General Paper

Revisiting the Nature of Si-O-Si Bridging

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Non-empirical calculation based on the Schrödinger equation is an appropriate tool for investigating the relationship among Si-O-Si angle, Si-O bond length, Si-O bond strength, and electronic structure. However, past studies could not reach a consensus about the equilibrium structure of the C_{2v} pyrosilicic acid molecule. Moreover, the structure of disiloxane, the simplest siloxane molecule, could not be reproduced using non-empirical molecular orbital calculations. In this study, I checked the reproducibility of various model chemistries and basis sets, and found that employing the post-Hartree-Fock method and a larger basis set (at least, aug-cc-pVTZ) is necessary for accurate calculation of the disiloxane molecule. In contrast to past studies on molecular orbitals, the present study reveals no significant occupancy in the Si 3d orbitals. The total energy landscape of the C_{2v} pyrosilicic acid molecule is calculated by using the coupled cluster method concerning three excited electrons and the aug-cc-pVTZ basis set. The stable bond length for Si-O_{br} is 1.604 Å, and the stable Si-O-Si angle is 159.449°. There are gentle curves around the stable angles for each bond length comparing with bond length direction. The stable angle for each bond length decreased with increasing Si-O_{br} bond length. The weakening of the Si-O_{br} bond with decreasing Si-O-Si bond angle can be explained by the decrease in the bond index and the increase in the orbital energy for Si-O_{br} σ-bond. Consequently, hybridization of the valence electrons of the bridging oxygen with decreasing Si-O-Si angle weakens the Si-O_{br} σ-bond. Electrostatic potential favors a straight configuration because of the repulsion between the SiO₄ tetrahedra, while the valence electrons of the bridging oxygen favor a bent configuration. These two competing behaviors can explain the bent configuration of pyrosilicic acid without considering d-p π bonding.

Keywords: Silicate, Pyrosilicic Acid, Disiloxane, Benchmark, Molecular Orbital Calculations

1 INTRODUCTION

Silicates, which are compounds comprising metal oxide and silica, have been studied in various fields such as mineralogy, materials science, and metallurgy. These compounds are characterized by the existence of SiO₄ tetrahedra, and corner-shared Si-O networks if the compounds are rich in SiO₂. The Si-O-Si angle in silicates can vary from 109.47° to 180° depending on differences in the composition, temperature, and pressure [1]. The variations in the Si-O-Si angle affect the Si-O bond strength, that is, a decrease in the Si-O-Si angle increases the Si-O bond length [2]. A decrease in the Si-O-Si angle in silicates has been identified by various high-pressure experiments [3–6], and this decrease is associated with the mechanical weakening of silicates [6–8]. The existence of d-p π bonding between the Si 3d and lone pair of electrons on the bridging oxygen is thought to result in bending configuration of Si-O-Si bridging, and a shift from the stable angle weakens the Si-O bond [9]. Non-empirical calculation based on the Schrödinger equation is an appropriate tool for investigating the relationship among the Si-O-Si angle, Si-O bond length, Si-O bond

strength, and electronic structure. Newton and Gibbs [10] reported that the pyrosilicic acid molecule (H₆Si₂O₇, C_{2v} point symmetry) shows the energy minimum at the Si-O-Si angle of 145°, which was supported by the significant overlap of the 3d orbital of silicon and the 2p orbital of oxygen. However, Tsuneyuki [11] reported that straight Si-O-Si bridging minimizes the energy of the pyrosilicic acid molecule. Our previous work [12] revealed that these contradictory results were due to poor calculation accuracy. The use of the Møller–Plesset second-order perturbation method [13] and Pople’s split valence triple-zeta basis set [14, 15] yielded a bending geometry of the C_{2v} pyrosilicic acid molecule. However, the stable Si-O-Si angle for disiloxane (H₆Si₂O) calculated using the above-mentioned method above was still larger than the experimental value [16]. Past research [17, 18] failed to reproduce the molecular structure accurately. Csonka & Réffy [19] report that employing of CCSD (T) and triple-zeta basis set yields bent configuration for disiloxane molecule. However, they also report non-consistent behavior that more expanded basis set gives extremely high energy barrier for linearization of that molecule. However, non-empirical calculations are still an appropriate method for understanding

