_J^{\text{MM}}) + F_J^{\text{MM}} \quad (1)$$

Term  $F_J^{\text{Smooth}}$  is total force acting on all particles in smoothing area,  $F_J^{\text{MM}}$  is the MM force of whole system,  $F_J^{\text{layer}}$  is force particle in QM region and  $S(r)$  is smoothing function that applied between radii  $r_0$  and  $r_1$ , where is:

$$S(r) = \begin{cases} 1, & \text{for } r \leq r_0 \\ \frac{(r_1^2 - r^2)^2 (r_0^2 + 2r^2 - 3r_1^2)}{(r_0^2 - r_1^2)^3}, & \text{for } r_0 < r < r_1 \\ 0, & \text{for } r > r_1 \end{cases} \quad (2)$$

As a consequence of eq. 2 the ligands are allowed to migrate between the QM and MM regions.

Mean residence time of ammonia ( $\tau$ ) in the first solvation shell is calculated by eq. 3 [25]:

$$\tau^{0.5} = \frac{t_{\text{simulation}} N_{\text{AV}}}{N_{\text{ex}}^{0.5}} \quad (3)$$

where  $t_{\text{simulation}}$  is total simulation time,  $N_{\text{AV}}$  is an average of coordinated ligand, and  $N_{\text{ex}}^{\text{AV}}$  is sum of coordinated ligand in 0.5 ps. Then the sustainability of solvation layer is calculated by eq. 4:

$$S_{\text{ex}} = \frac{N_{\text{ex}}^{0.5}}{N_{\text{ex}}^0} \quad (4)$$

where  $N_{\text{ex}}^0$  is sum of all migration ligand that occurred between first and second solvation shell.

## Simulation Protocol

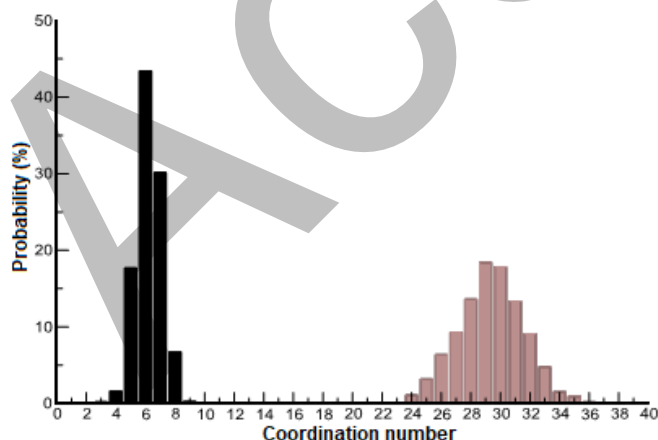
One potassium ion was put in the center of simulation box containing 593 ammonia molecules where the length of the box is 29.03 Å. The density of system is considered to be equal to density of pure liquid ammonia in 235.16 K which is 0.690 g/cm<sup>3</sup>. The NVT ensemble was employed and the temperature was kept to constant by Berendsen algorithm [29] at 235.16 K with relaxation time of 0.1 ps. The radius of the QM region that consist of core and solvation shell was set to 6.6 Å and radius for smoothing zone was set to 0.2 Å for boundary between QM and MM region. The QM region was treated using Hartree-Fock level of theory with DZP Dunning [5] for ammonia and LANL2DZ ECP [27] for K(I) ion. Sampling of simulation was performed during 20 ps after equilibration in 4 ps.

## NBO Analysis

Trajectory data of the simulation was visualized by the molecular dynamic visualizer using VMD package. Then, the position of ligand in first solvation shell was captured base on the maximum coordination number distribution of the simulation. Position of this molecule was then calculated using Gaussian09. The population Mulliken analysis with NBO was chosen, and the Wiberg bond index was employed. The basis set for the molecules were DZP Dunning and LANL2DZ ECP basis set to ammonia molecules and the ion, respectively.

