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# Calculation of the Vibration Frequencies of $\alpha$ -Quartz: The Effect of Hamiltonian and Basis Set

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**Abstract:** The central-zone vibrational spectrum of  $\alpha$ -quartz ( $\text{SiO}_2$ ) is calculated by building the Hessian matrix numerically from the analytical gradients of the energy with respect to the atomic coordinates. The nonanalytical part is obtained with a finite field supercell approach for the high-frequency dielectric constant and a Wannier function scheme for the evaluation of Born charges. The results obtained with four different Hamiltonians, namely Hartree–Fock, DFT in its local (LDA) and nonlocal gradient corrected (PBE) approximation, and hybrid B3LYP, are discussed, showing that B3LYP performs far better than LDA and PBE, which in turn provide better results than HF, as the mean absolute difference from experimental frequencies is 6, 18, 21, and 44  $\text{cm}^{-1}$ , respectively, when a split valence basis set containing two sets of polarization functions is used. For the LDA results, comparison is possible with previous calculations based on the Density Functional Perturbation Theory and usage of a plane-wave basis set. The effects associated with the use of basis sets of increasing size are also investigated. It turns out that a split valence plus a single set of  $d$  polarization functions provides frequencies that differ from the ones obtained with a double set of  $d$  functions and a set of  $f$  functions on all atoms by on average less than 5  $\text{cm}^{-1}$ .

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**Key words:** vibration frequencies;  $\alpha$ -quartz; Hartree–Fock; LDA; PBE; B3LYP; basis set

## Introduction

The calculation of vibrational spectra of molecular systems is a well-known procedure, today implemented in most of the relevant molecular computer codes.<sup>1,2</sup> The method is based on the calculation of the Hessian matrix, either numerically or analytically.<sup>3</sup> The case of crystalline systems is different, as the development of reliable and accurate computer codes is at an earlier stage than in molecular quantum chemistry and, as a matter of fact, only a few *ab initio* codes permit the calculation of vibrational spectra. So far, to our knowledge, the most consistent implementations are those employing Density Functional Perturbation Theory methods and plane waves as a basis set.<sup>4–6</sup> Our implementation in the periodic *ab initio* CRYSTAL code,<sup>7</sup> that uses a basis of local functions, is more similar to the computational scheme of molecular codes. It is based on a recent implementation of the calculation of the analytical gradients of the total energy with respect to the nuclear

positions<sup>8,9</sup> (R. Orlando, V. R. Saunders, R. Dovesi, in preparation). The Hessian matrix is then obtained by numerical differentiation.

The effect of Hamiltonian, basis set, and numerical parameters of the calculation is well documented in the case of small molecules,<sup>10–13</sup> but not in the case of periodic systems, where the algorithms are much less consolidated, and a variety of methods has been proposed.

In a previous article<sup>14</sup> the effect of the computational parameters on the accuracy of the vibration frequencies of  $\alpha$ -quartz calculated with CRYSTAL at the  $\Gamma$  point was discussed at length. The aim of the present article is to extend such an analysis to the effect of the Hamiltonian and basis set. Four different Hamiltonians are considered, namely Hartree–Fock (HF), Density Functional Theory (DFT) both in the local (LDA) and the nonlocal

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(PBE) formulation, and B3LYP, a hybrid scheme that has been shown to provide excellent frequency values for molecular<sup>10</sup> and crystalline systems.<sup>15–20</sup> Convergence with the basis set size is also investigated. This will permit a proper comparison with previous LDA calculations by Gonze et al.<sup>5</sup> and Umari et al.,<sup>6</sup> who used a plane-wave basis set in a Density Functional Perturbation Theory scheme.

## Computational Method

In the CRYSTAL program<sup>7</sup> the forces on the atoms are computed analytically<sup>8,9</sup> (V. R. Saunders and R. Orlando, in preparation), and the Hessian matrix is computed by numerical differentiation of the gradient vector.<sup>14</sup> A two-point formula is used with 0.001 Å as a step. The nonanalytical correction to the Hessian, that must be added in the case of ionic compounds to take long-range Coulomb effects due to coherent displacement of the crystal nuclei into account (see sections 5, 10, 34, and 35 in ref. 21, and eqs. (3) and (6) in ref. 6), depends essentially on the electronic (clamped nuclei) dielectric tensor  $\epsilon^\infty$  and the *Born effective charge tensor* associated with every atom. The former is evaluated by applying a saw-tooth finite field along the direction of interest,<sup>22</sup> the latter through well-localized Wannier functions.<sup>23–26</sup>