Figure 1. Geometry of (a) disiloxane molecule, $\text{H}_6\text{Si}_2\text{O}$, C_{2v} and (b) pyrosilicic acid molecule, $\text{H}_6\text{Si}_2\text{O}_7$, C_{2v} optimized using CCSD (T)/aug-cc-pVTZ. Upper and lower Figures are projected to two different planes parallel to vertical mirror. No particular physical significance is ascribed to those sphere sizes. The Figures are drawn using Winmostar [56].

vibration spectra of silicate liquids/glass [20–22]. In this study, I propose the appropriate model chemistry and basis set for disiloxane based on systematic calculations, and apply the method to pyrosilicic acid to discuss the nature of siloxane bridging.

2 COMPUTATIONAL PROCEDURE-DISILOXANE BENCHMARK

Molecular orbital calculations were performed using the Gaussian 16W code [23]. I first calculated the optimized structure of the disiloxane molecule (**Figure 1a**) by the Hartree-Fock (HF) method [24], second-order Møller–Plesset perturbation theory (MP2) [13, 25], coupled-cluster method including triplet excitation (CCSD (T)) [26–29], 4 density functional theories (DFT) [30, 31] (LSDA [32, 33], PBE [34], BLYP [35, 36], and TPSS [37]), and 2 hybrid functionals (PBE0 [38], B3LYP [39]). I also investigated the effect of the basis set using the Dunning-Huzinaga type full-double zeta basis set (D95) [40] augmented by polarization and two diffuse functions [41, 42], augmented Pople-type split-valence triple-zeta basis set (6-311) [14, 15], augmented Dunning-type correlation-consistent double/triple-zeta basis set with a frozen core (cc-pVnZ) [43–45] (note that this type is consistently adopted for post-HF calculations, so it is suboptimal for DFT), and Ahlrichs and co-workers type quadruple-zeta basis set (QZVP) [46]. To analyze the nature of the orbitals, I applied the natural bonding orbital (NBO) analysis method [47–49], because Mulliken population analysis [50] has been carried out considering the minimal-basis set [51]; consequently, this would lead to a confusing result [52, 53]. NBO analysis has emerged as an effective tool for studying the hybridization and covalency effect in molecular wave functions. The calculated molecular orbitals are decomposed and recomposed as a visualized bond orbital that represents the picture of interatomic bonds and lone pairs. Thus, the orbital energy of bonding, overlap-

Figure 2. Plots of the difference in (a) Si-O length, (b) Si-H length, and (c) Si-O-Si angle in disiloxane molecule ($\text{H}_6\text{Si}_2\text{O}$) compared with experimental data reported by Almenningen et al. [16]. Experimental values for Si-O length, Si-H length, and Si-O-Si angle are 1.634 Å, 1.486 Å, and 144.1°, respectively. Note that the number of basis (N_{basis}) in the Figure implies the number of contracted basis, not primitive functions.

weighted bond order, and atomic charge can be determined.

3 RESULTS AND DISCUSSION-DISILOXANE BENCHMARK

Figure 2 shows the deviations of the calculated structural parameters for the disiloxane molecule from the experimental data. The D95 and cc-pVDZ basis sets strongly overestimate the Si-O bond length. The 6-311 basis sets successfully reproduce the Si-O bond length; however, the singly augmented one, namely, 6-311++G (d,p)

Table 1. Optimized parameters for the C_{2v} pyrosilicic acid molecule using CCSD (T)/aug-cc-pVTZ.

