

## Total Cluster Energy Calculation of Lithium Ion Conductors by the DV- $X\alpha$ Method

Y.Kowada\*, W.Nishitani\*, and K.Ogasawara\*\*

\*Hyogo University Teacher Education

\*\*Department of Chemistry, Kwansei Gakuin University

E-mail: [ykwada@hyogo-u.ac.jp](mailto:ykowada@hyogo-u.ac.jp)

Recently several programs for the total cluster energy calculation have been developing in the DV- $X\alpha$  method. In this study, we have tried to calculate and compare total cluster energies of several diatomic molecules and model clusters of ionic conductors. The total cluster energies of diatomic molecules have minimum near the equilibrium atomic distance of each molecules though the absolute value of the total cluster energy were slightly different each other. In the case of the model cluster of the  $\text{Li}_3\text{N}$  crystal, which is one of the typical Li ion conductors, we have obtained the energy change as a function of the site during the movement of a Li ion. The energy change with the movement of the Li ion along the conduction path was considerably smaller than along other paths, consistent with the results by the band calculation and experiments. The total cluster energy calculation method was enough useful for the discussion of the cluster energy.

Key words: Li ion conductor, theoretical calculation, First principle MO method, the DV- $X\alpha$  cluster method

## 1. Introduction

Nanomaterials are hopeful to give new vistas in wide fields from basic science to industry. Therefore theoretical calculations, which can precisely evaluate stable structures of nanomaterials, are demanded. The DV- $X\alpha$  molecular calculation is well known to be advantageous to calculate the valence band structures of from atom-cluster through nano-particle to meso-substance composed of from light through transition metal to actinide element. However, there were a few study about total energy calculation by the DV- $X\alpha$  method, since total energy calculation by the DV- $X\alpha$  method was difficult associated with the numerical basis functions. Fukushima et al. has reported the GQ- $X\alpha$  method for the calculation of total energy of diatomic molecules.[1] The GQ- $X\alpha$  method was very useful to obtain the total energy of diatomic molecules. The obtained theoretical total energy was good agreement with the experiments. However, the program development of this method was frozen almost thirty years ago. Then we couldn't calculate any energy about the complicated model clusters including more than three atoms. Recently, Ogasawara has developed "Coulomb" and improved the total energy calculation based on the numerical basis

functions. By the program Coulomb, we can use any model clusters which can be calculated by the DV-X  $\alpha$  calculation program code named "scat." In the present study, stable structure of simple molecules and path of ions in solid-state electrolyte were investigated by using "Coulomb" for the first time.

We have investigated the electronic state of the ion movement in the solid-state materials and found that the moving cations had a very small change of the covalent bonding with movement. [2-7] The smaller change of the covalent bonding means smaller change in the covalent bonding energy. Usually the cations can move in the solid-state electrolyte with energy change, called activation energy. Then, we would like to obtain the variation of the energy with the movement of the cations.

In this study, we tried to calculate the energy change as a function of the site during the movement of a lithium ion in the lithium nitride crystal, which is one of the typical solid-state electrolytes, by using Coulomb, which is one of the total energy calculation programs.

There are several studies concerning the high Li ion conductivity of  $\text{Li}_3\text{N}$  crystal by experimental measurements and theoretical calculations [8-11]. Several

experimental studies reported that the  $\text{Li}_3\text{N}$  crystal contained  $\text{H}^+$  ion impurities in interstitial positions and they make a certain concentration of the Li ion vacancies. These vacancies are yield on the planes, which contain both Li and N ions, called  $\text{Li}_2\text{N}$  plane. It was reported that the activation energy of the movement of the Li ion on  $\text{Li}_2\text{N}$  planes was 0.004 eV by the band calculation. [11] Also, in the  $\text{Li}_3\text{N}$  crystal there is the other kind of the Li ions on the planes containing only the Li ions, which connect between the  $\text{Li}_2\text{N}$  planes. This kind of the Li ions hardly moves, compared with that on the  $\text{Li}_2\text{N}$  plane.