The geometry of  $\alpha$ -quartz, that is, the inner coordinates<sup>27</sup> and two cell parameters, has been fully optimized for each Hamiltonian considered (HF, LDA,<sup>28,29</sup> PBE,<sup>30</sup> and B3LYP<sup>31</sup>). The B3LYP equilibrium geometry has also been recalculated with different basis sets. Inner coordinates and cell parameters have been optimized separately within an iterative procedure based on the total energy gradients calculated analytically with respect to the nuclear coordinates and numerically with respect to the cell parameters. Convergence has been tested on the root-mean-square (RMS) and the absolute value of the largest component of both gradients and nuclear displacements. The thresholds for the maximum and the RMS forces and the maximum and the RMS atomic displacements (in a.u.) have been set to 0.00045, 0.00030, and 0.00180, 0.00120, respectively. Optimization is considered complete when the four conditions are simultaneously satisfied both for the fractional coordinates and the cell parameters. The level of accuracy in evaluating the Coulomb and exchange series is controlled by five parameters.<sup>7</sup> The values used in the present calculations are 6, 6, 6, 6, and 12. For the DFT part, 55 radial and 434 angular points have been used for every atomic grid, corresponding to an unpruned Lebedev quadrature with  $\ell = 13$ . The reciprocal space has been sampled according to a regular sublattice with a shrinking factor of 3, corresponding to 7 independent  $\mathbf{k}$  points in the irreducible Brillouin zone. Choice of the present computational conditions allows accuracy within  $2 \text{ cm}^{-1}$  in the evaluation of the vibration frequencies of  $\alpha$ -quartz.<sup>14</sup>

Regarding the basis sets, modified Pople's 6-21G\* and 6-31G\* for Si and O, respectively, have been used as reference basis sets, which will collectively be labeled as  $1d$ . The exponents (in bohr<sup>-2</sup>) of the most diffuse *sp* and *d* orbitals have been optimized at the HF level (0.09 and 0.60 for Si and 0.29 and 0.47 for O). A more flexible basis set, labeled as  $2d$ , has been obtained by adding a second set of *d* orbitals; the exponents of the two *d* shells are: 2.56 (Si), 0.54 (Si), 2.00 (O), and 0.41 (O). For completeness, two

**Table 1.** Equilibrium Geometry and Total Energy ( $E$ ) of  $\alpha$ -Quartz as a Function of the Basis Set Size (see Text for Definitions) at the B3LYP Level.

	$0d$	$1d(\text{Si})$	$1d$	$2d$
$a$	5.132	5.124	4.943	4.926
$c$	5.675	5.593	5.429	5.421
$V$	129.423	127.170	114.894	113.945
$\text{Si}_x$	0.47342	0.49623	0.46766	0.46835
$\text{O}_x$	0.42570	0.42878	0.41307	0.41197
$\text{O}_y$	0.26402	0.20717	0.27249	0.27103
$\text{O}_z$	0.12690	0.17245	0.11474	0.11560
Si–O1	1.6571	1.5949	1.6245	1.6197
Si–O2	1.6608	1.6380	1.6275	1.6225
Si–O–Si	148.88	157.12	142.14	142.16
$E$	–1319.79557	–1320.07810	–1320.12194	–1320.15705

Cell parameters ( $a$  and  $c$ ) and distances (Si–O1 and Si–O2) are in Å, the volume ( $V$ ) in Å<sup>3</sup>, the Si–O–Si angle in degrees,  $E$  in hartree;  $\text{Si}_x$  and  $\text{O}_x$  are fractional coordinates.

smaller basis sets,  $0d$  and  $1d(\text{Si})$ , have also been considered, with the first corresponding to the complete elimination of *d* orbitals from  $1d$  and the latter to suppressing only oxygen *d* orbitals. The importance of *f* functions has also been tested.

## Results and Discussion

### Geometry and Total Energy: Basis Set and Hamiltonian Effects

The effect of the basis set on the equilibrium geometry and total energy has been investigated in the case of the B3LYP Hamiltonian (Table 1). The two smallest basis sets,  $0d$  and  $1d(\text{Si})$ , provide poor geometries. For example, the predicted volume is 129 and 127 Å<sup>3</sup>, respectively, to be compared to 114 Å<sup>3</sup> of  $2d$ , whereas the Si–O–Si angle is 149 and 157 degrees, to be compared to 142 in the case of  $2d$ . Also, the total energy is much higher (about 360 mhartree) with  $0d$  than with  $2d$ , the addition of *d* atomic orbitals to the Si basis set being particularly important. For these reasons  $0d$  and  $1d(\text{Si})$  are expected to reproduce frequencies poorly. Even so, these basis sets will be considered in the calculation of vibration frequencies as well, to check the influence of a poor determination of the equilibrium geometry on the vibration spectrum.

$1d$  and  $2d$  basis sets provide very similar geometries, with a volume difference below 1%, the Si–O–Si angle differing by less than 1 degree and the Si–O distances by about 0.005 Å. Of the energy gain (55 mhartree per cell) from  $1d$  to  $2d$  only 0.2 mhartree are associated with the geometry optimization from  $1d$  to  $2d$  (see  $\Delta E$  in Table 2), leading to the conclusion that performing such an optimization would not be strictly necessary.