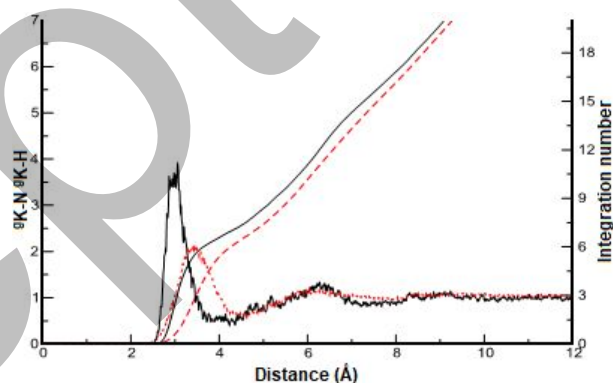
## RESULT AND DISCUSSION

The simulation produced trajectory data that can be analyzed in terms of RDF (radial distribution function), ADF (angular distribution function), CND (coordination number distribution) and MRT (mean residence time).

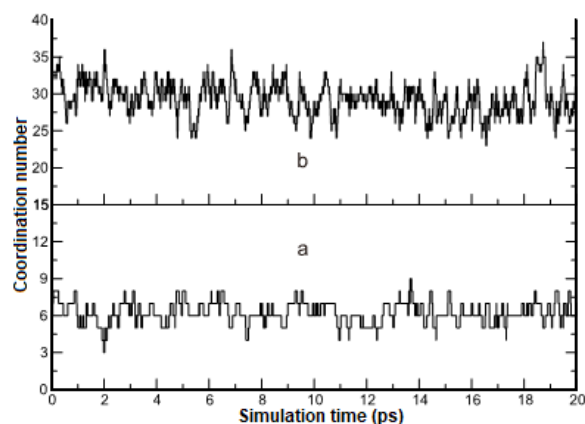


**Fig 2.** Coordination number distribution of first solvation shell (black) and second solvation shell (grey)

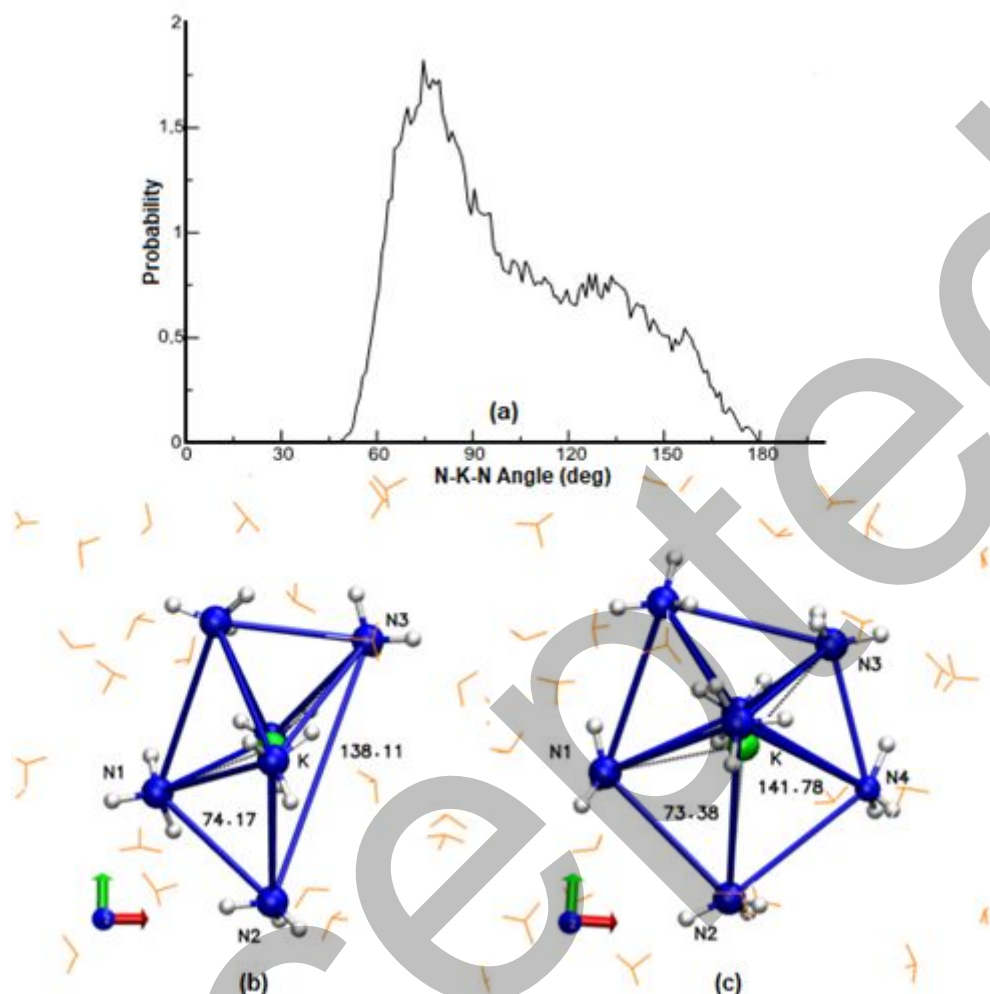
The RDF of K-N ammonia, depicted by Fig. 1 shows that there is two solvation regions. The region between 2.5 and 3.7 Å indicates the first solvation shell and the average distance of K-N is located at 3.05 Å. This value is closed to the experiment result by Wasse et al. [6] using neutron diffraction with K-NH<sub>3</sub> distance of 2.85 Å and Qian et al. [30] using X-ray diffuse scattering in graphite the K-NH<sub>3</sub> distance of 2.89 Å. Previous simulation of K(I) in liquid ammonia by Tongraar et al. [5] using QM/MM gave 2.88 Å of K-NH<sub>3</sub>, while in preferential system by Kabbalee [31] using ONIOM XS MD simulation, the distance is 2.95 Å. Using optimized drude potential model in QM/MM simulation, Orabi et al. [3] found K-NH<sub>3</sub> distance of 2.94 Å. The board peak between 3.7 to 7.1 Å confirms the second solvation shell region of the system. The a distance of the second solvation shell is 6.4 Å. The non-zero valley of K-N radial distribution function indicates the ligand exchange processes.



