# Basis Set Dependency of Energy Components in Hartree-Fock MO Theories. II.[1] Conservability of Virial Ratio between Different Conformations

Hiroshi ICHIKAWA* and Atsushi SHIGIHARA
Hoshi College of Pharmacy, Ebara, Shinagawa, Tokyo 142

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The authors examined 22 different basis sets in order to determine exactly how they reproduce the relative kinetic and potential energies. In an attempt to find the calculation error of such energy components, the virial relationship has been used between two conformations in which all bond lengths are optimized with respect to the total energy: i.e., the relationship, $\Delta V=-2\Delta T$, where $\Delta V$ and $\Delta T$ are the differences in the potential and kinetic energies. The degree of error was compared in terms of the relative virial error $((\Delta E+\Delta T)/\Delta E)$ to the difference in the total energies ($\Delta E$). STO-*N*G was found to give a large amount of casual error, up to 500% to $\Delta E$. Such an error could be dramatically improved by using a split-valence method. It should be noted that 4-31G and 6-31G methods resulted in a small amount of error and that the inclusion of polarization functions does not always improve the amount of error.

Ruedenberg and co-workers have pointed out that the nature of the chemical bond can be fully understood by only taking into account the kinetic and potential energies.[2-4] The basic energies which govern chemical phenomena are electrostatic potentials and kinetic energies of nuclei and electrons. The kinetic energy of nuclear motion may be considered separately;[5] thus, the major and important energies in a molecule are the potential energy and the kinetic energy of electrons. Therefore, it is possible, in principle, to interpret chemical phenomena in terms of the potential and kinetic energies in a system using MO theories.

Quantum chemists have provided a large number of basis sets for ab initio MO calculation.[6] However, care concerning components of the totel energy has been neglected or considered to be less important. Besides, it has been shown that the kinetic and potential energies are very sensitive to the scaling factor of the wave function, indicating that one must be more careful when analyzing the energy components than when analyzing the total energy.[7,8] The purpose of this paper is to show whether or not the potential energy and the kinetic energy of electrons are meaningful to quote and how they are dependent on the adopted basis set. For this purpose, we have examined 22 different basis sets in the GAUSSIAN 80 program.[9,10]

## Theory

**Evaluation of the Kinetic and Potential Energies.** Since via a Fock matrix three- and four-center integrals out of two-electron integrals can be reduced to two-center terms, the kinetic energy ($T$) and the electronic potential energy ($V$) can be expressed in terms of the density ($P_{rs}$), kinetic energy ($T_{rs}$), and Fock ($F_{rs}$) matrices as follows;

$$T=\sum_{r,s} P_{rs}\, T_{rs} \tag{1}$$

and

$$V=1/2 \sum_{r,s} P_{rs}\,(F_{rs}-T_{rs})+\sum_{A<B} E_{AB}{}^{N}, \tag{2}$$

where $E_{AB}{}^{N}$ is the internuclear repulsion between atoms $A$ and $B$, and where $r$ and $s$ run over all atomic orbitals. Details are shown elsewhere.[11]

Since the scaling factor to the wave function applies to the electronic coordinates as well as to the nuclear coordinates, the condition or threshold of geometry optimization is predicted to seriously affect components of the total energy. Therefore, the threshold of geometry optimization was set to be 0.000075 (maximum) and 0.00005 (rms) Hartree/Bohr or radian, which are less than one fifth of the standard geometry optimization.

As Eqs. 1 and 2 show, the convergence on the density matrix may be another important condition. The SCF criterion was set such that every element of the density matrix was to converge within $10^{-10}$, 1000-times more severe than the standard SCF criterion. The effects of geometry optimization and the SCF convergence will be discussed in a later section.

**Criteria of Energy Components.** The first criterion of the adopted basis set is to compare the relative total energy ($\Delta E$) with the experiment (criterion 1). However, this cannot apply to the components of the total energy.