If the same basis set optimized at the HF level is used with DFT Hamiltonians, as is usually done in molecular quantum chemistry, we obtain the equilibrium geometries and total energies reported in Tables 1 (last column) and 2 (columns 1–3). The B3LYP, PBE, and HF equilibrium geometries are close to the experiment, as

**Table 2.** Equilibrium Geometry and Total Energy of  $\alpha$ -Quartz.

	This work			Umari et al. <sup>a</sup>	Gonze et al. <sup>b</sup>	Exp <sup>c</sup>
	HF	PBE	LDA	LDA	LDA	
<i>a</i>	4.915	4.926	4.765	4.870	4.815	4.916
<i>c</i>	5.405	5.409	5.300	5.346	5.321	5.405
<i>V</i>	113.077	113.668	104.215	109.804	106.836	113.123
Si <sub><i>x</i></sub>	0.47079	0.46571	0.45652	0.471	0.461	0.470
O <sub><i>x</i></sub>	0.41460	0.40872	0.40492	0.415	0.410	0.413
O <sub><i>y</i></sub>	0.26627	0.27595	0.29097	0.265	0.281	0.267
O <sub><i>z</i></sub>	0.12058	0.11015	0.09986	0.121	0.108	0.119
Si–O1	1.6047	1.6319	1.6136	1.58	1.60	1.607
Si–O2	1.6068	1.6347	1.6188	1.59	1.61	1.613
Si–O–Si	144.34	139.67	135.12	144.8	139.1	143.7
<i>E</i>	−1316.70108	−1319.54190	−1313.91555			
$\Delta E$	−0.00018	−0.00017	−0.00026			

The present results have been calculated with basis set *2d* (see text) optimized at the HF level.  $\Delta E$  denotes the amount of energy gain for the optimization performed with the *2d* basis set starting from the geometry optimized with the *1d* basis set. Other symbols and units as in Table 1.

<sup>a</sup>Ref. 6. <sup>b</sup>Ref. 5. <sup>c</sup>Ref. 32.

expected, with PBE performing slightly worse, with slightly longer Si–O distances and smaller Si–O–Si angles by 4 degrees. On the contrary, LDA provides a volume that is about 10% smaller, as a consequence of the Si–O–Si angle being just 135 degrees instead of 143.

The effect of adapting the basis set to the Hamiltonian has also been investigated by reoptimizing the outer *sp* and *d* exponents in the *1d* basis set specifically for LDA, PBE, and B3LYP. The B3LYP and PBE results, given in Table 3, are not so different from the ones obtained with the basis set optimized at the HF level, nor are the corresponding geometries. Upon optimization with

B3LYP, for example, Si–O distance varies only by 0.002 Å (compare the *1d* column in Table 1 with the B3LYP column in Table 3), and the Si–O–Si angle by 2.3 degrees, with about 3 Å<sup>3</sup> increase in the volume and an energy gain of the order of 10 mhartree.

In the case of LDA, modifications in the basis set (compare the exponents given earlier and in Table 3) are more important, and the corresponding energy gain is about twice as large. The change in the equilibrium geometry is, however, negligible (e.g., the change in volume is below 1%). Nevertheless, for completeness, data corresponding to basis sets and geometries in Table 3 will also be reported.

### The Dielectric Tensor and the Born Charges

The use of a supercell<sup>22</sup> in the calculation of the dielectric tensor with the method mentioned in the previous section requires a preliminary analysis of the convergence trend as a function of the supercell size. The results in Table 4 refer to HF calculations performed with the *1d* basis set. They show that *N* = 8 (size of the supercell) provides well converged results.

In Table 5, the dielectric tensor components evaluated at *N* = 8 for *1d* and *2d* with four different Hamiltonians are reported and

**Table 3.** Equilibrium Geometry and Total Energy of  $\alpha$ -Quartz Obtained with *1d*-Type Basis Sets Optimized for Each Hamiltonian.

	HF	LDA	B3LYP	PBE
<i>a</i>	4.960	4.767	4.984	4.978
<i>c</i>	5.444	5.318	5.479	5.481
<i>V</i>	115.991	104.668	117.876	117.595
Si <sub><i>x</i></sub>	0.47398	0.45475	0.47139	0.46817
O <sub><i>x</i></sub>	0.41710	0.40419	0.41469	0.41131
O <sub><i>y</i></sub>	0.26134	0.29112	0.26570	0.27174
O <sub><i>z</i></sub>	0.12487	0.10119	0.12060	0.11453
Si–O1	1.6086	1.6190	1.6262	1.6391
Si–O2	1.6106	1.6240	1.6291	1.6423
Si–O–Si	146.31	135.35	144.40	141.66
<i>sp</i> <sub>Si</sub>	0.08048	0.24073	0.08249	0.08336
<i>d</i> <sub>Si</sub>	0.60399	0.72299	0.60906	0.60221
<i>sp</i> <sub>O</sub>	0.28915	0.25052	0.27271	0.27280
<i>d</i> <sub>O</sub>	0.47331	0.31499	0.39446	0.36200
<i>E</i>	−1316.67477	−1313.89968	−1320.13054	−1319.51644

*sp*<sub>Si</sub> denotes the exponent (in bohr<sup>−2</sup>) of the outermost *sp* set of atomic orbitals of silicon. Other symbols and units as in Table 1.

