## NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(3), 807—808 (1976)

# The Many-body Effects in $(N_2)_n$ Systems

Masao Hashimoto
*The Chemical Research Institute of Tohoku University, Sendai, 980*

(Received July 14, 1975)

**Synopsis.** Many-body effects in $(N_2)_n$ systems are discussed on the basis of CNDO/2-Clementi SCF calculations of the deviation from the pairwise additivity. The many-body effects cancel each other out, and this makes the deviation from the pairwise additivity only a small percentage of the pairwise interaction in the rather high $n$-mers.

The total energy of an interacting $n$-molecular system can be described as follows (the so-called multibody expansion[1]):

$$E = \sum_{r} E_r + \sum_{r<s} E_{rs} + \sum_{r<s<t} E_{rst} + \cdots + \sum_{r<s<t<\cdots<n} E_{rst\cdots n} \quad (1)$$

The first term of Eq. (1) is the summation of the self-energies of individual molecules. The second term is the summation of the two-body interaction energies, the third term is that of the three-body interaction energies, and so on. Rewriting Eq. (1) in terms of the (2) and (3) defintitions, we obtain the defintition for the deviation from the pairwise additivity, $\sigma(n)$:

$$\varDelta E_n = E - \sum_{r} E_r \quad (2)$$

$$\varDelta E_2 = \sum_{r<s} E_{rs} \quad (3)$$

$$\sigma(n) = \varDelta E_n - \varDelta E_2 = \sum E_{rst} + \cdots + \sum E_{rst\cdots n} \quad (4)$$

It is expected that the three-body effects contribute most significantly to $\sigma(n)$.

Recently, there have appeared several papers on SCF calculations of $\sigma(n)$ in various configrations of rare gas trimers and, in a few cases, tetramers.[2] Novaro and Beltran-Lopez made a calculation of the system of $(He)_4$ and found that the four-body effects were not small compared with the three-body effects. Therefore, the superiority of three-body effects in Eq. (4) may be questionable in general.

TABLE 1. MANY-BODY EFFECT IN $\alpha$-$N_2$, IN ELECTRON VOLTS

| $n$ | Species | $\varDelta E_n$ | $\varDelta E_2$ | $\sigma(n)$ | $n$-Body effect |
|---|---|---|---|---|---|
| 2 | (2, 5) | 0.00000 | | | |
| | (1, 2) | −0.01072 | | | |
| | (1, 10) | −0.01894 | | | |
| | (2, 3) | −0.00004 | | | |
| 3 | (1, 2, 3) | −0.02754 | −0.02148 | −0.00606 | −0.00606 |
| | (2, 1, 5) | −0.02284 | −0.02144 | −0.00140 | −0.00140 |
| | (2, 3, 5) | −0.00010 | −0.00008 | −0.00002 | −0.00002 |
| 4 | (1, 2, 3, 5) | −0.03404 | −0.03224 | −0.00180 | 0.01174 |
| | (2, 3, 4, 5) | −0.00018 | −0.00016 | −0.00002 | 0.00006 |
| | (7, 10, 6, 11) | −0.04588 | −0.04296 | −0.00292 | 0.02132 |
| 5 | (1, 2, 3, 4, 5) | −0.04700 | −0.04304 | −0.00396 | −0.02386 |
| | (1, 7, 10, 6, 11) | −0.12111 | −0.08584 | −0.03527 | 0.00401 |
| 7 | (1············ 7) | −0.14232 | −0.15040 | 0.00808 | |
| 9 | (1············ 9) | −0.25089 | −0.25784 | 0.00691 | |
| 13 | (1············13) | −0.53288 | −0.56472 | 0.03184 | |

TABLE 2. MANY-BODY EFFECT IN $\gamma$-$N_2$ CRYSTAL, IN ELECTRON VOLTS

| $n$ | Species | $\varDelta E_n$ | $\varDelta E_2$ | $\sigma(n)$ | $n$-Body effect |
|---|---|---|---|---|---|
| 2 | (1, 2) | −0.02898 | | | |
| | (3, 4) | −0.00281 | | | |
| | (2, 4) | −0.03734 | | | |
| | (2, 5) | −0.00243 | | | |
| 3 | (2, 3, 5) | −0.07421 | −0.07711 | 0.00290 | 0.00290 |
| | (2, 3, 4) | −0.08068 | −0.07749 | −0.00319 | −0.00319 |
| | (1, 3, 5) | −0.09460 | −0.09530 | 0.00070 | 0.00070 |
| | (1, 3, 4) | −0.05731 | −0.06077 | 0.00346 | 0.00346 |
| | (1, 2, 5) | −0.05419 | −0.06039 | 0.00620 | 0.00620 |
| 4 | (2, 3, 4, 5) | −0.15722 | −0.13788 | −0.01934 | −0.01876 |
| | (1, 3, 2, 4) | −0.15856 | −0.16443 | 0.00587 | 0.00420 |
| | (1, 2, 4, 5) | −0.14807 | −0.16405 | 0.01598 | 0.00548 |
| 5 | (1········5) | −0.25773 | −0.27052 | 0.00279 | −0.00897 |
| 7 | (1········7) | −0.34965 | −0.36582 | 0.01617 | |
| 9 | (1········9) | −0.51269 | −0.53580 | 0.02311 | |