The ratio $V/T$ should be exactly $-2$ in any *equilibrium* geometry. Nelander has pointed out that the angular coordinates give no contribution to the ratio if all bond lengths are optimized with respect to the total energy.[12] The energy difference between any two sets of geometry-optimized conformations satisfies the relationship $\Delta V=-2\Delta T$, where $\Delta T$ and $\Delta V$ are the differences of the kinetic energy and the potential energy. Therefore, if the total energy increases when the geometry changes from one conformation to another, the potential energy must increase while the kinetic energy of electrons must decrease (criterion 2) and the ratio $-\Delta V/\Delta T$ should be exactly 2, as to the appropriate Hartree-Fock wave function. Although the actual wave functions obtained by an SCF MO theory do not always give the required ratio exactly, it could be said that the closer the calculated ratio is to 2, the more the adopted basis set is appropriate for the considered system. This can be another criterion. However, it involves such a difficulty that when $\Delta T$ appears to be zero or very close to zero, the ratio becomes infinity or a very large number, overrating the error.

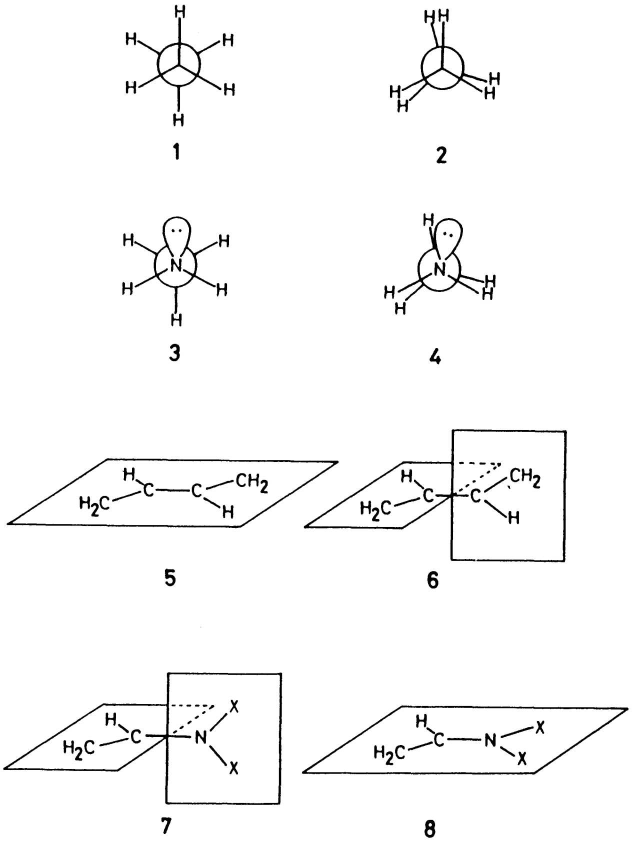
The $\Delta E+\Delta T$ value $(=\Delta V+2\Delta T)$ should be zero; the closeness to zero shows exactly how energy components are calculated by the adopted basis set. We call the difference from zero the "virial error" for now. Since the virial error should be compared with respect to $\Delta E$, we adopted the relative value $(\Delta E+\Delta T)/\Delta E$ as a quantitative measure for the error of the energy-component calculation (criterion 3).

## Results and Discussion

We have chosen the following compounds: $CH_3$-$CH_3$, $CH_3$-$NH_2$, $CH_2$=CH-CH=$CH_2$, $CH_2$=CH-$NH_2$, and $CH_2$=CH-$NO_2$. The first and second compounds represent the aliphatic compounds and the others are interesting in that a change in the conformation of the functional group breaks up the conjugation between $\pi$ systems or between a $\pi$ system and its substituent.

**Ethane.** Ethane favors the staggered conformation **1** and the experimental rotational barrier was reported to be 12.3 kJ mol$^{-1}$.[13] Table 1 shows the results for ethane where the total energies, kinetic energies, and potential energies for the staggered conformation are listed. As for the eclipsed conformation **2**, only the differences from the staggered conformation are shown.

The calculated energy barrier ($\Delta E$) ranges from 11 to 13 kJ mol$^{-1}$, a good agreement with the experiment,



Scheme 1.