**Table 4.** Dielectric Tensor Components of  $\alpha$ -Quartz Calculated at the HF Level with Supercells of Increasing Size.

<i>N</i>	$\epsilon_{xx}$	$\epsilon_{zz}$
2	—	1.717
4	1.645	1.961
6	1.925	1.961
8	1.935	1.961

Supercells are obtained by multiplying *a* (for  $\epsilon_{xx}$ ) or *c* (for  $\epsilon_{zz}$ ) by integer *N*.

**Table 5.** Calculated Dielectric Tensor Components of  $\alpha$ -Quartz with Various Hamiltonians and Basis Sets.

	$\epsilon_{xx}$				$\epsilon_{zz}$			
	0d	1d(Si)	1d	2d	0d	1d(Si)	1d	2d
HF			1.935	2.018			1.961	2.071
B3LYP	2.025	1.909	2.213	2.258	2.070	1.935	2.256	2.302
PBE			2.389	2.426			2.447	2.479
LDA			2.479	2.525			2.547	2.593
LDA <sup>a</sup>				2.429				2.457
LDA <sup>b</sup>				2.527				2.566
Exp. <sup>c</sup>				2.356				2.383

Experimental and plane-wave LDA calculated data are reported for comparison.

<sup>a</sup>Ref. 6.

<sup>b</sup>Ref. 5.

<sup>c</sup>Ref. 32.

compared with experiment and two previous plane-wave LDA calculations.<sup>5,6</sup> 0d and 1d(Si) results are also reported in the case of B3LYP. The four Hamiltonians provide quite different values for the two constants, the difference being greater than 20% in some case. As expected, HF strongly underestimates the experimental constants, as a consequence of the low polarizability of the corresponding wave function. Conversely, LDA overestimates the experimental finding, but by about 50% of the HF error. PBE and B3LYP perform better, and differ by less than 0.10 from the measured values. The effect of the basis set, when going from 1d to 2d is smaller than 2% in all but one case (HF), where it reaches 4%. As expected, 0d and 1d(Si) perform poorly, with errors as large as 15% with respect to 2d. The difference between the two tensor components is small (of the order of 0.06, or below) and slightly larger than according to Gonze<sup>5</sup> and Umari<sup>6</sup> or the experiment (about 0.03). Regarding the comparison of the present and previous LDA calculations, our data appear closer to the older result by Gonze than to the more recent data by Umari et al.

Born charges are reported in Table 6. Basis set and Hamiltonian effects are relatively small, especially for diagonal terms (less than 5%). Relative differences in the off-diagonal terms can be as large

**Table 6.** Born Charges of Si and O Atoms Calculated with Various Basis Sets and Hamiltonians.

Basis set	Hamiltonian	Born tensors					
		Si			O		
1d	B3LYP	3.738	0.000	0.350	-1.937	0.554	-0.625
		0.000	3.041	0.000	0.506	-1.460	0.431
		-0.303	0.000	3.501	-0.586	0.509	-1.755
2d	B3LYP	3.720	0.000	0.339	-1.929	0.561	-0.645
		0.000	3.030	0.000	0.517	-1.442	0.449
		-0.301	0.000	3.488	-0.600	0.519	-1.749
2d	HF	3.706	0.000	0.229	-1.933	0.513	-0.615
		0.000	3.164	0.000	0.464	-1.456	0.400
		-0.221	0.000	3.493	-0.560	0.444	-1.762
2d	PBE	3.715	0.000	0.419	-1.924	0.590	-0.657
		0.000	2.954	0.000	0.546	-1.427	0.470
		-0.369	0.000	3.476	-0.622	0.559	-1.735
2d	LDA	3.626	0.000	0.427	-1.863	0.519	-0.545
		0.000	2.947	0.000	0.506	-1.461	0.456
		-0.358	0.000	3.467	-0.527	0.534	-1.733
PW <sup>a</sup>	LDA	3.671	0.000	0.224	-1.915	0.519	-0.615
		0.000	3.021	0.000	0.564	-1.413	0.505
		-0.257	0.000	3.450	-0.648	0.447	-1.715
PW <sup>b</sup>	LDA	3.633	0.000	0.324	-1.999	0.429	-0.679
		0.000	3.016	0.000	0.480	-1.326	0.298
		-0.282	0.000	3.453	-0.718	0.222	-1.726

The last two entries refer to previous Plane-Wave (PW) LDA data calculated in the same cartesian frame.

<sup>a</sup>Ref. 6.

<sup>b</sup>Ref. 5.

Table 7. Dependence of B3LYP Vibration Frequencies (in  $\text{cm}^{-1}$ ) of  $\alpha$ -Quartz at  $\Gamma$  on the Basis Set Size.