Si-O _{br} (Å)	1.604
Si-O _{nbr} (Å)	1.647
O-H (Å)	0.957
Si-O-Si (degrees)	159.449
Si-O-H (degrees)	118.482

largely overestimates the Si-O-Si bond angle, while doubly/triply augmented ones slightly underestimate the bond angle. The larger pVTZ and QZVP basis sets seem to show good agreement with the experimental data. Consequently, precise calculation that includes Si-O-Si bridging needs at least Aug-cc-pVTZ-class high-cost basis sets. Model chemistries also influence the structural parameters. HF systematically underestimates bond lengths and overestimates bond angles. DFTs, except for LSDA, would result in longer bond lengths but fine bond angles. Despite the simple behavior of the GGAs and meta-GGA functional, LSDA shows inconsistent behavior, especially for singly polarization-augmented Pople-type split-valence triple-zeta basis. This inconsistency also appears in the calculations of the pyrosilicic acid molecule. A hybrid functional cures the bond lengths but increases the bond angle as compared to the post-HF calculations. MP2 and CCSD (T) generally show good agreement with the experimental data. It could be stated that the appropriate method pair for siloxane/silicate molecules is MP2/CCSD (T) with aug-cc-pVTZ or higher. The atomic charge calculated by NBO analysis is -1.33013 , 1.46050 , and -0.26868 for oxygen, silicon, and hydrogen, respectively. The contribution of the Si d-orbital to Si-O bonding is 2.04%, while Newton and Gibbs [10] reported an extremely large contribution of 28.5% in the case of the pyrosilicic acid molecule. This large discrepancy is thought

to be caused by use of the minimal basis set, which does not allow flexible presentation of the orbitals, in their study. Thus, the bent configuration of the disiloxane molecule would result from the balance of the oxygen valence orbital preference and the Coulombic repulsion between tetrahedrally coordinated hydrogen atoms, as described in our previous work [12].

4 COMPUTATIONAL PROCEDURE-PYROSILIC ACID

Hereafter, I use the CCSD (T)/Aug-cc-pVTZ method as reference and landscape calculation for the C_{2v} pyrosilicic acid molecule. (Figure 1b) I first calculated the optimized geometry of the C_{2v} symmetry pyrosilicic acid molecule at the CCSD (T)/aug-cc-pVTZ level, using z-matrix notation to keep the symmetry and to avoid the effect of hydrogen bonds. Second, I verified the differences among the model chemistries and basis sets for the stable structure and electronic structure of the pyrosilicic acid. The model chemistries and basis sets were the same as those used in the calculations of the disiloxane molecule. Then, I calculated the energy landscape of the C_{2v} pyrosilicic acid molecule with varying bond lengths between silicon and bridging oxygen (Si-O_{br} hereafter, similarly, the bond between silicon and non-bridging oxygen is abbreviated Si-O_{nbr}) and Si-O-Si bond angles. The atomic charge, bond index, and orbital energy assigned lone/bonding pairs are also determined in landscape calculations.

5 RESULTS AND DISCUSSION-PYROSILIC ACID

Table 1 displays the optimized parameters for the C_{2v} pyrosilicic acid molecule. We obtained the bent geometry for stable Si-O-Si

Figure 3. Plots of the differences in the optimized structural parameters of pyrosilicic acid molecule ($H_6Si_2O_7$, C_{2v}) from the CCSD (T) model using various model chemistries with the aug-cc-pVTZ basis set. Closed symbols for Si-O_{br}, Si-O_{nbr}, and O-H are in angstrom (left axis), and open symbols for Si-O-Si bridging angle are in degree (right axis)

Figure 4. Plots of the differences in (a) absolute atomic charge and (b) overlap-weighted bond index of pyrosilic acid molecule ($H_6Si_2O_7$, C_{2v}) using various DFTs with the aug-cc-pVTZ basis set in the CCSD (T) optimized configuration.

bridging, as in our previous study [12]. **Figure 3** shows the differences in the structural parameters of the pyrosilic acid molecule for different model chemistries, in comparison with those at the CCSD (T)/aug-cc-pVTZ level. The HF method, which is widely used in these types of studies, only shows a bent configuration when the minimal basis set is employed. That naturally prefers straight configuration no matter how more basis added. MP2 shows a similar structure as CCSD (T). LSDA yields a shorter Si-O length, longer O-H length, and reasonable Si-O-Si angle. Despite the inconsistent behaviors of LSDA, GGAs and meta-GGA systematically give a longer bond length. The equilibrium Si-O-Si angles are different, namely, PBE shows good reproducibility but the others do not. The Hybrid DFT cures the reproducibility of bond length but worsens that of the Si-O-Si angle. **Figure 4** shows the difference in the atomic charge and bond index of the pyrosilic acid molecule calculated using DFTs in comparison with those for the CCSD (T) electronic structure with the optimized geometry using CCSD (T). DFT generally leads to a lower charge, implying that charge transfer will be underestimated. These smaller atomic charges are consistent with the smaller bridging angle, and the hybrid DFT increases the bridging angle while decreasing the bond length. Surprisingly, GGAs and meta-GGA yield a larger overlap-weighted bond index whereas the bond lengths generally lengthen. The lack of an exact exchange term would lead to a larger bond index.

