

Comprehensive Electronic Structure of Si Nanocrystal

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Abstract

The properties of oxidized surface and core have been investigated. using of STO-3G(Slater Type Orbitals)foundation is made to be able to compare RHF(Roothaan-Hartree-Fock)method with semiempirical methods using the complete neglect of differential overlap (CNDO)which uses Slater type orbitals (STO). outcomes revealed that the electronic properties converge to some limit as the size of the nanocrystal increases. Increasing the size of the core of a nanocrystal resulted in anraise of energy gap (3.54 eV), valance band width (14.21 eV), and cohesive energy (9.15 eV).The lattice constant of the core and oxidized surface parts illustrate a decreasing movement as the nanocrystal increases in size that converges to 0.528 nm. Surface and core convergence to the same lattice constant reflects good adherence of oxide layer at the surface.

The nanocrystal surface shows smaller gap (1.08 eV) and higher valence band whilst compared to the core part due to the oxygen atoms at the surface the diminution of structural symmetry.

KeyWords:energy gap,cohesive energy,valance band width.

Subject Classification : QC 170-197

Introduction

Si nanocrystals(nc_s) have claimed a lot of interest in the last years due to the promising applications in advanced electronic devices based on nanoscale technology [1]

Silicon nanocrystals have many industrialized applications. It is the base of elements of most semiconductor devices; the largest part importantly integrated circuits[2] Silicon which is commonly used in semiconductor devices because it remains a native oxide is easily grown in a furnace and a better semiconductor/dielectric interface forms than several other material[3,4]. The applications of silicon are in the flash memory, photonic applications, lighting applications, solar cells, bioapplications and sensors applications [4,5]. Fully compatible with the existing technologies makes of Si nanocrystals easier and more attractive than other kinds of nanoparticles [6,7].

In a Si(nc_s), the greater part of Si atoms are on or near the surface and likely to be affected by surface effects or passivation, which can, in turn, significantly modify its electronic structure. Actually, modern theoretical studies have shown that the surface can heavily affect the electronic property of Si (nc_s)[8, 9].

The chemical and physical properties of solids, molecules and nanomaterials depend on a subtle interchange of the spatial collection of the ions and the calculations distribution of electrons density, which afford the binding forces of the structure[10]. Ab-Initio is a Latin term for "first principles"[11]. The aim of ab-initio methods is the choice of what is well-known like the model chemistry[12]. The Quantum model chemistry have described a mathematical approach to solving the Schrödinger equation for any particle[13,14]. In choosing the Quantum chemistry, one proposes a altitude of theory (such as a Hartree-Fock method) and a basis set (described earlier)[15]. At its most basic level, ab initio methods affirm that if one knows the molecule, one should be able to carry out a complete results of that molecule completely from mathematical principles [16-22].

we have used Gaussian (G03) program, this program predicts the electronic properties

$$\sum_i C_i \int \bar{X}_\mu^*(1) \hat{F}(1) \hat{X}_i(1) d\tau_1 = \sum_i C_i \int \hat{X}_\mu^*(1) \hat{X}_i(1) d\tau_1 \dots\dots\dots (4)$$

The Hartree -Fock Roothaan equation can be written in the matrix form:

$$\sum_\mu F_\mu C_i = \sum_i S_\mu C_i \dots\dots\dots (5)$$

Or in simple form as matrices

$$FC = SC \dots\dots\dots (6)$$

including the energies, molecular structures and vibration frequencies for molecular systems, Gaussian is a federally registered trademark of Gaussian and Gauss view program supports G03 to draw the result.[6 , 23].