Table 1. Total, Kinetic, and Potential Energies in Ethane

| | $E^{a)}$ | $T^{a)}$ | $V^{a)}$ | $\Delta E^{b)}$ | $\Delta T^{b)}$ | $\Delta V^{b)}$ |
|---|---|---|---|---|---|---|
| STO-3G | −78.306180 | 77.672593 | −155.978772 | 12 | 12 | 0 |
| STO-4G | −78.863187 | 78.621105 | −157.484292 | 12 | 8 | 4 |
| STO-5G | −79.018148 | 78.918412 | −157.936560 | 12 | 10 | 2 |
| STG-6G | −79.066024 | 79.021753 | −158.087777 | 12 | 10 | 2 |
| 3-21G | −78.793948 | 78.644574 | −157.438523 | 12 | −20 | 32 |
| 4-21G | −79.061649 | 79.093991 | −158.155640 | 11 | −20 | 31 |
| 6-21G | −79.138022 | 79.209755 | −158.347777 | 11 | −20 | 31 |
| 3-21G* | −78.824494 | 78.614277 | −157.438771 | 13 | −15 | 28 |
| 4-21G* | −79.091958 | 79.062910 | −158.154868 | 13 | −16 | 28 |
| 6-21G* | −79.168213 | 79.180491 | −158.348704 | 13 | −16 | 29 |
| 3-21G** | −78.844210 | 78.475882 | −157.320092 | 13 | −15 | 28 |
| 4-21G** | −79.109019 | 78.952629 | −158.061647 | 13 | −15 | 27 |
| 6-21G** | −79.184285 | 79.103225 | −158.287510 | 13 | −15 | 27 |
| 4-31G | −79.115933 | 79.249285 | −158.365218 | 12 | −13 | 25 |
| 6-31G | −79.197572 | 79.340650 | −158.538222 | 12 | −12 | 24 |
| 4-31G* | −79.151624 | 78.671024 | −157.822648 | 13 | −15 | 28 |
| 6-31G* | −79.228755 | 79.199474 | −158.428229 | 12 | −16 | 28 |
| 4-31G** | −79.162010 | 78.678248 | −157.840258 | 13 | −16 | 28 |
| 6-31G** | −79.238235 | 79.199114 | −158.437349 | 13 | −16 | 29 |
| 6-311G | −79.211802 | 79.284061 | −158.495863 | 12 | −11 | 22 |
| 6-311G* | −79.242829 | 79.263740 | −158.506569 | 12 | −8 | 21 |
| 6-311G** | −79.251707 | 79.217743 | −158.469450 | 13 | −11 | 24 |

a) In terms of au (1 au=2625.5 kJ mol$^{-1}$). b) kJ mol$^{-1}$.

regardless of the adopted basis set satisfying criterion 1. In the STO-*N*G methods, however, it is seen that both kinetic and potential energies increase as the geometry changes from the staggered conformation to the eclipsed one. This does not meet criterion 2. All other methods satisfy such a requirement.

Regarding criterion 3, as Fig. 1 shows, only STO-*N*G gave a relative virial error of more than 100% to the difference of the total energies. All other methods gave reasonably correct values where, interestingly, the inclusion of polarization functions did not improve the error. For example, the relative errors by 6-311G, 6-311G*, and 6-311G** were 0.08, 0.33, and 0.15, respectively, where the basis set without polarization functions gave the best result among them. Except for STO-*N*G, the difference of energy components, $\Delta T$