	0d		1d(Si)		1d	2d		2d + f		Exp.	
A1-TO	174.8	-44.2	32.3	-186.7	219.6	0.6	216.0	-3.0	223.3	4.3	219.0
	333.8	-24.2	366.7	8.7	348.8	-9.2	350.4	-7.6	356.5	-1.5	358.0
	414.1	-54.9	460.0	-9.0	464.3	-4.7	465.1	-3.9	466.9	-2.1	469.0
	1087.6	5.6	1133.0	51.0	1090.8	8.8	1085.4	3.4	1085.8	3.8	1082.0
A2-TO	354.3	-7.0	423.4	62.1	351.8	-9.5	352.3	-9.0	360.7	-0.6	361.3
	453.9	-45.1	460.7	-38.3	499.4	0.4	500.9	1.9	502.3	3.3	499.0
	782.2	4.2	819.2	41.2	787.0	9.0	783.8	5.8	787.6	9.6	778.0
	1109.4	37.4	1151.2	79.2	1084.4	12.4	1076.4	4.4	1077.3	5.3	1072.0
E-TO	135.4	2.4	123.2	-9.8	135.2	2.2	132.5	-0.5	141.3	8.3	133.0
	241.1	-27.9	253.2	-15.8	261.8	-7.2	263.6	-5.4	265.2	-3.8	269.0
	380.9	-12.6	430.6	37.1	390.5	-3.0	391.3	-2.2	394.8	1.3	393.5
	428.8	-23.7	444.1	-8.4	446.9	-5.6	447.0	-5.5	456.4	3.9	452.5
	667.4	-30.6	699.7	1.7	703.0	5.0	702.9	4.9	704.7	6.7	698.0
	728.4	-70.6	780.5	-18.5	808.2	9.2	810.5	11.5	807.5	8.5	799.0
	1103.2	37.2	1144.5	78.5	1077.2	11.2	1068.2	2.2	1069.2	3.2	1066.0
	1152.6	-5.4	1241.6	83.6	1167.9	9.9	1163.1	5.1	1166.4	8.4	1158.0
A2-LO	379.7	-5.3	427.3	42.3	377.3	-7.7	377.1	-7.9			385.0
	557.8	4.8	578.3	25.3	556.7	3.7	555.9	2.9			553.0
	788.0	-3.0	822.9	31.9	800.8	9.8	797.1	6.1			791.0
	1273.6	43.6	1337.6	107.6	1261.2	31.2	1252.1	22.1			1230.0
E-LO	135.4	2.4	123.4	-9.6	135.3	2.3	132.6	-0.4			133.0
	241.6	-27.4	253.2	-15.8	263.7	-5.3	265.5	-3.5			269.0
	395.2	-6.8	430.7	28.7	400.2	-1.8	400.0	-2.0			402.0
	524.4	12.4	541.7	29.7	510.7	-1.3	508.0	-4.0			512.0
	668.1	-32.9	701.8	0.8	705.8	4.8	705.7	4.7			701.0
	746.2	-65.3	801.5	-10.0	820.9	9.4	822.8	11.3			811.5
	1151.6	-3.4	1235.0	80.0	1165.1	10.1	1160.2	5.2			1155.0
	1262.7	35.7	1330.4	103.4	1253.1	26.1	1243.3	16.3			1227.0
$ \bar{\Delta} $	24.1		43.4		7.9		5.8		4.7		
$\bar{\Delta}$	-10.9		20.4		4.0		1.9		3.7		
$\Delta_{\min}$	-70.6		-186.7		-9.5		-9.0		-3.8		
$\Delta_{\max}$	43.6		107.6		31.2		22.1		9.6		

The exponents of the most diffuse  $sp$  and  $d$  shells have been optimized at the HF level. Analytical and global differences with respect to the experimental frequencies<sup>33</sup> are also given. The global indices  $|\bar{\Delta}|$ ,  $\bar{\Delta}$ ,  $\Delta_{\min}$ , and  $\Delta_{\max}$  (see text for definition) extend to both TO and LO frequencies, with the exception of  $2d + f$ , referred to TO modes only.

as 50% (see the  $xz$  component of the Si tensor), although absolute differences are of the same order of magnitude as in diagonal terms. Similar considerations apply to the comparison of the three LDA calculations.

#### The Frequencies: Basis Set and Hamiltonian Effects

There are 24 transverse-optical (TO) and 20 longitudinal-optical (LO) vibration modes in  $\alpha$ -quartz. The variability of the calculated vibration frequencies  $\nu_v$  as depending on the basis set and Hamiltonian will be estimated through four global indices evaluated with respect to a reference set of frequencies  $\nu_v^{\text{ref}}$  as follows:

$$|\bar{\Delta}| = \sum_v |\nu_v - \nu_v^{\text{ref}}|$$

$$\bar{\Delta} = \sum_v \nu_v - \nu_v^{\text{ref}}$$

$$\Delta_{\max} = \max(\nu_v - \nu_v^{\text{ref}}) \quad \nu = 1, 2, \dots$$

$$\Delta_{\min} = \min(\nu_v - \nu_v^{\text{ref}})$$

The effect of the basis set has been explored at the B3LYP level of theory and with reference to the experiment (Table 7) and to the data calculated with the  $2d$  basis set (Table 8). The calculations have been performed at the geometries optimized with each basis set, namely  $0d$ ,  $1d(\text{Si})$ ,  $1d$ ,  $2d$ . As expected,  $0d$  and  $1d(\text{Si})$  basis sets produce poor frequencies, with a mean difference  $|\bar{\Delta}|$  (Table 8) of 23 and 42  $\text{cm}^{-1}$ , respectively, from the frequencies calculated with  $2d$  (the error is about the same when reference is made to the