In the present study, we have tried to calculate the energy change as a function of the site during the movement of the Li ion in the cluster models that were used for the chemical bonding analyses, since the energy change was very important to discuss the fast movement of the Li ion. In the case of the cluster model, the meaning of the energy of the cluster is slightly different from the total energy of the molecules and the energies obtained by the band calculation and of the molecules. Usually the cluster model was cut from the crystal structure and had dangling bonds on its surface. The energy obtained by the DV- $X\alpha$  cluster method is corresponding to the total energy of

the small particle, which has the same structure as the cluster model. Thus the energy of the cluster model is not the same as and couldn't be directly compared with that in the band calculation. Then, we would propose "Total cluster energy" (TCE) for the energy of the cluster model obtained by the program Coulomb in the DV- $X\alpha$  method.

## 2. Calculation method

The DV- $X\alpha$  cluster method [12-15], which is one of the first principle molecular orbital calculation methods, was used for the calculation of the electronic state of the  $\text{Li}_3\text{N}$  crystal. In this method, Slater's exchange potential and the numerical basis functions were used. We have used the program set named "scat" and the default parameters, such as the minimal basis functions, i.e.  $1s$ ,  $2s$ , and  $2p$  for Li and N ions. After the DV- $X\alpha$  MO calculation, we have used one of the energy calculation program, named "Coulomb", to obtain the energy change as a function of the site during the movement of the Li ion. In The DV- $X\alpha$  cluster method, the molecular orbitals were

obtained by the SCC approximation.[12] For the energy calculation, the MOs were re-calculated by the SCF approximation. In the Coulomb, the SCF molecular orbital calculation was achieved in the following procedure. The wave functions of molecular orbitals calculated by the DV-X $\alpha$  cluster method were used for the basis functions in the SCF calculation.

$$\phi_\ell = \sum_i C_{i\ell} \chi_i \quad (1)$$

The electron density  $\rho(r)$  was obtained from the molecular orbitals and the Coulomb potentials between two electrons,  $V_{ee}$ , were calculated.

$$\rho(r) = \sum_\ell f_\ell \phi_\ell^2(r) \quad (2)$$

$$V_{ee}(r_1) = \int \frac{\rho(r_2)}{r_{12}} dr_2 \quad (3)$$

The eigenvalues and  $C_{ij}$  were obtained by following equations.

$$(\tilde{\mathbf{H}} - \tilde{\epsilon} \tilde{\mathbf{S}}) \tilde{\mathbf{C}} = 0 \quad (4)$$

$$(H)_{ij} = (K.E.)_{ij} + (V_{Ze})_{ij} + (V_{ee})_{ij} + (V_{ex})_{ij} \quad (5)$$

$$(K.E.)_{ij} = \int \chi_i(r_1) \left\{ -\frac{1}{2} \nabla_1^2 \right\} \chi_j(r_1) dr_1 \quad (6)$$

$$(V_{Ze})_{ij} = \int \chi_i(r_1) \left\{ \sum_{n=1}^{\infty} \frac{(-Z_V)}{r_{1V}} \right\} \chi_j(r_1) dr_1 \quad (7)$$

$$(V_{ee})_{ij} = \int \chi_i(r_1) \int \frac{\rho(r_2)}{r_{12}} dr_2 \chi_j(r_1) dr_1 \quad (8)$$

$$(V_{ex\uparrow})_{ij} = -3\alpha\left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \int \chi_{i\uparrow}(r_1)(\rho_{\uparrow}(r_1))^{\frac{1}{3}} \chi_{j\uparrow}(r_1) dr_1 \quad (9)$$

After the SCF calculation, the energy of the cluster was calculated.

$$E = E_{K.E.} + E_{ze} + E_{ee} + E_{ex} + E_{zz} \quad (10)$$

where  $E_{K.E.}$ ,  $E_{ze}$ ,  $E_{ee}$ ,  $E_{ex}$  and  $E_{zz}$  mean the kinetic energy of the electrons, the energy of the nuclear-electron attraction, the energy of the electron-electron repulsion, the energy of the exchange term, and the energy of the nuclear-nuclear repulsion, respectively.

Each energy term was calculated by the weighted sum of the each value on the sample

points except  $E_{zz}$ . In the program Coulomb, there are two major improvements

for the energy calculation. The first is the improvement of the estimation of the

Coulomb potential. In the DV- $X\alpha$  molecular calculation of "scat", the electron

density was calculated as the spherically symmetric charge densities centered on the

nuclei of the molecule. In the Coulomb, however, the Coulomb potential was

estimated by the electron distribution based on each molecular orbital. The second is

the SCF calculation, which makes the molecular orbitals of the lowest energy with the linear combination of the fixed atomic orbitals obtained by the SCC calculation.