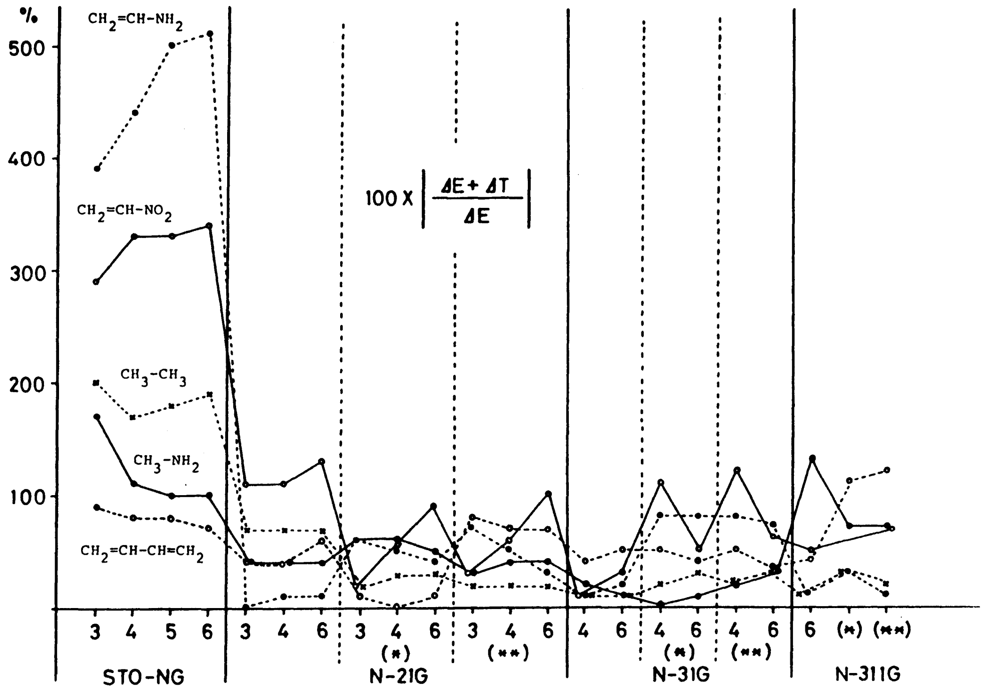


Fig. 1. Relative virial errors.

Table 2. Total, Kinetic, and Potential Energies in Methylamine

| | $E$[a] | $T$[a] | $V$[a] | $\Delta E$[b] | $\Delta T$[b] | $\Delta V$[b] |
|---|---|---|---|---|---|---|
| STO-3G | −94.032863 | 93.218512 | −187.251375 | 12 | 8 | 4 |
| STO-4G | −94.704379 | 94.353756 | −189.058136 | 12 | 2 | 10 |
| STO-5G | −94.887253 | 94.731303 | −189.618556 | 12 | 0 | 12 |
| STO-6G | −94.943358 | 94.862177 | −189.805535 | 12 | 0 | 12 |
| 3-21G | −94.681656 | 94.460890 | −189.142546 | 8 | −5 | 13 |
| 4-21G | −94.995400 | 94.990298 | −189.985699 | 8 | −5 | 14 |
| 6-21G | −95.084985 | 95.143410 | −190.228395 | 9 | −5 | 13 |
| 3-21G* | −94.721827 | 94.450702 | −189.172528 | 12 | −5 | 16 |
| 4-21G* | −95.035133 | 94.978065 | −190.013198 | 12 | −5 | 17 |
| 6-21G* | −95.124511 | 95.131635 | −190.256145 | 12 | −5 | 17 |
| 3-21G** | −94.744616 | 94.357714 | −189.102330 | 11 | −8 | 18 |
| 4-21G** | −95.055857 | 94.903976 | −189.959833 | 11 | −7 | 18 |
| 6-21G** | −95.144436 | 95.082366 | −190.226802 | 11 | −6 | 17 |
| 4-31G[c] | −95.071663 | 95.196402 | −190.268065 | 11 | −13 | 24 |
| 6-31G[c] | −95.170903 | 95.293703 | −190.464606 | 11 | −12 | 23 |
| 4-31G* | −95.117328 | 94.482331 | −189.599659 | 10 | −11 | 21 |
| 6-31G* | −95.209828 | 95.103524 | −190.313353 | 10 | −11 | 21 |
| 4-31G** | −95.130398 | 94.491786 | −189.622183 | 10 | −12 | 22 |
| 6-31G** | −95.221864 | 95.106854 | −190.328718 | 10 | −13 | 22 |
| 6-311G | −95.193323 | 95.307019 | −190.500342 | 7 | 2 | 5 |
| 6-311G* | −95.231752 | 95.305991 | −190.537744 | 10 | −3 | 13 |
| 6-311G** | −95.242514 | 95.255665 | −190.498179 | 10 | −3 | 12 |

a) In terms of au. b) kJ mol$^{-1}$. c) HNH was set to be the experimental value (105°52′) since the stationary angle was not obtain.