Figure 5. (a) Plots of the differences in the optimized structural parameters of pyrosilic acid molecule ($H_6Si_2O_7$, C_{2v}) from the aug-cc-pVTZ basis set using various basis sets with the CCSD (T) model. Note that Pople-1p, 2p, 3p denotes augmentation using 1, 2, and 3 polarization and diffusion functions, respectively. Closed symbols for $Si-O_{br}$, $Si-O_{nbr}$, and O-H are in angstrom (left axis), and open symbols for Si-O-Si bridging angle are in degree (right axis). (b, c) Plots of the differences in (b) absolute atomic charge and (c) overlap-weighted bond index of pyrosilic acid molecule ($H_6Si_2O_7$, C_{2v}) using various basis sets in the CCSD (T)/aug-cc-pVTZ optimized configuration.

Figure 5a shows the differences in the equilibrated structures using various basis sets in comparison with the results for aug-cc-pVTZ using CCSD (T). **Figures 5b and 5c** show the differences in the atomic charges and bond index in CCSD (T)/aug-cc-pVTZ geometry for various basis sets. Augmentation to Pople's split-valence triple-zeta basis set significantly lowers bridging angle with keeping bond length, whereas it just cures the reproducibility in the case of the disiloxane molecule. The augmented Dunning-Huzinaga-type full-double-zeta basis shows a larger bond length and a smaller bridging angle, while the bond index is smaller and

Figure 6. Total energy landscape of pyrosilic acid molecule (C_{2v}) for varying Si-O_{br} lengths and Si-O-Si angles at the CCSD (T)/aug-cc-pVTZ level. Open star indicates the point of lowest energy.

atomic charge is larger. Dunning's correlation-consistent-type double-zeta basis set shows a significantly longer bond distance and lower bond index, implying weaker bonding. The increase in the number of contracted Gaussians typically leads to greater accuracy, but it does not hold for an intermediate-size basis set, namely, basis sets smaller than cc-pVTZ.

Figure 6 displays the total energy landscape of the pyrosilic acid molecule (C_{2v}) for varying Si-O_{br} lengths and Si-O-Si angles using the CCSD (T)/aug-cc-pVTZ level. There are gentle curves around the stable angles for each bond length comparing with bond-length direction. The stable angle for each bond length decreased with increasing Si-O_{br} bond length. Thus, the energy landscape becomes an inclined ravine from shorter bond length/larger bridging angle to larger bond length/smaller bridging angle. **Figures 7a and 7b** show the atomic charges of silicon and bridging oxygen, respectively. The absolute values of the atomic charges increased with increasing bond length and bridging angle. **Figure 7c** displays the electrostatic energy landscape calculated using the atomic charge. The electrostatic energy decreases with increasing bridging angle and decreasing Si-O_{br} bond length. Because the repulsion between two tetrahedra increases the energy for the bent configuration, the

Figure 7. Contour maps of (a) atomic charge of silicon (q_{Si}), (b) atomic charge of bridging oxygen (q_{O}), (c) electrostatic potential calculated by atomic charge (E_{esp}) in MJ/mol, and (d) bond index of Si-O_{br} bonding with varying Si-O_{br} bond lengths and Si-O-Si angles.