These improvements gave enough accuracy for the total cluster energy. The number of the sample points used in the energy calculation was 2000 per atom, which was 4 times larger than that in the chemical bonding analyses, for the enough precision of the wave functions of molecular orbitals.

### 3. Results and discussion

The total energy of several diatomic molecules, such as  $F_2$ ,  $N_2$  and  $NaCl$ , were calculated to discuss the accuracy of the total energy obtained by the program Coulomb. In this case, we have used both a minimum and an extended basis sets to compare the influence of the expanse of the basis function to the total energy. Fig. 1 shows the relationship between the total energy and the distance of F atoms in a  $F_2$  molecule. In this figure, closed circle shows the total energy of the minimum basis set and the closed square shows that of the extended basis set. The distance between two atoms was normalized with the equilibrium nuclear distance,  $1.412\text{\AA}$ , as 100% and was changed



from 50 to 150%. The total energy of the minimum basis set was -194.9457 atomic unit (a.u.) at 50 % and decreased as a function of the distance. The energy shows a minimum around at 103% and was -197.9385 a.u. In the case of the extended basis set, the total energy change was similar to that of the minimum basis set, that is, it was decreased with an increase in the distance and showed a minimum at 101%, -197.8128 a.u. The total energy of the extended basis set, however, became slightly larger than that of the minimum basis set at longer distance region than 120%. This difference was caused by the larger interaction of the extended atomic orbitals. Fig. 2 shows the total energy of a N<sub>2</sub> molecule. The equilibrium nuclear distance of the N<sub>2</sub> molecule was 1.098 Å. In this molecule, the total energy was decreased and had a minimum, -108.1649 a.u., at 110% for the minimum basis set and 105%, -108.2216 a.u., for the extended basis set. The change of the total energy are very similar each other. Then the difference was dependent on the small energy change around the energy minimum, which is a well-known characteristic of the density functional calculation method.

Fig. 3 shows the energy change of a NaCl molecule with the atomic distance. In this molecule, the energy change of the minimum basis set was similar to that of the

extended basis set like the  $N_2$  molecule. The minimum value of total energy is -620.177 a.u. at 95 % in minimum basis set and -620.223 a.u. at 100% in extended basis set.

The results of the total energy calculations of the diatomic molecules suggested that the total energy obtained by the program Coulomb could be useful to discuss the energy change at the different position of the atoms. Then, we have applied the program Coulomb to discuss the movement of the Li ion in the  $Li_3N$  crystal.

The model clusters for the total energy calculations of the  $Li_3N$  crystal were constructed by the crystal structure of the  $Li_3N$  crystal. [9] This crystal is assigned to the space group of  $P_{6/mmm}$  and the lattice constants a and c are 3.65 and 3.88 Å, respectively. The schematic diagrams of the model clusters are shown in Fig. 4.

Fig. 4(a) shows the model clusters for the conduction path in  $Li_2N$  plane. In this model, one Li ion was removed from the  $Li_2N$  plane so that the neighboring Li ion can move to the vacancy. The movement of the Li ion was simulated by using five model clusters with the different positions of the Li ion along the estimated conduction path, since it is fundamentally very difficult to manipulate the movement of the atoms and

ions in the molecular orbital calculations. This method was already reported and was really very useful for the simulations of the movement of the Ag ions in the  $\alpha$ -AgI crystal.[5] Fig. 4(b) shows the model cluster for the movement of the Li ions on the Li plane. In this model cluster one Li ion was moved to the neighboring vacancy of the Li sites. This path is not a suitable conduction path for the Li ion in the  $\text{Li}_3\text{N}$  crystal reported by several experimental studies.

The moving Li ion in the  $\text{Li}_3\text{N}$  crystal was expected to show the small change of the bonding energy with its movement. Since there are several programs for the energy calculation, among them we tried the program Coulomb to obtain the energy change of the movement of the Li ion in the clusters (a) and (b). Figs. 5 and 6 show the variation of the TCE with the different positions of the moving Li ion in the cluster (a) and (b), respectively. In this figure, the ordinate shows the TCE of the clusters in a.u. and the abscissa shows the relative position of the moving Li ion. In the case of cluster (a), the energy changes very small with the positions of the moving Li ion, that is, the difference between the minimum and the maximum was 0.031 a.u. This value is larger than the result of the band calculation [11], since the TCE usually includes

larger interaction with surface atoms. On the other hand, the energy change with the Li position in the cluster (b) is 3.796 a.u. and is much larger than that in the cluster (a). This difference of the energy change is consistent with the results of the chemical bonding analyses.[16] Thus the TCE evaluated by the Coulomb could be useful to discuss the movement of the Li ion in the Li ion conductors, although the cluster size, the number of sample points, the basis functions and the other computational parameters should be clarified to obtain the qualitative total energy of the cluster.