Table 3. Total, Kinetic, and Potential Energies in Butadiene

| | $E^{a)}$ | $T^{a)}$ | $V^{a)}$ | $\Delta E^{b)}$ | $\Delta T^{b)}$ | $\Delta V^{b)}$ |
|---|---|---|---|---|---|---|
| STO-3G | −153.020365 | 151.994848 | −305.015213 | 23 | −2 | 26 |
| STO-4G | −154.124511 | 153.827631 | −307.952142 | 23 | −4 | 28 |
| STO-5G | −154.427447 | 154.412477 | −308.839924 | 23 | −5 | 28 |
| STO-6G | −154.521944 | 154.616226 | −309.138170 | 23 | −6 | 29 |
| 3-21G | −154.059459 | 153.744461 | −307.803920 | 23 | −15 | 37 |
| 4-21G | −154.598599 | 154.649834 | −309.248433 | 23 | −14 | 37 |
| 6-21G | −154.752984 | 154.892001 | −309.644985 | 23 | −9 | 33 |
| 3-21G* | −154.124030 | 153.624492 | −307.748522 | 47 | −43 | 91 |
| 4-21G* | −154.660728 | 154.548828 | −309.209557 | 49 | −47 | 96 |
| 6-21G* | −154.814130 | 154.813666 | −309.627796 | 51 | −48 | 99 |
| 3-21G** | −154.148618 | 153.468784 | −307.617401 | 41 | −8 | 49 |
| 4-21G** | −154.681789 | 154.427391 | −309.109180 | 43 | −12 | 55 |
| 6-21G** | −154.833862 | 154.731145 | −309.565007 | 46 | −13 | 60 |
| 4-31G | −154.699966 | 154.903200 | −309.603166 | 25 | −34 | 58 |
| 6-31G | −154.864579 | 155.055757 | −309.920336 | 25 | −38 | 63 |
| 4-31G* | −154.764143 | 153.771430 | −308.535574 | 24 | −12 | 37 |
| 6-31G* | −154.919656 | 154.808417 | −309.728073 | 24 | −16 | 40 |
| 4-31G** | −154.775600 | 153.782106 | −308.557706 | 24 | −12 | 37 |
| 6-31G** | −154.930326 | 154.814169 | −309.744495 | 24 | −16 | 41 |
| 6-311G | −154.892899 | 155.018421 | −309.911320 | 24 | −33 | 57 |
| 6-311G* | −154.949276 | 154.966953 | −309.916229 | 45 | −96 | 141 |
| 6-311G** | −154.960846 | 154.939571 | −309.900417 | 45 | −100 | 145 |

a) In terms of au. b) kJ mol$^{-1}$.

and $\Delta V$, were calculated to be 10 to 20 and 20 to 30 kJ mol$^{-1}$, respectively.

**Methylamine.** We have chosen two conformations: the staggered conformation **3** and the eclipsed conformation **4**. The rotational barrier of methylamine has been reported to be 8.3 kJ mol$^{-1}$.[14] The calculated rotational barriers shown in Table 2 were from 7 to 12 kJ mol$^{-1}$, in reasonable agreement with the experiment. However, the components by STO-*N*G appeared to be unsatisfactory, even qualitatively. The split-valence methods gave results which reasonably well satisfy criteria 1, 2, and 3. Very exceptionally, 6-311G gave a large relative virial error in addition to failure of criterion 2, although it was improved by the inclusion of polarization functions. As expected, the contraction number of the primitive Gaussian functions for the inner-shell atomic orbitals did not affect the ratio very much. It is also noted that the inclusion of polarization functions to the first-row atom and to the hydrogen atom seems not always to improve the relative virial error.

**Butadiene.** The rotational barrier from the trans to cis structures has been observed to be a value ranging between 24 and 32 kJ mol$^{-1}$.[15–17] We have chosen the planar trans structure with the lowest energy **5** and the orthogonal structure with the highest energy **6**.

As shown in Table 3, the calculated rotational barriers varied from 23 (STO-*N*G) to 51 kJ mol$^{-1}$ (6-21G*), significantly larger than the observed values. This may stem from the difference of the electron-correlation energy between the orthogonal and planar structures: in the orthogonal structure the conjugation between two $\pi$ systems are broken.

