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Ab initio study of high tridymite by the formalism generator coordinate Hartree–Fock

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Abstract

The Generator Coordinate Hartree–Fock (GCHF) Method is applied to generate extended 14s 8p and 17s 11p Gaussian basis sets for the atoms O and Si, respectively. The role of the weight functions in the assessment of the numerical integration range of the GCHF is shown. The Gaussian basis sets are contracted to [6s4p] O atom and [8s5p] Si atom by the Dunning's segmented contraction scheme. To evaluate the quality of our contracted [6s4p] and [8s5p] bases in molecular calculations we accomplish calculations of total and orbital energies in the Hartree–Fock–Roothaan method for O_2 and SiO molecules. We compare the results obtained with the our (14s 8p) and (17s 11p) bases sets with the of 6-311G basis and with values from the literature. The addition of one d polarization function in the silicon basis and its utilization with the basis for oxygen leads to the calculation of electronic properties and IR Spectrum of high tridymite in space group D_{3d} . © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Electronic properties of high tridymite; IR Spectrum of high tridymite; Generator coordinate HF method

1. Introduction

Detailed information on the Generator Coordinate Hartree – Fock (GCHF) method can be found in the article by Mohallem et al. [1]. The GCHF method has become one of the most powerful technique in the design of basis sets for atomic and molecular calculations and the first application was in the generation of Gaussian and Slater type orbital (GTO, STO) universal bases [2,3]. The method has been used by Silva et al. [4] in generation of universal basis for H to Xe, with further application in the calculation of electronic properties of molecular systems [5]. Also, Costa and co-workers extended the GCHF formalism to

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molecular systems [6,7]. Custódio and co-workers introduced in the literature the use of optimized integral discretization technique for the GCHF [8,9]. More recently, Silva, Malli and Ishikawa developed a universal Gaussian basis for relativistic calculations [10,11] and Jorge and Silva introduced, in the literature, the GCHF formalism to closed-shell Dirac–Fock equations [12]. A first application of GCHF method to the choice of contracted basis was made by Pinheiro et al. [13].

Metastable crystalline silica, at ordinary temperatures, crystallize as quartz, tridymite or cristobalite. Tridymite is stable between 870°C and 1470°C, however, it can also be maintained in a metastable state at lower temperatures. The density of tridymite is 2.27 g cm⁻³ because of its very open structure. There are also high-and-low temperature tridymite forms, nevertheless the low-temperature form is

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Fig. 1. The p weight functions for oxygen and silicon obtained with the basis sets 14s 8p and 17s 11p, respectively.

Table 1	
Discretization parameters (which	define the exponents) for oxygen
and silicon $(A = 6.00)$	

Symmetry	Oxygen $arOmega_{ ext{min}}$	$\Delta \Omega$	Ν	Silicon $arOmega_{\min}$	$\Delta \Omega$	N
s	- 0.285	0.148	14	-0.528	0.151	17
p	- 0.368	0.147	8	-0.505	0.148	11

metastable and does not appear in the equilibrium phase diagram [14]. The transformation between high- and low-temperature polymorphs is displacive, rapid and unquenchable.

Transition metal doped inorganic materials are of considerable industrial interest for catalysts, pigments, optics and electro-electronic, chromium and manganese

doped silicates, for instance, are potential materials for tunable solid state laser devices and optical amplisiers media in the $1-2 \mu m$ region [15,16]. The Cr⁺⁴ or Mn⁺⁵ ions, substitutes for Si⁺⁴ in tetrahedral sites of silicates [17] or non-crystalline silica [18] and its luminescence properties are very sensitive to ion local symmetry. Vibrational studies of these systems are very important to understand and determine the vibrational progession in the luminescence spectra. A hightridymite structure seems to be adequate as a d² ion doped matrix.

In this work we present high quality Gaussian basis sets based on the GCHF method for the calculation of electronic properties and IR spectrum of high trydimite in the space group D_{3d} . This is the first application of this method in the choice basis sets concerning polyatomic molecules.

Table 2 Total and orbital energies (a.u.) of O_2 at 2.28 a.u.

