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A Comparative Study of *ab-initio* Effective Core Potential and All-Electron Calculations for Molecular Structures and Transition States

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The reliability of the *ab-initio* effective core potential method for calculating molecular geometries was tested for several polyatomic molecules by using the energy gradient technique. The calculated geometries are in good agreement with those of all-electron calculation not only for equilibrium but also for transition states. The heat of reaction and the activation barrier height compare very well with those of all-electron calculation as well.

Key words: Effective core potential – Molecular geometry – Transition state.

1. Introduction

The *ab-initio* effective core potential (ECP) method is probably the most reliable approximation for calculating electronic structures of systems which contain heavy atoms or are too large for all-electron *ab-initio* calculations. Though the application of the method is gaining popularity, its reliability for molecular calculations, especially for structures of polyatomic molecules, has not been fully established. Among many ECP schemes, we in this work carry out a rigorous test of the Kahn–Goddard–Melius–Topiol's scheme [1, 2] for calculating geometries of polyatomic molecules. This ECP scheme has also successfully been applied to transition metal complexes [3, 6]. Pullman et al. [7] have tested the scheme for intermolecular interactions. These studies have indicated a high reliability of the ECP method. We determined both with and without the ECP approximation geometries of transition states as well as equilibrium geometries of various systems using the energy gradient technique [4, 5]. One will find an excellent agreement between the ECP and the all-electron calculations both for geometries and energetics.

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2. Method of Computations

The ECP parameters employed were those of Topiol et al. [8] using the scheme of Kahn–Goddard–Melius–Topiol. The valence 31G [9] basis set was used for the ECP calculations, and correspondingly the split-valence (n-31G) set [10] was used for all-electron calculations. The following is the model Hamiltonian:

$$H^{\mathrm{ECP}}=\sum_i\left[-\tfrac{1}{2}\nabla_i^2-\sum_\alpha V_{\alpha i}^{\mathrm{ECP}}\right]+\sum_{i>j}\frac{1}{r_{ij}}+\sum_{\alpha>\beta}\frac{(Z_\alpha-N_\alpha^c)(Z_\beta-N_\beta^c)}{R_{\alpha\beta}} \tag{1}$$

where i and j run over valence electrons and α and β over nuclei. N_α^c is the number of core electrons on atom α. The last term of Eq. (1) is the approximate "core–core" interaction introduced for molecular calculations. This completely shielded core–core potential gives a smaller repulsion than the actual interaction between core electrons. The error introduced by this approximation, however, is very small around normal bond distances [2, 11].

All calculations were for singlet ground states at the RHF level. Geometrical parameters were fully optimized using the energy gradient. Numerical calculations were carried out with the IMSPACK *ab-initio* MO program system [12] which includes the ECP integral package and its derivative routines [4].

3. Results and Discussions

For a comparative study, we have arbitrarily chosen several systems which had been studied by all-electron calculations with the n-31G basis set. Those include unimolecular reactions of fluroformaldehyde [13], addition reaction of acethylene with fulminic acid [14], as well as some organosilicon compounds [15].

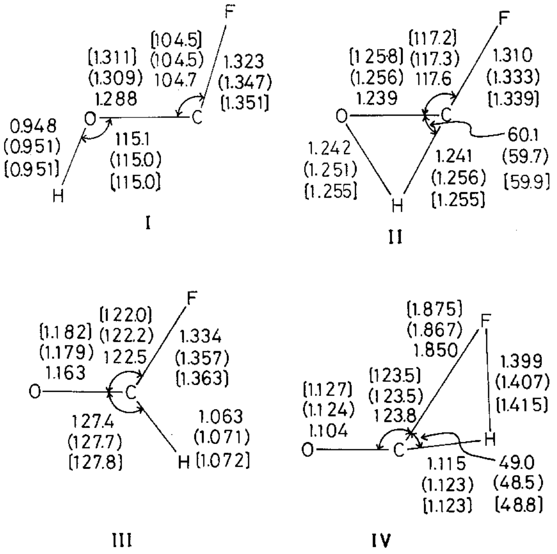

Fig. 1. Optimized equilibrium (I and III) and transition state (II and IV) geometry. The 4-31G results in ( ) are taken from Ref. [13]. The 6-31G results are given in [ ]

The optimized geometries with ECP are summarized in Figs. 1 to 3 along with those of all-electron calculations. Fluoroformaldehyde and its isomerization product FCOH as well as two transition states are shown in Fig. 1. The 4-31G results in Fig. 1 were taken from ref. [13] and the reoptimization with the 6-31G basis set was performed in this work. Isoxazole and its parent molecules are shown in Fig. 2. Silaacetylene and disilyne are shown in Fig. 3. Both linear HSiCH and HSiSiH are "super-saddle" points where two normal coordinates have imaginary frequencies [15]. The 4-31G set for Si [16] seems to be less accurate compared to the basis set for other atoms of the same series. Therefore, we only refer to the 6-31G results for silicon compounds and the 4-31G results for all other molecules. For all systems studied here, one sees an excellent