**Table 8.** Statistical Analysis of the Dependence of B3LYP Vibration Frequencies of  $\alpha$ -Quartz at  $\Gamma$  on the Basis Set Size Referred to the  $2d$  Set of TO and LO Frequencies.

	$0d$	$1d(\text{Si})$	$1d$	$2d + f$
$ \bar{\Delta} $	22.7	42.2	3.0	3.9
$\bar{\Delta}$	-12.8	18.5	2.1	3.5
$\Delta_{\min}$	-82.1	-183.7	-2.3	-3.0
$\Delta_{\max}$	35.0	87.1	9.8	9.4

Statistics relative to  $2d + f$  are restricted to TO modes. Symbols as in Table 8.

experiment), and a maximum difference as large as 80 and 180  $\text{cm}^{-1}$ , respectively.  $1d$  frequencies are, however, much closer to  $2d$ , as  $|\bar{\Delta}|$  reduces to 3  $\text{cm}^{-1}$ , and they are also systematically closer to experiment. A preliminary calculation of the TO vibration frequencies has been performed with an even larger basis,  $2d + f$ , obtained from the original  $2d$  basis set by including an additional set of  $f$  functions (seven components) for every atom, with the exponents being 0.53 and 0.73 for Si and O, respectively. The equilibrium geometry considered in this case is, again, the one determined with  $2d$ . The four global indices (Table 7) show proximity of  $2d + f$  frequencies to  $2d$ , about in the same order of  $1d$ . However, when compared to the experimental data,  $|\bar{\Delta}|$  is 6.7, 4.8, and 4.7 for the TO frequencies computed with  $1d$ ,  $2d$ , and

**Table 9.** Vibration Frequencies of  $\alpha$ -Quartz Obtained at  $\Gamma$  with Four Different Hamiltonians and the  $2d$  Basis Set Optimized at the HF Level.

	HF		B3LYP		LDA		PBE	
A1-TO	216.7	-2.3	216.0	-3.0	261.6	42.6	220.8	1.8
	381.3	23.3	350.4	-7.6	332.3	-25.7	332.0	-26.0
	504.9	35.9	465.1	-3.9	482.1	13.1	451.8	-17.2
	1144.4	62.4	1085.4	3.4	1089.1	7.1	1050.3	-31.7
A2-TO	395.4	34.1	352.3	-9.0	326.3	-35.0	326.3	-35.0
	544.1	45.1	500.9	1.9	504.6	5.6	481.6	-17.4
	823.4	45.4	783.8	5.8	791.1	13.1	764.6	-13.4
	1132.4	60.4	1076.4	4.4	1086.4	14.4	1038.5	-33.5
E-TO	138.8	5.8	132.5	-0.5	143.4	10.4	128.8	-4.2
	286.5	17.5	263.6	-5.4	263.5	-5.5	252.8	-16.2
	427.4	33.9	391.3	-2.2	376.9	-16.6	372.4	-21.1
	490.6	38.1	447.0	-5.5	443.8	-8.7	424.0	-28.5
	740.9	42.9	702.9	4.9	721.7	23.7	681.5	-16.5
	847.7	48.7	810.5	11.5	835.0	36.0	797.0	-2.0
	1125.2	59.2	1068.2	2.2	1070.3	4.3	1030.8	-35.2
	1235.8	77.8	1163.1	5.1	1141.7	-16.3	1117.9	-40.1
A2-LO	423.3	38.3	377.1	-7.9	351.3	-33.7	350.2	-34.8
	609.2	56.2	555.9	2.9	543.9	-9.1	528.9	-24.1
	837.0	46.0	797.1	6.1	816.8	25.8	778.2	-12.8
	1315.2	85.2	1252.1	22.1	1249.6	19.6	1210.4	-19.6
E-LO	138.8	5.8	132.6	-0.4	143.7	10.7	128.8	-4.2
	288.1	19.1	265.5	-3.5	266.9	-2.1	255.4	-13.6
	436.6	34.6	400.0	-2.0	389.1	-12.9	380.4	-21.6
	558.9	46.9	508.0	-4.0	497.2	-14.8	479.8	-32.2
	743.2	42.2	705.7	4.7	726.5	25.5	685.2	-15.8
	865.7	54.2	822.8	11.3	844.7	33.2	806.2	-5.3
	1232.7	77.7	1160.2	5.2	1137.3	-17.7	1115.4	-39.6
	1310.8	83.8	1243.3	16.3	1234.7	7.7	1201.4	-25.6
$ \bar{\Delta} $		43.7		5.8		17.5		21.0
$\bar{\Delta}$		43.5		1.9		3.4		-20.9
$\Delta_{\min}$		-2.3		-9.0		-35.0		-40.1
$\Delta_{\max}$		85.2		22.1		42.6		1.8

The differences with respect to the experimental data<sup>33</sup> are also reported. Symbols and units as in Table 7. The global indices are evaluated with respect to the experimental frequencies.