Figure 8. Energy landscapes of (a) Si-O_{br} σ -bonding orbital, (b) lone pair orbital of the bridging oxygen on the symmetry axis, (c) lone pair orbital of the bridging oxygen perpendicular to the symmetry axis, and (d) sum of valence orbital energies (two different lone pairs, two symmetric σ -bonding, and doubled considering α/β electrons) with varying Si-O_{br} bond lengths and Si-O-Si angles in MJ/mol.

increase in the absolute atomic charge with decreasing Si-O_{br} bond length lowers the energy. **Figure 7d** shows the bond index of the Si-O_{br} bond contour map for varying Si-O-Si bond angles and Si-O_{br} bond lengths. The bond index increases by not only the decrease in the bond length but also the increase in bond angle. The orbital energy of Si-O_{br} σ -bonding, calculated by NBO analysis, decreases with increasing bond angle and decreasing bond length. **Figure 8a** displays the energy landscape of the Si-O_{br} bonding orbital. These changes simply correspond to the weakening of σ -bonding with increasing hybridization index and decreasing Si-O_{br} bond length, with increasing Si-O-Si bridging angle. The orbital energy of the lone pair orbital of bridging oxygen, which is on the symmetry axis, decreases with increasing bond length and decreasing bond angle (**Figure 8b**). **Figure 8d** shows the energy landscape summing the energy of the valence orbital of bridging oxygen (**Figures 8a-c**). The energy sum decreases slightly with increasing bond angle and remarkably with decreasing bond length, because changes in the orbital energy of lone pair are much larger than that of the two σ -bonding orbitals. The sum of the valence orbital energy and

electrostatic energy calculated by atomic charge, which shows conflicting behavior with varying Si-O_{br} bond lengths and Si-O-Si angles, can lead to energy minima corresponding to the changes in the Si-O-Si angle for certain bond lengths (**Figures 9a-c**). There is no energy minimum for the Si-O_{br} bond length of 1.54 Å (**Figure 9a**). However, the minimum appears at 160° for the Si-O_{br} bond length of 1.60 Å, and the angle correspond to the energy minimum decreases with increasing Si-O_{br} bond length (**Figures 9b, c**). The existence of d-p π bonding is negligible in these calculations because a sum of occupancies of all d orbitals of Si is 0.05 whereas Newton and Gibbs [10] report significant contribution (up to 33%) of Si d-orbital to Si-O bonding. Once d-orbital becomes valence orbital, the d-p π bonding can be observed in X-ray diffraction experiment [54, 55], however Si d-orbitals are Rydberg (remaining) orbitals. The sum of these two competing energies still cannot explain the minimum in the Si-O_{br} bond length; however, this might be explained by short-range repulsive interactions.

Figure 9. Plots of energy calculated by summing electrostatic potential of atomic charges and sum of the valence orbital energy of bridging oxygen at varying Si-O-Si angles for (a) Si-O_{br} bond length of 1.54 Å, (b) Si-O_{br} bond length of 1.60 Å, and (c) Si-O_{br} bond length of 1.72 Å.

6 CONCLUSION

I present the results and discussions for molecular orbital calculations of disiloxane and pyrosilic acid molecules. The post-HF method and a larger basis set (at least, aug-cc-pVTZ) would be necessary for accurate calculations of the disiloxane molecule. In contrast to past molecular orbital studies, there is no significant occupancy in the Si-3d orbitals. The total energy landscape of the C_{2v} pyrosilic acid molecule is calculated by using the coupled cluster method concerning three excited electrons and aug-cc-pVTZ basis set. The stable bond length for Si-O_{br} is 1.604 Å, and the stable Si-O-Si angle is 159.449°. There are gentle curves around the stable angles for each bond-length comparing with bond-length direction. The stable angle for each bond length decreases with increasing Si-

O_{br} bond length. The weakening of the Si-O_{br} bond with decreasing Si-O-Si bond angle can be explained by the decrease in the bond index and the increase in the orbital energy for Si-O_{br} σ-bonding. Consequently, hybridization of the valence electrons of the bridging oxygen with decreasing Si-O-Si angle weakens the Si-O_{br} σ-bonding. Electrostatic potential favors a straight configuration because of the repulsion between SiO₄ tetrahedra, while the valence electrons of the bridging oxygen favor a bent configuration. These two competing behaviors can explain the bent configuration of pyrosilic acid without concerning d-p π bonding.