Theory

The approaches are based on fundamental physical constants like the mass and charge of an electron and no atom definite parameters are introduced, these methods are called "ab-initio" or "first principles"[2, 3,24]

Ab-Initio methods are independent of any experimental data, but can using values of several physical constants, such as, velocity of light, Planck's constant, electrons and nuclei masses, Ab-initio methods have advanced sufficiently to give the researches with calculations of molecular properties, this application requires a detailed algorithm or program to transform the mathematical formalism into instructions appropriate for implementation on computer [3,4,37]

Ab-initio methods are based on the variation theory which requires an evaluation of energy:

$$E(\psi) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \dots\dots\dots (1)$$

Ab-initio methods are used for any type of structure, closed or open shell systems of atoms and molecules to explain the dynamics of systems studied and to work out the molecular properties from the creation with out any neglect, such as, excited electronic states, structure properties and energies [4,38] While Roothaan Equation transform the Hartree-Fock equations into the Roothaan equations by introducing a foundation set, refer to the atomic orbital basis functions as \bar{X} which have the expansion [37, 39]:

$$X_i = \sum_{\mu=1}^K C_{\mu i} \bar{X}_\mu \dots\dots\dots (2)$$

For every spin orbital i .therefore:

$$\hat{F}(1) \sum_i C_i \bar{X}_i(1) = \sum_i C_i \bar{X}_i(1) \dots\dots\dots (3)$$

Multiplying equation (3) by $\bar{X}_\mu^*(1)$ from left and integrating together sides , obtained :

Where $S_{\mu i}$ is a diagonal matrix of the orbital energies ϵ_i , and S , F are the overlap and Fock matrix , respectively , can be defined as :

$$S_{\mu i} = \int \bar{X}_\mu^*(1) \bar{X}_i(1) d\tau_1 \dots\dots\dots (7)$$

$$F_{\mu i} = \int \bar{X}_\mu^*(1) \hat{F}(1) \bar{X}_i(1) d\tau_1 \dots\dots\dots (8)$$

Fock matrix elements in atomic orbital basis are written as:

$$F_{\mu} = \langle X_{\mu} | \hat{h} + \sum_{j=1}^{n/2} (2\hat{J}_j - \hat{K}_j) | X_{\mu} \rangle \quad \dots\dots(9)$$

$$F_{\mu} = h_{\mu} + \sum_{j=1}^{n/2} [2(\mu / ij) - (\mu j / j \epsilon)] \dots\dots(10)$$

Solving the eigenvalue equation by diagonalizing Fock matrix, and the solution of Hartree-Fock- Roothaan equations call the self consistent field (SCF) method.

The large unit cell (LUC) is various kind of super cell methods, was recommended and first applied for the examination of electronic band structure of bulk materials and principally in semiconductors elemental in the 70s of the last century [4,5,26].

Energy gap is the most essential electronic properties of structures, it's given by formula [31]:-

$$E_g = E_{LUMO} - E_{HOMO} \dots\dots(11)$$

Where E_g is the forbidden energy gap.

E_{LUMO} is the energy of the lowest unoccupied molecular orbital.

E_{HOMO} is the energy of the highest occupied molecular orbital.

The total energy calculation of the large unit cell given the result of cohesive energy, the large unit cell is unruffled of (8, 16, 54, 64, 128, 216 and

250 atoms) for Si (nc_s) LUC. The cohesive energy E_{Coh} is given by [16, 25].

$$E_{Coh} = (E_{Tot} / N) - E_{free} - E_{One} \dots\dots(12)$$

Where E_{Tot} : is the total energy

N: is the number of atoms

E_o : is the correction of cohesive energy for the zero- point motion of the nuclei, this is a pure quantum mechanical effect and it is straight related to the uncertainty principle [27]. Its value is 0.07eV for Si [28], E_{free} : is the free atom energy, which means the energy of one atom for Si (nc_s). And equals (-285.7035832) in the present work. The cohesive energy is the ground state binding energy, atomic structure and cohesive energy are basically based on Linear Combination of Atomic Orbitals model [29]. A crystal is formed by independent atoms according to this model, number of orbital still the same and retains much of their atomic character, on the other hand, there are continuous changes in the energies of the orbital with atomic separation, as the atoms are brought closer together, the orbits instigate to interact and hence their bond strength modifies which determines eventually the physical properties of the crystal [30].

The relation between the number of atoms per LUC and cohesive energy is given in Fig. (1).