**Vinylamine.** We consider the orthogonal structure **7** (X=H) and the planar structure **8** (X=H). Vinylamine is the fundamental unit of enamines. The electronic effect of enamine has been explained as being a strong contribution of the structure $CH_2^-$-CH=$NH_2^+$.[18]

Since vinylamine favors to take the imino form, the experimental rotational barrier may not be obtained, excluding the way to check the difference of total energies. However, the rotational barrier has been calculated to be between 26 and 32 kJ mol$^{-1}$.[19] Table 4 shows the energies for the planar structure and the differences for the orthogonal structure from the planar structure.

The total energy of the optimized orthogonal structure was calculated to be 25 to 35 kJ mol$^{-1}$ higher than that of the planar structure by all MO methods, perhaps satisfying the first criterion. However, the components were divergent.

A comparison of the relative virial errors by *N*-21G*, *N*-21G**, *N*-31G*, and *N*-31G** leads to the fact that, contrary to the case of methylamine, the number of the primitive Gaussian functions for the inner-shell electrons is slightly concerned with the energy components: as a rule, the larger the number of functions, the better the results.

**Nitroethene.** Nitroethene has a planar structure with an electric dipole moment of 3.7 d,[20] indicating that a considerable number of electrons move to the nitro group. In an orthogonal structure **7** (X=O) such a conjugation is forced to cease. The conjugation energy is observed to be 20.2 kJ mol$^{-1}$,[21] suggesting a strong contribution of the cannonical structure $CH_2^+$-CH=$NO_2^-$.

Table 5 shows that the calculated conjugation energy ranges between 20 and 40 kJ mol$^{-1}$. The potential energies calculated by all methods increase in accordance with the corresponding total energies. However, the kinetic energy behaves differently according to the calculation method. This time, STO-*N*G gave the correct signs of $\Delta T$, but $\Delta T$'s by *N*-21G, 6-21G**, 4-31G*, and 4-31G** failed to meet the second criterion. Criterion 3 is necessary for a quantitative discussion. Interestingly, such a requirement is satisfied by such rather smaller basis sets as 4-31G and 6-31G; the inclusion of polarization functions does not always improve the relative virial error.

**Effect of the Conditions of Geometry Optimization and SCF Convergence. (a) Threshold of Geometry Optimization.** It has been known that the kinetic and potential energies change in the first order of the error of the scaling factor to the wave function, while the total energy does only in the second order.[7,22] Since

Table 4. Total, Kinetic, and Potential Energies in Vinylamine

| | $E^{a)}$ | $T^{a)}$ | $V^{a)}$ | $\Delta E^{b)}$ | $\Delta T^{b)}$ | $\Delta V^{b)}$ |
|---|---|---|---|---|---|---|
| STO-3G | −131.395801 | 130.361665 | −261.757466 | 25 | 73 | −48 |
| STO-4G | −132.341207 | 131.933730 | −264.274936 | 25 | 85 | −60 |
| STO-5G | −132.598103 | 132.448926 | −265.047029 | 25 | 99 | −74 |
| STO-6G | −132.677501 | 132.628438 | −265.305938 | 25 | 104 | −79 |
| 3-21G | −132.326444 | 132.018646 | −264.345089 | 33 | −33 | 66 |
| 4-21G | −132.775409 | 132.774694 | −265.550103 | 32 | −30 | 63 |
| 6-21G | −132.903865 | 132.990267 | −265.894132 | 32 | −28 | 61 |
| 3-21G* | −132.380162 | 131.954477 | −264.334638 | 26 | −11 | 37 |
| 4-21G* | −132.827356 | 132.718805 | −265.546161 | 25 | −13 | 38 |
| 6-21G* | −132.955071 | 132.946404 | −265.901475 | 25 | −15 | 40 |
| 3-21G** | −132.404789 | 131.858017 | −264.262806 | 27 | −9 | 36 |
| 4-21G** | −132.849484 | 132.644363 | −265.493847 | 26 | −13 | 40 |
| 6-21G** | −132.976248 | 132.900359 | −265.876606 | 26 | −17 | 43 |
| 4-31G | −132.875211 | 133.031032 | −265.906243 | 35 | −31 | 65 |
| 6-31G | −133.015746 | 133.156180 | −266.171926 | 35 | −27 | 62 |
| 4-31G* | −132.930283 | 132.025368 | −264.955651 | 26 | −6 | 32 |
| 6-31G* | −133.061699 | 132.901443 | −265.963142 | 25 | −6 | 31 |
| 4-31G** | −132.944430 | 132.040734 | −264.985164 | 26 | −6 | 32 |
| 6-31G** | −133.074921 | 132.912700 | −265.987621 | 26 | −7 | 33 |
| 6-311G | −133.044367 | 133.176830 | −266.221197 | 33 | −29 | 62 |
| 6-311G* | −133.091500 | 133.151130 | −266.242630 | 26 | −19 | 45 |
| 6-311G** | −133.103747 | 133.114557 | −266.218304 | 26 | −25 | 51 |