#### 4. Conclusion

In this study, we have investigated the total energy calculation program Coulomb in the DV-X $\alpha$  method and shown the usefulness of this program. In the calculation of diatomic molecules, The results of default parameters, the extended basis set and 2000 sample points per atom in the cluster showed the equilibrium distance within 5 % compared with experimental results.

The next, we tried to obtain the local cluster energy of the model cluster to discuss the energy change with the movement of the Li ion. The movement of the Li ion was

simulated by using several model clusters with different positions of a Li ion, which was located on the conduction path. The model clusters for the other non-conduction paths were adopted for the comparison. As the results, the TCE showed that the movement of the Li ion through the conduction path made the smaller energy change than another path. This result suggested that the energy calculation program Coulomb is very useful to analyze the energy change of the cluster models for ionic conductors.

#### References

- [1] K. Fukushima, J. Mizuno, K. Fujima and H. Adachi, *J. Phys. Soc. Jpn.* **51** (1982) 4028.
- [2] Y. Kowada, H. Adachi, and T. Minami, *J. Ceram. Soc. Jpn.*, **101** (1993) 1330-4.
- [3] Y. Kowada, H. Adachi, M. Tatsumisago, T. Minami, *J. Non-Cryst. Solids*, **232-234** (1998) 497-501.
- [4] N. Imanaka, S. Tamura, G. Adachi, Y. Kowada, *Solid State Ionics*, **130** (2000) 179-182.
- [5] Y. Kowada, Y. Yamada, M. Tatsumisago, T. Minami, and H. Adachi, *Solid State Ionics*, **136-137** (2000) 393-397.
- [6] R. Araki, A. Hayashi, Y. Kowada, M. Tatsumisago, T. Minami, *J. Non-Cryst. Solids*, **288** (2001) 1-7.
- [7] Y. Kowada, M. Okamoto, I. Tanaka, H. Adachi, M. Tatsumisago, T. Minami, *J. Non-Cryst. Solids* **345&346** (2004) 489-493.
- [8] J. Wahl and U. Holland, *Solid State Commun.* **27** (1978) 237.
- [9] H. Schulz, K. H. Thiemann, *Acta Crystallogr. A* **35** (1979) 309.

- [10] Y. Koyama, Y. Yamada, I. Tanaka, S. R. Nishitani, H. Adachi, M. Murayama, R. Kanno, *Mater. Trans.*, **43**(7) (2002) 1460-1463.
- [11] J. Sarnthein, K. Schwarz, P. E. Bloechl, *Phys. Rev. B: Condens. Matter*, **53**(14) (1996) 9084-91.
- [12] H. Adachi, M. Tsukada, C. Satoko, *J. Phys. Soc. Japan* **45** (1978) 875.
- [13] J. C. Slater, *Quantum Theory of Molecules and Solids*, Vol. 4 (McGraw-Hill, New York, 1974).
- [14] E. J. Baerends and P. Ros, *Chem. Phys.* **2** (1973) 52.
- [15] E. J. Baerends and P. Ros, *Molec. Phys.* **30** (1975) 1735.
- [16] Y. Kowada, M. Tatsumisago, T. Minami, and H. Adachi, *Adv. Quant. Chem.*, **54** (2008) 255-270.

Figure captions

Fig.1 Energy change and bond distance of  $F_2$ .

Fig.2 Energy change and bond distance of  $N_2$ .

Fig.3 Energy change and bond distance of  $NaCl$ .

Fig. 4 Schematic diagram of the  $Li_3N$  model clusters. (a)  $Li_2N$  plane, (b) Li plane. These figures were drawn with VESTA developed by K. Momma and F. Izumi

Fig. 5 The relationship between the position and total cluster energy of  $Li_2N$  plane.

Fig.6 The relationship between the position and total cluster energy of Li plane.