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REFERENCES

- [1] M. O’Keeffe, B. G. Hyde, *Acta Crystallogr. B*, **34**, 27 (1978). DOI:10.1107/S0567740878014557
- [2] G. V. Gibbs, C. T. Prewitt, K. J. Baldwin, *Z. Kristallogr.*, **145**, 108 (1977). DOI:10.1524/zkri.1977.145.1-2.108
- [3] R. A. B. Devine, R. Dupree, I. Farnan, J. J. Capponi, *Phys. Rev. B*, **35**, 2560 (1987). DOI:10.1103/PhysRevB.35.2560
- [4] R. M. Hazen, L. W. Finger, R. J. Hemley, H. K. Mao, *Solid State Commun.*, **72**, 507 (1989). DOI:10.1016/0038-1098(89)90607-8
- [5] T. Sakamaki, Y. Wang, C. Park, T. Yu, G. Shen, *J. Appl. Phys.*, **111**, 112623 (2012). DOI:10.1063/1.4726246
- [6] D. Wakabayashi, N. Funamori, T. Sato, *Phys. Rev. B*, **91**, 014106 (2015). DOI:10.1103/PhysRevB.91.014106
- [7] A. Navrotsky, K. L. Geisinger, P. McMillan, G. V. Gibbs, *Phys. Chem. Miner.*, **11**, 284 (1985). DOI:10.1007/BF00307406
- [8] K. N. Matsukage, Y. Nishihara, F. Noritake, K. Kawamura, N. Tsujino, M. Sakurai, Y. Higo, J. Nakajima, A. Hasegawa, E. Takahashi, *Am. Mineral.*, **100**, 1856 (2015). DOI:10.2138/am-2015-5240
- [9] D. W. J. Cruickshank, *J. Chem. Soc.*, **0**, 5486 (1961). DOI:10.1039/JR9610005486
- [10] M. D. Newton, G. V. Gibbs, *Phys. Chem. Miner.*, **6**, 221 (1980). DOI:10.1007/BF00309858
- [11] S. Tsuneyuki, *Mol. Eng.*, **6**, 157 (1996). DOI:10.1007/BF00161726
- [12] F. Noritake, K. Kawamura, *J. Comput. Chem. Jpn.*, **14**, 124 (2015). DOI:10.2477/jccj.2015-0009
- [13] C. Möller, M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934). DOI:10.1103/PhysRev.46.618
- [14] A. D. McLean, G. S. Chandler, *J. Chem. Phys.*, **72**, 5639 (1980). DOI:10.1063/1.438980
- [15] K. Raghavachari, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1980). DOI:10.1063/1.438955