Basis	Total energy	$1\sigma_{\alpha}$	$1\sigma_{n}$	$2\sigma_{\alpha}$	$2\sigma_{\rm u}$	$3\sigma_{\alpha}$	$1\pi_{n}$	$1\pi_{a}$
	85	5	· u	5	· u	- 5	··· u	5
[6s4p] (14s 8p) 6-311G ^a	-149.588807780 -149.6017621 -149.5782586 -149.638186 ^b -149.662506 ^c	-20.74398 -20.73830 -20.7396	-20.74292 -20.73724 -20.73390	-1.66609 -1.66789 -1.66788	-1.06755 -1.07063 -1.0669	-0.716672 -0.71630 -0.71325	-0.67476 -0.87388 -0.67272	-0.15305 -0.15246 -0.15149

^a Basis from [24].

^b GTO [7s5p1d] basis from Ref. [13].

^c GTO [7s6p3d] basis from Ref. [25].

2. The generator coordinate Hartree–Fock method and the development of the Gaussian basis sets for oxygen (14s 8p) and silicon (17s 11p)

In the GCHF method, the one-electron functions are chosen as

$$\varphi_i(1) = \int \phi_i(1,\alpha) f_i(\alpha) \, \mathrm{d}\alpha, \qquad i = 1, 2, \dots, n. \tag{1}$$

The ϕ_i , α and f_i in Eq. (1) are the generator functions, the generator coordinate and the weight functions, respectively. Using Eq. (1) to build the Slater determinant for a many-electron wave function, and minimizing the total energy, *E*, with respect to f_i , the HF– Griffin–Wheeler (HFGW) equation can be written as

$$\int [F(\alpha, \beta) - \varepsilon_i S(\alpha, \beta)] f_i(\beta) \, \mathrm{d}\beta = 0,$$

$$i = 1, 2, \dots, n.$$
(2)

The integration of the HFGW equation is performed through a procedure referred to as integral discretization [19], implemented through a relabeling of the generator coordinate space, α ,

$$\Omega = \ln \alpha / A, \, A > .1 \tag{3}$$

Then the Ω space is discretized (for each symmetry) in an equally space mesh $\{\Omega_m\}$ so that

$$\Omega_m = \Omega_{\min} + (m-1)\,\Delta\Omega, \qquad m = 1, 2, \dots, N. \quad (4)$$

In Eq. (4) N is an option which allows the definition of the size of the basis sets, and $\Delta\Omega$ the numerical integration interval.

The values of Ω_{\min} (lowest value) and the highest value $\Omega_{\max} = \Omega_{\min} + (N-1)\Delta\Omega$ are chosen so as to adequately encompass the integration range of $f(\Omega)$. This is clearly visualized by drawing the weight functions from a preliminary calculation with arbitrary discretization parameters. This is illustrated in Fig. 1. Fig. 1 shows the 2p weight functions for oxygen and 2p and 3p for silicon. The lowest values at the left and the decay at the right indicate clearly the integration range relevant for the correct numerical integration of the HF-GHW equations.

Plots of weight functions were thus used to build rather large basis GTO sets for the referred atoms. The size (14 for s symmetry and 8 for p symmetry for oxygen, and 17 for s and 11 for p symmetries for

Total and orbital (snergies (a.u.) of Sit) at 2.853 a.u.								
Basis	Total energy	1σ	2σ	3σ	4σ	1π	5σ	6σ	2π	7σ
[8s5p]/[6s4p] (17s 11p/14s 8p) 6-311G ^a	- 363.7545016 - 363.7699615 - 363.7514233 - 363.8347 ^b - 363.8551 ^c	- 68.84820 - 68.85158 - 68.84692	-20.55073 -20.54512 -20.53971	-6.20029 -6.20369 -6.19820	-4.30696 -4.30611 -4.30161	-4.30373 -4.30297 -4.29813	-1.29431 -1.29668 -1.29210	-0.61337 -0.61395 -0.61074	-0.47928 -0.47877 -0.47557	-0.44010 -0.44028 -0.43623
^a Basis from Re ^b GTO [10s6p16	f. [24]. Jl/[7s5p1d] basis fro	om Ref. [13].								

Fable 3

Numerical HF value from Ref. [26]



Fig. 2. Geometry of high tridymite (symmetry D_{3d}).

silicon) ensured the error for the total Hartree–Fock ground state energy was 2.03×10^{-3} and 1.02×10^{-3} % to oxygen and silicon, respectively, compared to numerical Hartree–Fock energies [20]. Table 1 shows the discretization parameters (which define the exponents) for the basis sets.