**Fig 1.** Radial distribution function of K(I) ion in liquid ammonia and running integration number from molecular dynamic simulation at 235.15 K. Solid line for K-N, dash line for K-H



**Fig 3.** Coordination number evolution over 20 ps of simulation time for the first solvation shell (a) and the second solvation shell

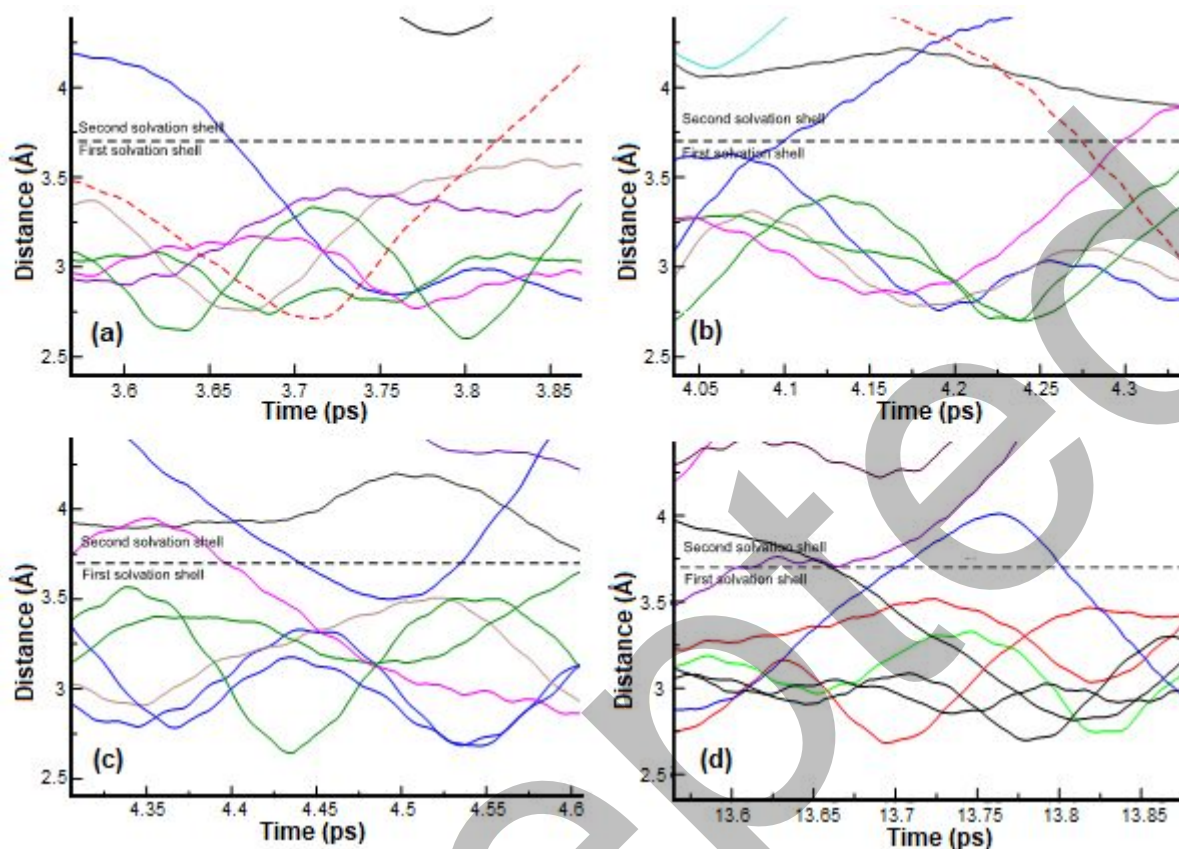


**Fig 4.** Angular distribution function of K-NH<sub>3</sub> in first solvation shell (a), top view of first shell solvation position with 6 coordination number where the angle of N(1)-K-N(2) is 74.7° and N(2)-K-N(3) is 138.11° (b), and top view with 7 coordination number (c). Green color is K(I) ion, blue and white are ammonia in the first shell, orange is ammonia in the second shell solvation

Fig. 2 shows the coordination number distribution of K(I) ion in liquid ammonia. In the first solvation shell, coordination number varied from 4 to 8 with the maximum probability of 6, which is close to neutron diffraction and QM/MM simulation data [3,6]. No experimental data exists to confirm the exact amount of ligands in the second solvation shell, while our work has the maximum probability of 29 ligands which is located at 6.3 Å. It is more reasonable than Orabi's work [3], where K(I) is surrounded by 39.6 ligand in second shell solvation. That seems to be an overestimation. The use of fluctuating charge that was calculated simultaneously and connected over QM (first and second shell are included) and MM region in QMCF successfully corrected previous methods to predict the coordination number in both of solvation shell regions. The evolution of coordination number over simulation time is displayed in Fig. 3. At the second solvation shell, the peak and

valley alternate rapidly, indicating the frequent exchange of the coordination number (Fig. 3b). It shows that the ligands in the second solvation shell are more labile and move rapidly than in the first shell. The evolution of coordination number at the first solvation shell is dynamically more constant than the second solvation shell (Fig. 3a).

The angular distribution function (ADF) confirms that the shape of first solvation shell is not rigid indicating non-symmetrical structure. The N-K-N angle shown in Fig. 4a depicts variety of bond angle ranging from 50° to 180° with maximum of around 75°. Nevertheless, the broad peaks also appear at around 130° exhibiting dynamical solvation structure of distorted octahedron. The N-K-N angle of 130° is as a consequence to accommodate one more ligand and changing from 6 to 7 coordinated ammonia (Fig. 4b and 4c). The octahedral structure was also reported in



**Fig 5.** Types of ligand exchange. A ligand come from second to first shell and other ligand go (a), a ligand leave a first region and other ligand entering the region (b), a ligand come to first shell region and then leave (c), a ligand leave first shell and then back again

neutron diffraction of potassium ammonia study by Wasse [6].