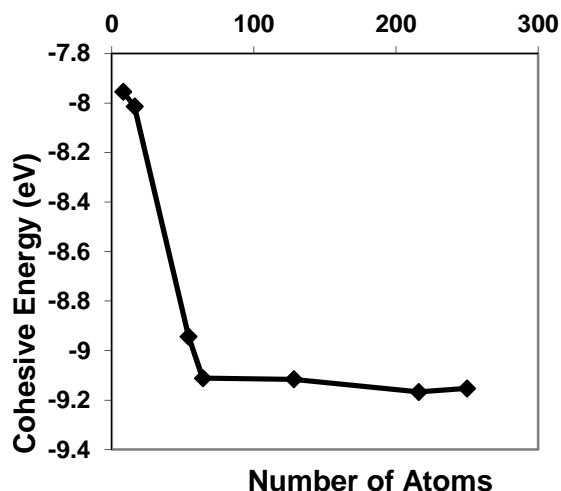


Fig.(1) Cohesive energy as a function of number of atoms for Si (nc_s) LUC.

Fig.(1) shows that the absolute value of the cohesive energy increases with increasing the number of atoms per LUC, reaching to 64 atoms in which the cohesive energy tends to stabilize, with increasing the number of atoms, due to the small silicon particle revealed more suspension bond and a high activation energy, the atoms on the particle's surface reconstructed to a more stable formation.

The Comprehensive Electronic Structure

The electronic structure properties of Si (nc_s) are calculated in table (1-a , - b , - c).

Table (1-a)]The electronic structure of Si (nc_s).

Property	Si (nc_s) Core Bart LUC			
	8 Atoms	16 atoms	54 atoms	64 atoms
Cohesive energy(eV)	-7.95	-8.01	-8.94	-9.11
Energy gap(eV)	2.74	2.83	3.29	3.533
Valence band width(eV)	13.65	13.73	14.23	14.22
Lattice constant (nm)	0.541	0.539	0.533	0.528

Table (1-b)

Property	Si (nc_s) Core Bart LUC		
	128 atoms	216 atoms	250 atoms
Cohesive energy(eV)	-9.11	-9.16	-9.15
Energy gap(eV)	3.52	3.57	3.54
Valence band width(eV)	14.21	14.22	14.21
Lattice constant (nm)	0.528	0.528	0.528

Table (1-c)

Property	Si (nc _s) Core Bart LUC	
	8 atoms	64 atoms
Cohesive energy(eV)	-7.78	-9.01
Energy gap(eV)	1.40	1.08
Valence band width(eV)	19.57	19.60
Lattice constant (nm)	0.534	0.528

In table (1-a,b ,c), it is shown that the core part has a converging changeable energy gap, valence band width and cohesive energy (absolute value). These fluctuations are correlated with the geometry of the nanocrystal. The surface part of nanocrystal has been controlled by the energy gap with the surface having damping oscillatory consecutive negative and positive layer charges. The core part has higher symmetry than the surface part with bigger energy gap and shorter valence band. Surface and core parts have the same lattice constant that in the

order of reflects the good adherence of oxide layer at the surface. The band gap which has high value can be attributed to the approximations complicated (the self-interaction of the electrons in the Hartree energy is fully removed) in HF method.

Also we can compare between the result of 8 atoms LUC of the core and the oxygenated (001)-(1x1) surface as shown in the table (2), and between the result of 64 atoms LUC of the core and the oxygenated (001)-(1x1) surface as shown in the table (3).

Table (2) Electronic structure for 8 atoms LUC of the core and the oxygenated (001)-(1x1) surface of silicon (nc_s).

Property	8 atoms LUC Of the core	8 atoms LUC oxygenated (001)-(1x1) surface
Energy gap(eV)	2.74	1.40
Valence band width(eV)	13.65	19.57
Lattice constant (nm)	0.541	0.534

Table (3) Electronic structure for 64 atoms LUC of the core and the oxygenated (001)-(1x1) surface of silicon (nc_s).