**Table 10.** Statistics Concerning DFT Frequencies Obtained for  $\alpha$ -Quartz at  $\Gamma$  with the  $1d$  Basis Set Optimized for HF and the  $1d$  Type Basis Sets Reoptimized for Each Hamiltonian (Reoptimized  $1d$ ) as Reported in Table 3.

Basis set	Global index	B3LYP	LDA	PBE
$1d$	$\overline{ \Delta }$	7.9	18.3	19.5
	$\bar{\Delta}$	4.0	3.4	-18.9
	$\Delta_{\min}$	-9.5	-37.1	-36.7
	$\Delta_{\max}$	31.2	41.8	8.4
Reoptimized $1d$	$\overline{ \Delta }$	10.2	20.9	26.7
	$\bar{\Delta}$	-2.7	7.5	-26.7
	$\Delta_{\min}$	-24.2	-39.0	-40.5
	$\Delta_{\max}$	26.7	41.0	-6.2

Symbols and units as in Table 7. The global indices are referred to experiment.

$2d + f$ , respectively, that is,  $2d + f$  data appear to approximate the experimental TO spectrum about as well as  $2d$ , although the error distribution is different. In fact,  $2d + f$  exhibits a more systematic overestimation of the experimental values, as is expected for B3LYP. When referred to the experimental TO frequencies,  $\bar{\Delta}$  results to be 3.7 and 0.1 for  $2d + f$  and  $2d$ , respectively.

These considerations about the dependence of vibration frequencies on the basis set size are in no way peculiar to B3LYP, and can be extended to the various Hamiltonians. For example, the mean absolute difference between  $1d$  and  $2d$  is 6.1, 3.0, 3.3, and 2.9 for HF, B3LYP, LDA, and PBE, respectively.

Frequencies in Table 9 have been obtained with the four Hamiltonians and the  $2d$  basis set, as optimized at the HF level. Statistics refer to the experimental data. The mean absolute error is 44, 6, 18, and 21  $\text{cm}^{-1}$  for HF, B3LYP, LDA, and PBE, respectively, indicating that B3LYP performs much better than LDA, that in turn, performs slightly better than PBE, whereas HF is by far the worst approximation of the experimental data.  $\Delta_{\max}$  shows a similar trend, being 85, 22, 42, and 40  $\text{cm}^{-1}$ , respectively.

As mentioned earlier, the valence part of the  $1d$  basis set has also been reoptimized for each DFT Hamiltonian, as reported in Table 3. The frequency values calculated with these modified basis sets at the corresponding equilibrium geometries have been analyzed in terms of the global indices defined above (Table 10), which can be compared with the results obtained with the  $1d$  basis set optimized for HF. The performance of these specifically reoptimized basis sets is not very different from the original  $1d$ , when compared with experiment. Actually, the new basis sets perform slightly worse:  $\overline{|\Delta|}$  increases by 2  $\text{cm}^{-1}$  for B3LYP and LDA and by about 8 for PBE; data, as measured by  $\Delta_{\min}$  and  $\Delta_{\max}$ , are also more randomly scattered with respect to the experimental measurements. On one hand, these indices show that specific reoptimization of the basis set for each Hamiltonian has no dramatic effect on the calculated frequencies but, on the other hand, the larger disagreement with respect to experiment seems to suggest that partial reoptimization of the basis set (restricted to valence functions only) may lead to some inconsistency, which is probably related to core-valence unbalancing. Thus, on the basis of this

analysis, the strategy of using standard basis sets optimized at the HF level in DFT calculations, which is commonly adopted in molecular quantum chemistry, appears to be the best choice. However, more extensive sets of data should be considered to draw general conclusions.

### Comparison with Previous LDA Calculations

As the last point, we compare the present data with the two previous LDA calculations.<sup>5,6</sup> The comparison in our previous article<sup>15</sup> is extended here to LO modes and larger  $2d$  basis set. The equilibrium geometry obtained with the three methods is reported in Table 2, the dielectric constants in Table 5 and Born charges in Table 6. Table 11 gives the obtained frequencies and the difference with respect to experiment. Overall, the three schemes seem to provide similar agreement with experiment,  $\overline{|\Delta|}$  being 17, 18, and 13  $\text{cm}^{-1}$ , and both  $\Delta_{\min}$  and  $\Delta_{\max}$  exhibiting a similar trend. However, closer inspection shows that differences are far from negligible as, for example,  $\bar{\Delta}$  is 3.4, 8.1, and -11.6 for the present calculations, Umari's and Gonze's, respectively. In particular, the large difference between the two plane-wave calculations is surprising. A more appropriate comparison is available in Table 12, where cross-comparisons between the calculated data are also reported, showing that the inclusion of the set of LO frequencies in the statistics does not alter the trend observed in Table 12 of ref. 14. In particular, it is confirmed that the present results compare slightly better with Gonze's work in all respects: predicted equilibrium geometry, dielectric constants, Born charges, and vibrational spectrum at  $\Gamma$ .