From bond evolution analysis, a lot of ligands attempt to exchange. Four different way of exchange are observed which is shown in Fig. 5. The first type of the exchange process is occurred when a ligand came from second shell region into first solvation region while coordination number changes from 6 to 7. At the same time, another ligand moves out from the first shell to the second shell region, therefore the coordination number is back to 6 (Fig. 5a). The second type of exchange is started when a ligand left the first shell and another ligand from the second shell came to replace it. Next, the third type, a ligand comes and goes in a short time from the second to the first solvation region (Fig. 5c). Lastly, the fourth type of exchange is occurred when a ligand leaves the first solvation region and then back again in a short time (Fig. 5d).

Mean residence time analysis shows that 185 times ligand attempt to exchange between second and first solvation region and 85 among of them are successful with mean residence time of 1.59 ps and sustainability coefficient of 0.318, confirming very labile

solvation structure. It is almost similar to the hydration of K(I) ion, where faster ligand movement was observed with mean residence time of 1.4 in QMCF-MD method [27].

As presented in Table 1, based on the second order perturbation NBO of donor-acceptor, interaction of ion-ligand involves several orbitals. For ammonia, that is the bond orbital of N-H (BD), core orbital of N (CR), and lone-pair orbital (LP) of N to the vacant valance antibonding orbital (LP\*) of K(I). Even in a very small amount of energy differences, the back-donation is occurred from the core orbital (CR) of K(I) ion to the valance antibond (BD\*) of N-H ammonia. Donation from LP of N and BD of N-H ammonia to LP\* of K(I) ion dominantly contribute to total stabilization energy of the solvation structure. It can be concluded that solute-solvent interactions were affected by access to lone pair of ammonia and the orientation of N-H bond of ammonia to K(I) ion. Partial Wiberg bond index of K-N is very low (less than 0.05) where a covalent single bond should be 1.0, indicating that the ion-ligand interactions in this system are weak electrostatic type [20].



**Table 1.** NBO analysis K(I) -ammonia in first solvation shell in octahedral structural

System	Wiberg bond index of K-N	Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis Donor – acceptor NBO		
		Donor NBO (I)	Acceptor NBO (j)	Stabilization energy (kJ/mol)
K – NH <sub>3</sub> (1)	0.0268	BD (N-H)	LP* (K)	10.28
		CR (N)	LP* (K)	2.47
		LP (N)	LP* (K)	33.15
		CR (K)	BD* (N-H)	0.75
K – NH <sub>3</sub> (2)	0.0304	BD (N-H)	LP* (K)	7.82
		CR (N)	LP* (K)	2.01
		LP (N)	LP* (K)	32.94
		CR (K)	BD* (N-H)	0.29
K – NH <sub>3</sub> (3)	0.029	BD (N-H)	LP* (K)	12.62
		CR (N)	LP* (K)	3.14
		LP (N)	LP* (K)	38.54
		CR (K)	BD* (N-H)	1.17
K – NH <sub>3</sub> (4)	0.0225	BD (N-H)	LP* (K)	15.22
		CR (N)	LP* (K)	3.14
		LP (N)	LP* (K)	30.39
		CR (K)	BD* (N-H)	1.63
K – NH <sub>3</sub> (5)	0.0274	BD (N-H)	LP* (K)	12.67
		CR (N)	LP* (K)	3.05
		LP (N)	LP* (K)	34.28
		CR (K)	BD* (N-H)	1.21
K – NH <sub>3</sub> (6)	0.0255	BD (N-H)	LP* (K)	19.40
		CR (N)	LP* (K)	4.56
		LP (N)	LP* (K)	40.04
		CR (K)	BD* (N-H)	4.01

## CONCLUSIONS

In summary, simulation of K(I) ion in liquid ammonia has been successfully studied using QMCF method and NBO analysis, to evaluate the ion-ligand interaction. For 20 ps of simulation time, maximum ion-ligand distance is 3.05 Å where K(NH<sub>3</sub>)<sub>6</sub><sup>+</sup> species in the first solvation shell was dominantly observed exhibiting distorted octahedral structure. In the second solvation, the maximum distance of ion-ligand is 6.3 Å with around 29 ligand attached. This seems to be more reasonable than other simulation by QM/MM methods. The RDF, ADF and CND are in good agreement with experimental data. Fast residence time is observed for the first solvation shell confirming a very labile solvation structure. Small Wiberg bond index affirms of weak electrostatic ion-ligand interaction.

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