Property	64 atoms LUC Of the core	64 atoms LUC oxygenated (001)-(1x1) surface
Energy gap(eV)	3.53	1.08
Valence band width(eV)	14.22	19.60
Lattice constant (nm)	0.528	0.528

This comparison shows that the energy gap decreases in the surface calculations, and the valence band width increases in the surface calculations. This result because of the broken bonds and the discontinuity by the side of the surface and the existence of new type of atoms (oxygen atoms). The calculated value of the energy gap of (1.08 eV) using a 64 atoms LUC of the oxygenated (001)-(1x1) surface is in good agreement with the experimental value of (1.15 eV)[15]. So the value of the energy gap is

controlled by the surface, in view of the fact that this gap is extremely lower for the surface [32]. The calculated value for the valence band width of (19.60 eV) using a 64 atoms LUC of the oxygenated (001)-(1x1) surface is in good agreement with the experimental value of (21 eV)[33]. 3-D structure diagrams for the (64, 128, 216, 250) atoms LUCs of Si (nc_s) core using GView program are shown in Figs. (2) – (5). All atoms in the LUCs are in periodic boundary conditions.

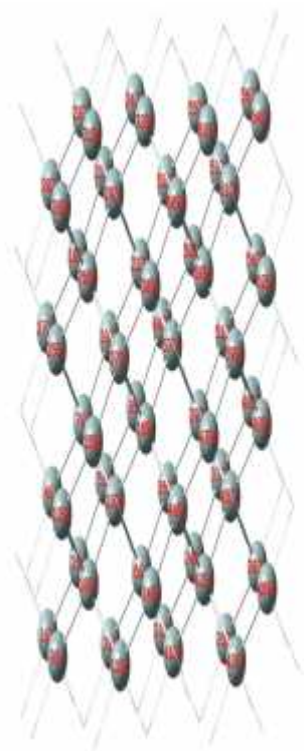


Fig.(2). The structure of 64 atoms LUC in periodic boundary conditions.

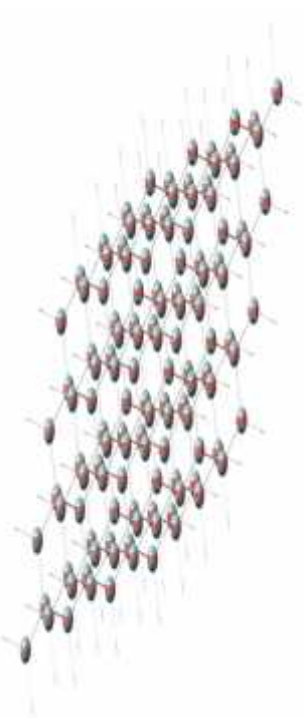


Fig.(3).The structure of 128 atoms LUC in periodic boundary condition.

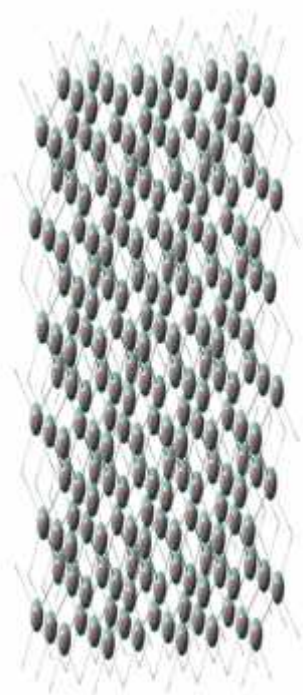


Fig.(4).The structure of 216 atoms LUC in periodic boundary conditions.

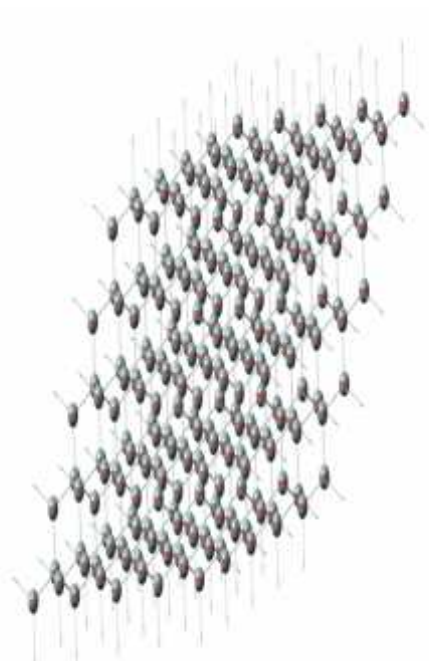


Fig.(5).The structure for 250 atoms LUC in periodic boundary conditions.