a) In terms of au. b) kJ mol$^{-1}$.

Table 5. Total, Kinetic, and Potential Energies in Nitroethene

| | $E^{a)}$ | $T^{a)}$ | $V^{a)}$ | $\Delta E^{b)}$ | $\Delta T^{b)}$ | $\Delta V^{b)}$ |
|---|---|---|---|---|---|---|
| STO-3G | −277.781977 | 275.262008 | −553.043984 | 20 | −78 | 98 |
| STO-4G | −279.784071 | 278.582771 | −558.366843 | 20 | −84 | 104 |
| STO-5G | −280.313391 | 279.764341 | −560.077732 | 20 | −85 | 105 |
| STO-6G | −280.475786 | 280.177739 | −560.653525 | 20 | −87 | 106 |
| 3-21G | −279.889056 | 279.275682 | −559.164738 | 41 | 3 | 38 |
| 4-21G | −280.811462 | 280.832774 | −561.644236 | 40 | 5 | 35 |
| 6-21G | −281.075628 | 281.294010 | −562.369639 | 40 | 10 | 30 |
| 3-21G* | −280.070296 | 279.283942 | −559.354238 | 37 | −31 | 67 |
| 4-21G* | −280.984154 | 280.825887 | −561.810042 | 36 | −16 | 52 |
| 6-21G* | −281.245313 | 281.286143 | −562.531456 | 36 | −3 | 39 |
| 3-21G** | −280.082650 | 279.203616 | −559.286266 | 37 | −25 | 62 |
| 4-21G** | −280.994616 | 280.763170 | −561.757785 | 36 | −13 | 49 |
| 6-21G** | −281.255073 | 281.243522 | −562.498595 | 36 | 0 | 36 |
| 4-31G | −281.064416 | 281.333970 | −562.398386 | 34 | −37 | 71 |
| 6-31G | −281.356993 | 281.575193 | −562.932185 | 34 | −46 | 80 |
| 4-31G* | −281.232693 | 279.302221 | −560.534914 | 31 | 3 | 28 |
| 6-31G* | −281.504092 | 280.949691 | −562.453784 | 30 | −14 | 45 |
| 4-31G** | −281.238623 | 279.306407 | −560.545030 | 31 | 5 | 25 |
| 6-31G** | −281.509570 | 280.951409 | −562.460979 | 30 | −12 | 43 |
| 6-311G | −281.435442 | 281.644113 | −563.079554 | 34 | −17 | 51 |
| 6-311G*$^{c)}$ | | | | | | |
| 6-311C** | −281.578367 | 281.659111 | −563.237477 | 30 | −10 | 40 |

a) In terms of au. b) kJ mol$^{-1}$. c) Optimized structure was not obtained because of SCF difficulty.

Table 6. Deviation of Energy Components by Incomplete Geometry Optimization (4-31G)

| $R$ | $r_0$(1.4216A) | $r_0$−0.0001 | $r_0$−0.0002 | $r_0$−0.0003 | $r_0$−0.0004 |
|---|---|---|---|---|---|
| $-\partial E/\partial R$[a)] | 0.00000 | 0.00014 | 0.00023 | 0.00031 | 0.00039 |
| $\Delta E$[b)] | 34.45 | 34.45 | 34.45 | 34.46 | 34.46 |
| $\Delta T$[b)] | −30.56 | −28.30 | −27.66 | −27.01 | −26.37 |
| $\Delta V$[b)] | 65.02 | 62.75 | 62.11 | 61.47 | 60.83 |
| $(\Delta E+\Delta T)/\Delta E$ | 0.11 | 0.18 | 0.20 | 0.22 | 0.23 |

a) au/Bohr. b) kJ mol$^{-1}$.

