The Development of a Program Visualizing Results of Vibrational Analysis Calculation Using *ab initio* Molecular Orbital Method

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We developed a computer program *MOLCAT* to visualize results of vibrational analysis calculation. This program can treat Z-matrix used in ab initio molecular orbital calculation, and shows the vibrational mode as arrows with the molecular structure. We applied this program to show transition vectors of the intramolecular inversion of ammonia and the water exchange reaction of hexaaquacalcium(II). We are preparing to distribute *MOLCAT* as a free software.

When we optimize a molecular geometry using ab initio molecular orbital method, the vibrational analysis is a strongly expected calculation at the optimized geometry to confirm whether it corresponds to a transition state structure or an energy minimum one on a potential energy surface. The vibrational mode of reactant gives the estimation what action of atoms in the molecule initiates the specific chemical reaction.[1] The vibrational analysis at a transition state of reaction gives a transition vector, a starting point of study of the reaction mechanism using IRC[2], and a theoretically estimated rate constant.[3] Though the vibrational analysis is one of indispensable methods to apply the molecular orbital calculation to chemical phenomena, it is difficult to imagine the molecular vibration intuitively from only numeric results of calculation except for simple systems like triatomic molecules.

MOLCAT uses the high performance for graphics of Apple Macintosh and visualizes the results of vibrational analysis calculations at optimized structures for transition states as well as for local energy minima. There are some applications like *MOLCAT*, for example, Chem3D, Molecular Editor, MacMolecule, NAMOD[5], etc. They mainly aim at visualization of molecular structures. On the other hand, *MOLCAT* is optimized for visualization of mode vectors. It can also display molecular structures without vibrational modes as the other ones do.

We used an Apple Macintosh Centris 660AV in the development of this program. All the routines were coded with FORTRAN except one where the picture image drawn in the main memory of computer is transferred to the screen at a time to avoid flicker.[4] This part was coded with C.

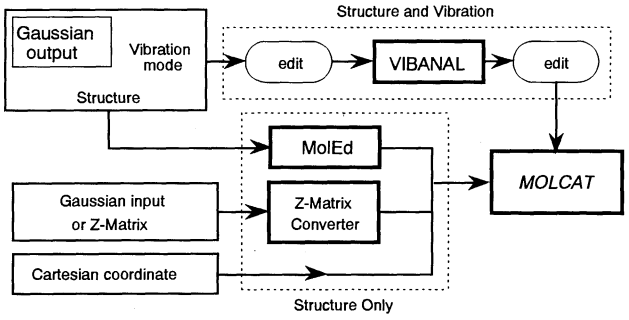

Figure 1. The relationship among *MOLCAT* and its helper routines.

We show the outline of *MOLCAT* in Figure 1. The treatable data are in the rectangles on the left side of Figure 1. They flow along the arrows and their treatment is dependent on their types. The rectangles enclosed by thick lines are *MOLCAT* and its helper routines. MolEd, Z-Matrix Converter and VIBANAL in the dotted rectangle modify data to suitable form for *MOLCAT*. Data for vibrational modes flow through the upper dotted rectangle, and data of molecular structures flow through the lower dotted one. It is possible to treat Cartesian coordinates, Z matrix usually used in ab initio molecular orbital calculation programs such as Gaussian series, and Gaussian outputs as an input of our program. Moled enables *MOLCAT* to treat Gaussian output whether it is in the final stage or halfway of geometry optimization calculation. Then if the calculation don't ended normally, the use of Moled makes us easily analyze the structural problems in the molecular orbital calculation. VIBANAL adjusts the relative length of vibrational vectors, and gives coordinates of the top of vectors with ones of each atom in the text format. The output data of VIBANAL can be edited by using usual text editors. If we would like to take into account the move of specific atoms according to the normal mode, we may notice only those coordinates of vibrational vector out of the output for the ease of understanding.