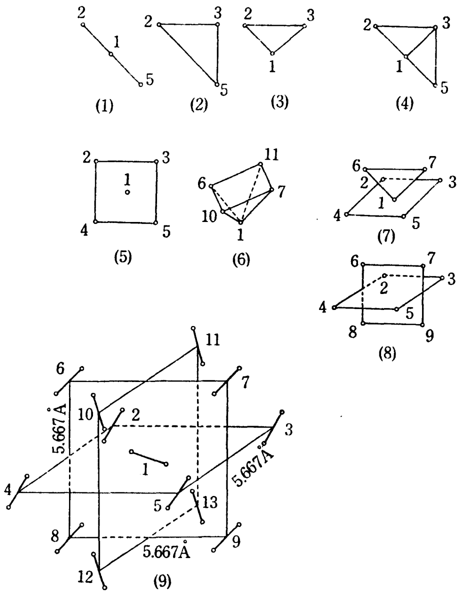

Fig. 1. The configurations of $n$-mers in $\alpha$-$N_2$ crystal. (1), (2), (3): 3-mer; (4): 4-mer; (5), (6): 5-mer; (7): 7-mer; (8): 9-mer; (9): 13-mer. In (1)—(8), only the positions of the centers of $N_2$ molecules are indicated.

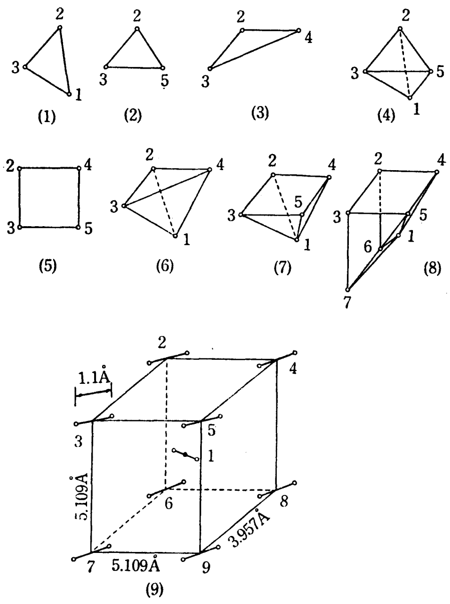

Fig. 2. The configurations of $n$-mers in $\gamma$-$N_2$ crystal. (1),(2),(3),: 3-mer; (4),(5),(6): 4-mer; (7): 5-mer; (8): 7-mer; (9): 9-mer. In (1)—(8) only the positions of the centers of $N_2$ molecules are indicated.

In the case of polyatomic molecular $n$-mer, there have not been any papers reported concerning this point.

In the present paper, we calculate $\sigma(n)$ for $(N_2)_n$ systems in the way previously used[3] for the calculation of $\sigma(3)$ in $(N_2)_3$ systems, and discuss the many-body effects higher than the three-body.

In Tables 1 and 2 the CNDO/2-Clementi SCF LCAO MO results are shown. The configurations of the molecules in $n$-mers in these Tables correspond to a part of the configurations of molecules in the real crystals, $\alpha$- and $\gamma$-$N_2$ (see Figs. 1 and 2).[4] The four-body effect in Fig. 1 (4) is calculated as the difference between $\sigma(4)$ and four three-body effects, which can be calculated easily:

$$\begin{aligned} E_{1235} &= \sigma(4) - \sum E_{rst} \\ &= \sigma(4) - (E_{215}+E_{235}+E_{123}+E_{135}) \\ &= -0.00180 - (-0.00140-0.00002 \\ &\quad -0.00606-0.00606) \\ &= 0.01174 \end{aligned} \tag{5}$$

The other four-body effects in Figs. 1 and 2 were calculated in the same way. The five-body effect in Fig. 1(5) was calculated using the four-body effects thus calculated:

$$\begin{aligned} E_{12345} &= \sigma(5) - (E_{2345}+E_{1235}\times 4+E_{123}\times 4+E_{235}\times 4 \\ &\quad +E_{215}\times 2) \\ &= -0.00396 - (0.00006+0.01174\times 4 \\ &\quad -0.00606\times 4-0.00002\times 4-0.00140\times 2) \\ &= -0.02386 \end{aligned} \tag{6}$$

The other five-body and higher-body effects could be calculated in the same way, but the effects higher than five-body were not evaluated since their calculations are rather time-consuming.

The $n$-body effects obtained throw doubt on the rapid convergence of multibody expansions shown in Eq. (1). However, because the signs of the components in Eq. (4) can be either positive or negative (as may be seen from Tables 1 and 2), there may occur cancellations between them. As a result, the deviations from the pairwise additivity, $\sigma(n)$'s, are of the order of a few percent of $\Delta E_2$ in the $n$-mers higher than the pentamers. This is another confirmation of the pairwise additivity in molecular crystals.

These discussions are, of course, justified only with respect to the intermolecular distance corresponding to the van der Waals minimum: at larger or smaller distances they are questionable. However, we are not interested in the latter region of distance, because we are concerned exclusively with molecular crystals.

All the numerical calculations were made by means of the NEAC-2200 model 700 computer system at the Computer Center of Tohoku University.

## References

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