Table 7. Deviation of Total Energy and Its Components by SCF Threshold (4-31G)

| Threshold[a)] | $10^{-10}$ | $10^{-7}$ | $10^{-6}$ | $10^{-5}$ | $10^{-4}$ | $10^{-3}$ |
|---|---|---|---|---|---|---|
| $E$[b)] | −132.875211 | −132.875211 | −132.875211 | −132.875211 | −132.875211 | −132.875074 |
| $T$[b)] | 133.031438 | 133.031441 | 133.031462 | 133.031690 | 133.031002 | 133.015878 |
| $V$[b)] | −265.906649 | −265.906652 | −265.906673 | −265.906900 | −265.906213 | −265.890952 |

a) Threshold at the density matrix, $P_{rs}$. b) In terms of au.

the scaling factor applies to the electronic coordinates as well as to the nuclear coordinates, the error of energy components can be grouped into two: the error due to electronic coordinates and that due to nuclear coordinates. The former may be improved by adopting a large basis set which allows a shrinking or expansion of the electronic distribution. The latter may be largely affected by the threshold of geometry optimization.

Table 6 shows how the energy-components are affected by the condition of geometry optimization. As an example, we investigated the case when the orthogonal structure of vinylamine is not properly optimized: namely, the energy difference between the optimized planar structure and the orthogonal structures in which the C–N bond is intentionally shifted from the equilibrium distance ($r_0$). A decrease of 0.0001A from $r_0$ makes no difference regarding the total energy. However, the differences of the kinetic or potential energy amount to 2.3 kJ mol$^{-1}$ and the relative virial error increases from 0.11 to 0.18. The force at this point is 0.00014 Hartree/Bohr. Judging from this result, a threshold less than 0.0001 Hartree/Bohr may be absolutely necessary. However, a far more severe optimization than that consumes a large amount of computation time and is likely to go into oscillation. Therefore, a threshold of 0.000075 Hartree/Bohr, which is adopted in the present study, may be a practical compromise.

**(b) Concerning the SCF Convergence.** As already mentioned, an incomplete convergence of the density matrix, $P_{rs}$, may create errors in the energy components. Table 7 shows the relationship between the threshold of SCF convergence and the total energy and its components.

The total energy is not very sensitive until a threshold of $10^{-3}$ at the density matrix. However, the components are susceptible enough, even at $10^{-6}$ (The deviation from the threshold of $10^{-10}$ is 0.1 kJ mol$^{-1}$). Therefore, at least a threshold of $10^{-7}$ may be desirable.

## Concluding Remarks

In the first paper of this series,[23)] we discussed the dependency of the electron density, the kinetic energy, and the potential energy of an atom on the adopted basis set. It was shown that the polarization functions must be added to atoms of the first row and the hydrogen atom in order to obtain well-balanced wave functions. The STO-*N*G method was also shown to give well-balanced wave functions. However, Fig. 1 shows that STO-*N*G gives a large amount of casual error, up to 500%. This error can be dramatically improved by using a split-valence method. This may be because in a split-valence method, the wave function has more spacial freedom for expansion or shrinking than that in the single zeta method, like STO-*N*G. The 4-31G and 6-31G methods resulted in a small amount of error, but the inclusion of polarization functions does not always improve the amount of error. This strongly suggests that the error in the split-valence method is caused by incomplete geometry optimization, rather than an incomplete basis set.

As we stated in the introduction, it may be worth investigating which energy, $T$ or $V$, plays the major role in chemical phenomena. For such a purpose, we only need qualitative $\Delta T$ and $\Delta V$, and any split-valence method seems to be eligible to be adopted. However, care must be taken regarding the calculated energy components, as always, in any kind of MO theoretical calculation.

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