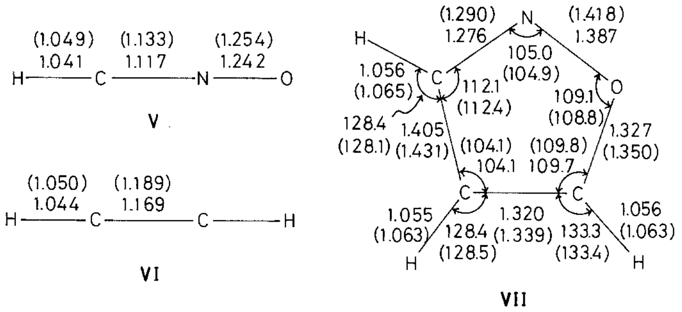

Fig. 2. Optimized geometries. The 4-31G results in ( ) are taken from Ref. [14]

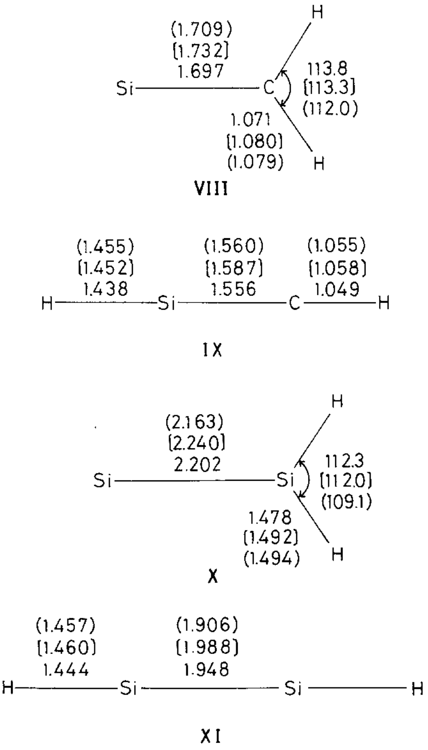

Fig. 3. Optimized geometries of equilibrium (VIII and X) and 'super-saddle' points (IX and XI). The 4-31G and the 6-31G results are in ( ) and [ ], respectively

Table 1. Calculated Energetics (kcal/mol)

system	ECP	4-31G	6-31G
I–III[a]	+41	+42[e]	+40
II–III[b]	+106	−106[e]	+105
IV–III[b]	+65	+63[e]	+63
VII–VI–V[c]	−78	−80[f]	—
IX–VIII[d]	+62	+44[g]	+60[g]
XI–X[d]	+37	+33[g]	+37[g]

[a] Relative energy of isomers.
[b] Activation barrier height.
[c] Heat of reaction.
[d] Energy of the "super-saddle" point.
[e] Recalculated at the geometries given in Ref [13].
[f] From Ref. [14].
[g] From Ref. [15].

agreement of the ECP results with the all-electron results. The difference between the optimized geometries are within 0.04Å in bond lengths and 0.5 degrees in bond angles, regardless whether they are equilibrium or transition states.

The calculated energetics are summarized in Table 1. The difference between the ECP and the all-electron calculations is not more than 2 kcal/mol for heats of reaction as well as for activation barrier heights. (As is mentioned previously, we do not refer to the 4-31G results for silicon complexes.) The ECP method, thus, reproduces the potential energy hypersurface of all-electron *ab-initio* method in a high degree of accuracy.

The deviations of the ECP results from the all-electron results are very small and are within the error due to the basis set dependency. One notices that the ECP underestimates bond distances systematically. The deviations are about 1, 1 to 2 and 2% for bond lengths between a first row atom and a hydrogen atom, between two first row atoms and between a first and a second row atom, respectively (Fig. 4). A frozen core approximation is expected to give a longer bond length. The ECP scheme introduces several approximations in replacing

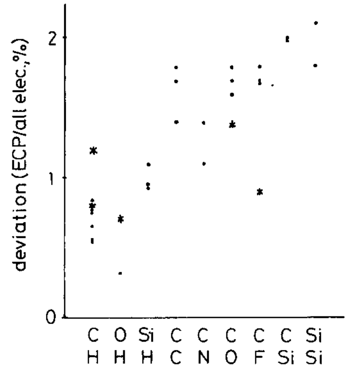

Fig. 4. Deviations of bond lengths for each type of bond. * shows elongated bond lengths at transition states

a frozen core with an effective potential [2]. Among the approximations employed, the completely screened core-core interaction is probably responsible to this underestimation.

We have shown that the ECP reproduces the all-electron *ab-initio* results very well. This does not necessarily exclude the possible drawback of ECP at a rather long internuclear distance, as has pointed out by Hay et al. [17]

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