It was argued in the previous section that reoptimization of the basis set for LDA is more troublesome than with other DFT Hamiltonians, as core functions should also be involved. Table 12 also suggests that the definition of the pseudopotentials, which has a crucial role in plane-wave calculations, can have some influence on results.

### Conclusions

In the present article it has been shown that it is possible to calculate the vibration frequencies of relatively large crystalline systems by using a local basis and standard quantum chemistry techniques with high accuracy at relatively low cost. This scheme is implemented in a version of the CRYSTAL03 code still under development. It has been shown that convergence with respect to the basis set size is easily achieved. The B3LYP Hamiltonian performs very well (mean absolute error of 6  $\text{cm}^{-1}$  and largest absolute error of 22  $\text{cm}^{-1}$ ), with an unprecedented accuracy in solid state, confirming previous experience with molecules. The LDA results are less satisfactory. PBE performs slightly worse than LDA and HF is affected by larger errors.

The full vibrational spectrum of a large class of materials is now within reach at relatively low cost.



Table 11. Calculated LDA Frequencies of  $\alpha$ -Quartz at  $\Gamma$ .

	This work		Umari et al. <sup>a</sup>		Gonze et al. <sup>b</sup>	
A1-TO	261.6	42.6	193.7	-25.3	238.9	19.9
	332.3	-25.7	355.0	-3.0	339.3	-18.7
	482.1	13.1	460.1	-8.9	461.7	-7.3
	1089.1	7.1	1123.3	41.3	1061.0	-21.0
A2-TO	326.3	-35.0	366.4	5.1	341.3	-20.0
	504.6	5.6	489.3	-9.7	493.4	-5.6
	791.1	13.1	792.2	14.2	762.4	-15.6
	1086.4	14.4	1115.4	43.4	1056.5	-15.5
E-TO	143.4	10.4	120.9	-12.1	133.3	0.3
	263.5	-5.5	257.3	-11.7	261.3	-7.7
	376.9	-16.6	390.0	-3.5	377.6	-15.9
	443.8	-8.7	448.0	-4.5	443.8	-8.7
	721.7	23.7	703.3	5.3	690.8	-7.2
	835.0	36.0	809.6	10.6	791.7	-7.3
	1070.3	4.3	1108.7	42.7	1045.0	-21.0
	1141.7	-16.3	1190.8	32.8	1128.1	-29.9
A2-LO	351.3	-33.7	391.4	6.4	365.7	-19.3
	543.9	-9.1	533.8	-19.2	540.5	-12.5
	816.8	25.8	815.0	24.0	784.7	-6.3
	1249.6	19.6	1272.6	42.6	1218.0	-12.0
E-LO	143.7	10.7	121.0	-12.0	133.4	0.4
	266.9	-2.1	258.5	-10.5	263.2	-5.8
	389.1	-12.9	398.6	-3.4	389.2	-12.8
	497.2	-14.8	500.2	-11.8	498.6	-13.4
	726.5	25.5	708.7	7.7	694.5	-6.5
	844.7	33.2	824.0	12.5	803.9	-7.6
	1137.3	-17.7	1185.7	30.7	1123.9	-31.1
	1234.7	7.7	1270.6	43.6	1209.5	-17.5
$ \bar{\Delta} $	17.5		17.8		13.1	
$\bar{\Delta}$	3.4		8.1		-11.6	
$\Delta_{\min}$	-35.0		-25.3		-31.1	
$\Delta_{\max}$	42.6		43.6		19.9	

The present results have been obtained with the  $2d$  basis set. The differences with respect to the experimental data<sup>33</sup> are also given. Symbols and units as in Table 7. Global indices are evaluated with respect to the experimental frequencies.

<sup>a</sup>Ref. 6.

<sup>b</sup>Ref. 5.

Table 12. Comparison of the LDA Sets of Frequency Values of  $\alpha$ -Quartz at  $\Gamma$  Reported in Table 11 through Global Index  $|\bar{\Delta}|$ .

	Umari et al. <sup>a</sup>	Gonze et al. <sup>b</sup>	Exp <sup>c</sup>
This work	23.2	17.8	17.5
Umari et al. <sup>a</sup>		26.3	17.8
Gonze et al. <sup>b</sup>			13.1

Each datum in a row has been computed with reference to the set of vibration frequencies of the corresponding column. Symbols and units as in Table 7.

<sup>a</sup>Ref. 6.

<sup>b</sup>Ref. 5.

<sup>c</sup>Ref. 33.

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