3. The contraction of the Gaussian basis sets for oxygen (14s 8p/6s 4p) and silicon (17s 11p/8s 5p)

A basis set for molecular calculations is usually developed in three stages: (i) the generation of the uncontracted basis set in atomic calculations; (ii) the generation of the contracted basis set using a segmented or general contraction scheme, and (iii) addition of supplementary functions of polarization and diffuse character. The first stage of the work was done by employing the GCHF method as discussed in Section 2. The second stage was implemented by employing the segmented contraction scheme of Dunning [21].

For oxygen, the (14s 8p) Gaussian primitives are contracted for [6s4p]. The 14s functions are grouped as 9, 1, 1, 1, 1, 1 and the 8p functions are grouped as 5,

1, 1, 1. For silicon the (17s 11p) Gaussian primitives are contracted to [8s5p]. Addition of one d polarization function of value 0.285361 to the contracted form result in the [8s5p1d] one. The polarization function value is extracted from the Gaussian primitive basis set. The adequate polarization function is chosen through successive calculations for the molecule by using different primitive functions and taking into account the minimum energy criterion. The 17s functions are grouped as 8, 3, 1, 1, 1, 1, 1, 1 and the 11p functions are grouped as 7, 1, 1, 1, 1.

For oxygen and silicon our results were compared to the Hartree–Fock numerical calculations of Fischer [20] and the deviations were of 1.03×10^{-3} and 4.88×10^{-3} , respectively.

The uncontracted and contracted Gaussian basis sets were obtained through a slightly modified version of the ATOMSCF program developed by Clementi and Pavani at IBM [22].

3.1. The evaluation of quality of the contracted [6s4p] and [8s5p] bases in molecular calculations

To evaluate the quality of our contracted [6s4p] and

Table 4 Population analysis and dipole moments for high tridymite

Total atom-atom overlap populations	Total atomic charges	Dipole moments (Debye)
$\begin{array}{rcrr} \hline populations \\ \hline \\ Si(1) - O(1) &= & + 0.80 \\ Si(1) - O(2) &= & + 0.80 \\ Si(1) - O(3) &= & + 0.74 \\ Si(1) - O(18) &= & + 0.72 \\ Si(2) - O(3) &= & + 0.74 \\ Si(2) - O(4) &= & + 0.80 \\ Si(2) - O(5) &= & + 0.80 \\ Si(2) - O(6) &= & + 0.72 \\ Si(3) - O(6) &= & + 0.72 \\ Si(3) - O(6) &= & + 0.74 \\ Si(3) - O(6) &= & + 0.74 \\ Si(3) - O(7) &= & + 0.74 \\ Si(3) - O(8) &= & + 0.74 \\ Si(3) - O(9) &= & + 0.74 \\ Si(3) - O(9) &= & + 0.72 \\ Si(4) - O(10) &= & + 0.80 \\ Si(4) - O(12) &= & + 0.74 \\ Si(5) - O(13) &= & + 0.80 \\ Si(5) - O(15) &= & + 0.72 \\ Si(6) - O(15) &= & + 0.74 \\ Si(6) - O(17) &= & + 0.74 \\ Si(6) - O(17) &= & + 0.74 \\ \end{array}$	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$D_x = 0.00$ $D_y = 0.00$ $D_z = 0.00$ $D_{tot} = 0.00$
Si(6) - O(18) = + 0.76	O(18) = -0.66	

[8s5p] bases in molecular calculations, we accomplish calculations of total and orbital energies of the molecules O_2 and SiO in the Hartree–Fock–Roothaan method [23]. We compare the results with that obtained with our (14s 8p) and (17s 11p) basis sets and with the of 6-311G basis of Hehre et al. [24].

Also, for O_2 we compare the total energy obtained with our [6s4p] basis with that Pinheiro, Silva and Trsic obtained with the GTO [7s5p1d] basis [13] and with the results Dingle, Huzinaga and Klobukowski obtained with the GTO [7s6p3d] basis [25]. For SiO the value of the total energy obtained with our [8s5p]/[6s4p] basis was compared with those of the GTO [10s6p1d]/[7s5p1d] basis obtained by Pinheiro et al. [13] and with the numerical HF value of Pekka Pykko et al. [26].

In Table 2 we show the total and orbital energies for O_2 . The total energy obtained with the [6s4p] basis described in this work is competitive with that of the 6-311G basis. The energy values are clearly close to

the obtained values from [7s5p1d] and [7s6p3d] basis. The percent difference for the energy of our (14s 8p) basis set is 8.66 × 10^{-3} %. The orbital energies obtained from our [6s4p] basis are competitive with those of the 6-311G basis and present the percent difference for the values of the (14s 8p) basis between 2.74 × 10^{-2} % and 3.84 × 10^{-1} %.