In Fig.(2) and Fig.(4), the structure of LUC is a compound of the Bravais cell of $\text{Si}(\text{nc}_s)$, this is a cubic and the face (001) which identical to the other faces of the surface. In Fig.(3) and Fig.(5), the structure of LUC is a compound of the primordial

cell of $\text{Si}(\text{nc}_s)$, this is a rectangular and the face (111) must be studied.

For the (001)-(1x1):O surface, the two most-conceivable configurations are the following: (a)

the “ketone” arrangement, in which the O atom is double -bonded to a particular surface Si atom(Si=O), and (b)the “ether,” arrangement in which the O atom bridges two surface Si atoms and makes a single bond to all of Si- O- Si

[34].This work calculated the electronic structure of 2D- slab of 8 and 64 oxygenated (001)-(1x1) surfaces (ketone arrangement). These structures are given in Fig.(6) and Fig.(7), respectively.



Fig.(6) 2D Slab calculations of (001) oxygenated a^2 area surface of $\text{Si}(\text{nc}_s)$.



Fig.(7) 2D Slab calculations of (001) oxygenated $4a^2$ area surface of $\text{Si}(\text{nc}_s)$.

In the double- bonded oxygen arrangement, an O atom is put over the top-layer Si atom, the space between the O atom and the top-layer Si atom for

the double- bonded oxygen arrangement is (0.154 nm).

Conclusions

1- The current method has a threefold outcome. The method be able to find the converged electronic formation of bulk, surface, and nanocrystals.

2- The lattice constant of all size of core Si (nc_s) decreases with increasing the number of atoms in the LUC. In the surface calculations, unit lattices that are nearer to the surface undergo lattice constant expansion in a direction vertical to the surface.

3- The present results show that the energy gap, valence band width and the cohesive energy (absolute value) increases as the Si (nc_s) LUC size

increases, for the core part. While the energy gap of oxygenated (001)-(1×1) surface decreases with increasing the LUC size.

4- The surface part of the nanocrystal have been controlled by energy gap. The core part has higher symmetry than the surface part with smaller energy gap and wider valence band.

5- Lattice constant for surface and core parts approximately is the same which reflects the good adherence of oxide layer at the surface.

References

[1] M. Luppi, "Multiple Si=O Bonds at the Silicon Cluster Surface", *Journal of Applied Physics*, 94(3), (2003).

[2] I. Z. Hassan, "Semiempirical Self-Consistent Field Calculations of III-V Zinc-Blende Semiconductors", Ph.D. Thesis, College of Science, Al-Nahrain University, (2001).

[3] P. Huang and E. A. Carter, "Advance in Correlated Electronic Structure Methods for Solids, Surface, and Nanostructures", *Rev. Phys. Chem.*, 59 (361), (2008).

[4] W. Hehre, L. Random, P. Schleyer, and J. Pople, "Ab-initio Molecular Orbital Theory", John Wiley and Sons (1986).

[5] I. O. Radi, Mudar A. Abdulsattar, and Ahmed M. Abdul-Lettif, *Phys. Status Solidi B* 244, 1304 (2007).

[6] Gaussian 03, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K.

Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, (2003).

[7] L. C. Kimerling, L. D. Negro, M. Stolfi, J. H. Yi, J. Michel, X. Duan, E. H. Sargent, T. W. Chang, V. Sukhovatkin, J. Haavisto, and J. Leblanc, "Si-Rich Dielectrics for Active Photonic Devices", Boston University, (2009).

[8] L. Pavesi, and R. Turan, "Si nanocrystals", Wiley-Vch, (2010).

[9] C. Delerue, M. Lannoo, and G. Allan, *Phys. Stat. Sol. (b)*, 1(115), (2001).

[10] L. Khriachtchev, "Silicon Nanophotonics", University of Helsinki, Finland, (2009).