In the Graphical User Interface manipulation the atomic radius and the view angle is changeable, and the picture of molecule is rotatable to observe the vibrational vectors from various points of view. This function is especially useful to study vibrational modes of complicated molecules. *MOLCAT* is able to treat molecular systems containing up to 100 atoms at a present version.

```
N     .000000     .000000     .000000
H     .000000    1.005500     .000000
H     .870789    -.502750     .000000
H    -.870789    -.502750     .000000
1     .000000     .000000    -.180000
2     .000000    1.005500     .855000
3     .870789    -.502750     .855000
4    -.870789    -.502750     .855000
```

Figure 2. The input data of *MOLCAT* to draw vibrational arrows and the molecular structure of ammonia inversion reaction. VIBANAL gave this data from Gaussian output.

This program was applied to the intramolecular inversion of ammonia. All of geometry optimizations and vibrational analysis calculations were made in RHF level using Gaussian92.[6] The used basis set was STO-3G. We show the input data of *MOLCAT* to draw vibrational arrows with the molecular structure of ammonia in Figure 2. This was given by using the routine VIBANAL. The coordinates of the top of vibrational

arrows are in rows numbered from 1 to 4. If we get data formed as shown in Figure 2 without using VIBANAL, we can use them directly as input data of *MOLCAT*. From these data *MOLCAT* drew the picture of vibration shown in Figure 3. The arrows suggest the direction of this reaction at the transition state.

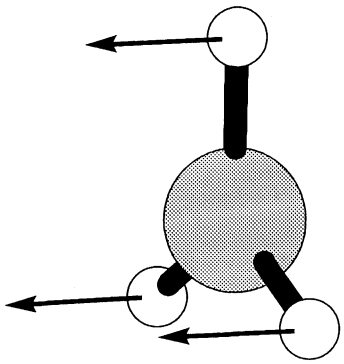

Figure 3. The transition vectors and the structure of ammonia at the transition state of intramolecular inversion drawn by *MOLCAT*.

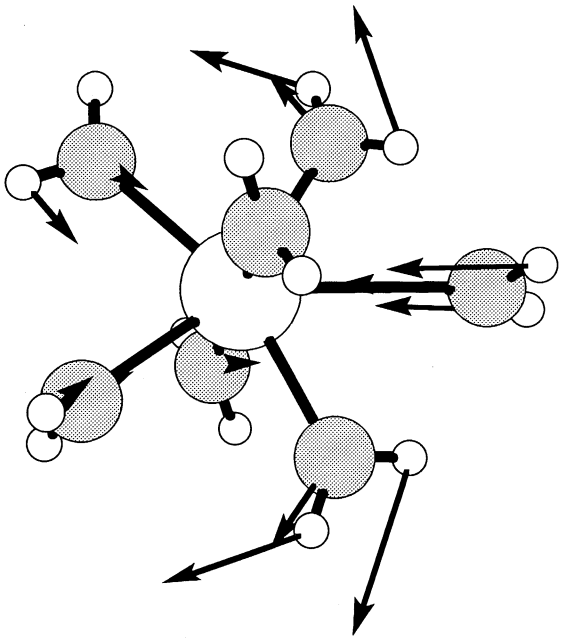

Figure 4. The picture of vibration drawn by *MOLCAT* at the transition state of a water exchange reaction of $[Ca(H_2O)_6]^{2+}$ and H_2O.

We also show the picture of vectors of $[Ca(H_2O)_7]^{2+}$ system at the transition state of a water exchange reaction of hexaaquacalcium(II) in Figure 4 as an example of more complicated molecular vibrations.

The molecular orbital calculation carried out for this reaction was at the same level as ammonia inversion except that the used basis set was DZ[7] augmented with three d functions and one p function for the calcium atom, and one d function for oxygen atoms. The exponents of d and p functions of calcium were 0.144, 0.446, 1.378 and 0.059, respectively. The exponent of d function for oxygen was 0.85. The visualization as this picture enables us to understand larger systems in detail where it is difficult to grasp the image of transition vectors from numeric data only.

We are preparing to distribute *MOLCAT* as a free software for widely uses in the molecular science.

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References and Notes

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