- [16] A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg, M. Trætteberg, *Acta Chem. Scand.*, **17**, 2455 (1963). DOI:10.3891/acta.chem.scand.17-2455
- [17] J. Sauer, B. Ĺurawski, *Chem. Phys. Lett.*, **65**, 587 (1979). DOI:10.1016/0009-2614(79)80297-3
- [18] M. R. Bär, J. Sauer, *Chem. Phys. Lett.*, **226**, 405 (1994). DOI:10.1016/0009-2614(94)00733-0
- [19] G. I. Csonka, J. Réffy, *Chem. Phys. Lett.*, **229**, 191 (1994). DOI:10.1016/0009-2614(94)01029-3
- [20] J. D. Kubicki, D. Sykes, *Phys. Chem. Miner.*, **19**, 381 (1993). DOI:10.1007/BF00202975
- [21] C. Carteret, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **64**, 670 (2006). DOI:10.1016/j.saa.2005.08.004
- [22] I. T. Moraru, P. M. Petrar, G. Nemeş, *J. Phys. Chem. A*, **121**, 2515 (2017). PMID:28282141, DOI:10.1021/acs.jpca.7b01208
- [23] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- [24] C. C. J. Roothaam, *Rev. Mod. Phys.*, **23**, 69 (1951). DOI:10.1103/RevModPhys.23.69
- [25] M. Head-Gordon, J. A. Pople, M. J. Frisch, *Chem. Phys. Lett.*, **153**, 503 (1988). DOI:10.1016/0009-2614(88)85250-3
- [26] J. Čížek, in *Advances in chemical physics*, Ed. P. C. Hariharam (Wiley Interscience, New York), **14**, 35 (1969).
- [27] G. D. Purvis, III, R. J. Bartlett, *J. Chem. Phys.*, **76**, 1910 (1982). DOI:10.1063/1.443164
- [28] G. E. Scuseria, C. L. Janssen, H. F. Schaefer, III, *J. Chem. Phys.*, **89**, 7382 (1988). DOI:10.1063/1.455269
- [29] G. E. Scuseria, H. F. Schaefer, III, *J. Chem. Phys.*, **90**, 3700 (1989). DOI:10.1063/1.455827
- [30] P. Hohenberg, W. Kohn, *Phys. Rev.*, **136**, 3B, B864 (1964). DOI:10.1103/PhysRev.136.B864
- [31] W. Kohn, L. J. Sham, *Phys. Rev.*, **140**, 4A, A1133 (1965). DOI:10.1103/PhysRev.140.A1133
- [32] J. Slater, *The self-consistent field for molecular and solids, quantum theory of molecular and solids* (McGraw-Hill, New York), **4** (1974).
- [33] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.*, **58**, 1200 (1980). DOI:10.1139/p80-159
- [34] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865 (1996). PMID:10062328, DOI:10.1103/PhysRevLett.77.3865
- [35] A. D. Becke, *Physical Review A*, **38**, 3098 (1988). DOI:10.1103/PhysRevA.38.3098
- [36] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, **37**, 786 (1988).
- [37] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.*, **91**, 146401 (2003). PMID:14611541, DOI:10.1103/PhysRevLett.91.146401
- [38] C. Adamo, V. Barone, *J. Chem. Phys.*, **110**, 6158 (1999). DOI:10.1063/1.478522
- [39] A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993). DOI:10.1063/1.464913
- [40] T. H. Dunning, Jr., P. J. Hay, in *Modern theoretical chemistry, Ed. H. F. Schaefer III* (Plenum, New York), **3**, 1 (1977).
- [41] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comput. Chem.*, **4**, 294 (1983). DOI:10.1002/jcc.540040303
- [42] M. J. Firsich, J. A. Pople, J. S. Binkley, *J. Chem. Phys.*, **80**, 3265 (1984). DOI:10.1063/1.447079
- [43] T. H. Dunning Jr., *J. Chem. Phys.*, **90**, 1007 (1989).
- [44] R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.*, **96**, 6796 (1992). DOI:10.1063/1.462569
- [45] E. R. Davidson, *Chem. Phys. Lett.*, **260**, 514 (1996). DOI:10.1016/0009-2614(96)00917-7
- [46] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **7**, 3297 (2005). PMID:16240044, DOI:10.1039/b508541a
- [47] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.*, **102**, 7211 (1980). DOI:10.1021/ja00544a007
- [48] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.*, **83**, 735 (1985). DOI:10.1063/1.449486
- [49] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, **88**, 899 (1988). DOI:10.1021/cr00088a005
- [50] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955). DOI:10.1063/1.1740588
- [51] W. J. Hehre, R. F. Stewart, J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). DOI:10.1063/1.1672392
- [52] B. T. Thole, P. T. Duijnen, *Theor. Chim. Acta*, **63**, 209 (1983). DOI:10.1007/BF00569246
- [53] J. Cisłowski, *J. Am. Chem. Soc.*, **111**, 8333 (1989). DOI:10.1021/ja00204a001
- [54] T. Yamanaka, Y. Nakamoto, F. Takei, M. Ahart, H. Mao, R. J. Hemley, *J. Appl. Phys.*, **119**, 075902 (2016). DOI:10.1063/1.4941383
- [55] T. Yamanaka, Y. Nakamoto, M. Ahart, H. Mao, *Phys. Rev. B*, **97**, 144109 (2018). DOI:10.1103/PhysRevB.97.144109
- [56] N. Senda, *Idemitsu Technol. Rep.*, **49**, 106 (2006).