[11] M. Fujii, Y. Yamaguchi, Y. Takase, K. Ninomiya, and S. Hayashi, *Applied Physics Letters*, 85(7), (2004).

[12] M. Nishida "Electronic Structure of Silicon Quantum Dots: Calculations of energy-gap red shifts due to Oxidation", *Journal of Applied Physics*, 98(023705), (2005).

[13] A. R. Wilkinson, "The Optical Properties of Silicon Nanocrystals and the Role of Hydrogen Passivation", Ph.D. Thesis, The Australian National University, (2006).

[14] C. Kittel, "Introduction to Solid State Physics", John Wiley and Sons, (2005).

- [15] C. Kittel, Introduction to Solid State Physics, 5th ed. John Wiley and Sons, New York, (1976).
- [16] D. A. Neamen, "Semiconductor Physics and Devices", University of New Mexico, (2003).
- [17] S. K. Tewksbury, "Semiconductor Materials", West Virginia University, (1995).
- [18] S. M. Sze and K. K. Ng, Physics of semiconductor devices, 3rd edition, Wiley (2007).
- [19] K. M. Lebecki¹, M J Donahue² and M W Gutowski¹, " Periodic boundary conditions for demagnetization interactions in micromagneticsimulations", Institute of Physics, (2007).
- [20] A. Arnoldy, M. Ehrhardt, and I. Sofronov, Comm. Matm. SCI., 1(3) , (2003).
- [21] C. Lamberti, " Characterization of Semiconductor Heterostructures and Nanostructures", Elsevier publications , 2008.
- [22] H. Fehske, R. Schneider, and A. Weibe , " Computational Many Particle Physics", Springer, Berlin Heidelberg, 2008.
- [23] Chemistry. Ncsm. Edubook //chap7//Ab-Initio.Pdf.
- [24] V. I. Minkin, Glossary of terms used in theoretical organic chemistry, Pure Appl. Chem., Vol. 71, No. 10, p. 1919, 1999.
- [25] O. Pulci, E. Degoli, F. Iori, M. Marsili, M. Palummo, R. Del Sole, and S. Ossicini, Superlattices and Microstructure, 47(178), (2010).
- [26] B. A. Mamedov, Evaluation of Two-Center Overlap Integral in Molecular Coordinate System over Slater Type Orbitals, Chinese Journal of Physics, V.42, no.2, 2004.
- [27] P. Norman and L. Ojamae, "Laborations in quantum chemistry", University of Linkoping, (2004).
- [28] W.R.L.Lambrecht, O.K.Andersen, Phys. Rev.B, 34 (2439), (1986).
- [29] X.P.Li, D.M.Ceperley and Richard.M. Martin, Physical Review B, 44(19), (1991).
- [30] S.K. Lamichhane, Kathmandu University Journal of Science, 5(I), (2008).
- [31] K.C. Fang, C.I.Weng, and S.P. Ju, Nanotechnology, 7(3909), (2006).
- [32] I. Kwon, R. Biswas, C.Z. Wang, k. m. Ho, and C.M. Soukoulis, Physical Review B, 49(11), (1993).
- [33] M. HeidariSaani, M. Kargarian, and A. Ranjbar, Phys. Rev. B 76(035417), (2007).
- [34] A.D.Zdetsis, Rev.Adv.Mater.Sci., 11(56), (2005).
- [35] D.E.Jiang and E.A.Carter, Physical Review B, 72(16), (2005).
- [36] S.J. Sque, R. Jones, and P.R. Briddon, Phys. Rev. B 73(085313), (2006).
- [37] 43.E.F.Valeev and C.Sherrill; "The Diagonal Born-Oppenheimer Correction beyond the Hartree-Fock Approximation", Journal of Chemical Physics, 118 , 9, (2003).
- [38] A.K.B.Bender; "Structure Modeling of Aluminosil-Sesquioxanes", Ph.D. Thesis, Berlin, Germany, (2000).
- [39] V.N.Glushkov ; "Alternative Techniques in open-shell SCF Theory", International Journal of Quantum Chemistry , 99 , pp.236-246 , (2004).

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