Table 3 shows the total and orbital energies for SiO. The total energy obtained from [8s5p]/[6s4p] basis of this work is competitive with that of the 6-311G basis. The obtained energy value is close to the result of the [10s6p1d]/[7s5p1d] basis. The percentage differences of 4.25 × 10⁻³% and 2.76 × 10⁻²% to the value obtained from our (17s 11p/14s 8p) basis set and with the numerical HF value, respectively. The orbital energies obtained from [8s5p]/[6s4p] basis are also competitive with those of the 6-311G basis and present deviations between 4.91 × 10⁻³% and 1.06 × 10⁻¹% when compared with the values of (17s 11p/ 14s 8p) basis set and numerical HF value, respectively.

Table 5 IR and Raman spectrum of high tridymite (D_{3d})

IR intens. (KM/mol)	Raman activ.
_	815.2
_	269.6
_	256.2
143.9	209.9
583.7	816.0
986.9	767.0
298.9	38.8
_	71.6
_	274.8
-	760.1
425.4	608.3
14.2	123.6
_	690.2
_	621.3
2.34	698.8
70.6	333.8
_	680.7
-	870.2
291.1	814.3
-	970.4
1073.4	44.0
292.9	637.0
_	841.2
_	831.2
39.4	508.6
273.1	19.5
_	322.9
_	689.9
183.5	19.2
-	481.3
13.7	511.2
1.12	321.3
	IR intens. (KM/mol)

4. Results and discussion

The crystal cell of high tridymite contains four molecular units the corresponding space group being D_{6h} . The calculation of the infrared and Raman spectra by the ab initio Molecular Orbital Theory methods of the symmetry species with space group D_{6h} of high tridymite is very demanding computationally. A generalized valence force field was previously used by Etchepare, Merian and Kaplan to calculate the spectrum infrared of the symmetry D_{6h} in high tridymite [27].

Our purpose is to study high tridymite in the symmetry D_{3d} by the ab initio Hartree–Fock–Roothaan method [23]. The crystal geometry shown in Fig. 2 was employed for structure [28]. The number of SiO₂ formula units is four in high tridymite.

The properties calculated are: atom-atom overlap populations bond orders, total atomic charges (obtained with Mulliken's Population Analysis [29]) and dipole moments, shown in Table 4. Infrared-Raman spectrum shown in Table 5. The molecular calculations performed in this work were done by using the Gaussian 94 routine [30].

The atom–atom overlap populations in high tridymite of symmetry D_{3d} (charge 0 and multiplicity 3) indicate a high electron density between atoms Si–O [29] in all structural frameworks. The total calculated atomic charges are consistent with an alternative charge occurring for Si and O atoms.

The vibrational spectrum was calculated by using a harmonic field [31]. The obtained frequencies were not scaled because the scaling frequencies are used to standard basis such as 3-21G [32] and 6-31G [33].

The infrared vibrational spectrum shows several bands above 530 cm^{-1} and those in the low frequency region. Raman activity is present in both low and high frequencies. The infrared spectrum shows two strong peaks at 389.0 cm⁻¹ while Raman activity is stronger at 721.1 and 808.6 cm^{-1} . Unfortunately, there is no specific infrared spectrum for high the tridymite symmetry D_{3d}, there are, however, experimental Raman spectrum results of D_{6h} symmetry [27]. Comparing these results there are five strong theoretical peaks at 214, 450, 520, 532 and 828 cm⁻¹, while in the experimental spectrum they appear at 205, 363, 407, 426, and 786 cm⁻¹. The discrepances are 4.2%, 19.3%, 21.7%, 19.9% and 5.1%, in which three values 19.3%, 21.7%, and 19.9% are near the approximately 10%–15% error [32] expected for the Hartree–Fock– Roothaan method and the other two values of 4.2 and 5.1 are consistent with the experimental results.

5. Conclusions

Among the electronic structure of high tridymite in the symmetry D_{3d} , the used atomic basis set indicates more explicitly a very good description of the electronic property. Obtained values of total atom– atom overlap populations show very strong overlap values of the Si–O bonding character. The Raman spectrum is in good agreement compared with the experimental spectrum of the symmetry D_{6h} . The atomic basis developed by the GCHF method is an effective alternative to investigate electronic and vibrational theoretical properties of tridymite.

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