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NEW ULTRASOFT PSEUDOPOTENTIALS FOR THE STUDY OF SILICATES

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New ultra-soft pseudopotentials (USP's) for Si and O suitable for studies of silicate materials are reported. The performance of the new USP's in density functional calculations on a number of model systems is documented and compared both to observed properties and to those computed in highly converged all-electron calculations. The new USP's are significantly more reliable and accurate than those previously developed and widely distributed. With the new USP's computed structural parameters follow well establised trends with regard to local and gradient corrected treatments of exchange and correlation. The correct order of stability of the α-quartz and sodalite structures is also reproduced although the energy difference is not in quantitative agreement with the all-electron calculations. A new Al USP is also generated and its performance in calculations on α-alumina documented. The importance of consistent treatments of exchange and correlation for core and valence electrons is established.

Keywords: USP; Silicate material; Density functional theory; Si and O; CASTEP

1. INTRODUCTION

Simulations using density functional theory (DFT) within the pseudopotential, plane-wave approximation (PP-PW) have dominated the application of first principles methods to materials simulation in recent years. For many chemical applications the accuracy of computed structures and energetics is crucial. In this case the choice of pseudopotential can be a governing factor in determining the reliability of results. We report the results of a systematic

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examination of the performance of a number of standard and widely used pseudopotentials (relative to all-electron DFT calculations) for computing the structure and phase stability of α-quartz. This system was selected as it is representative of the chemically and geologically important class of silicate minerals. Our target has been to establish the reliability of the ultrasoft pseudopotentials (USP) proposed by Vanderbilt [1] when used within a generalised gradient approximation (GGA) to DFT. The optimal procedure resulting from this study will then be used in further studies of chemical reactions in zeolite materials. In addition to using α-Quartz (α-QUA) and silica polymorphs to establish the reliability of Si and O USP's we have also studied α-Al$_2$O$_3$ to establish the accuracy of the Al USP. We have used as a reference the library of USP's distributed by Molecular Simulations Inc. with the CASTEP software [2]. We demonstrate that the standard Si and Al potentials give rather poor results when used in conjunction with GGA functionals. New potentials which provide significantly more reliable results have been generated and their performance is documented here.

2. METHODS AND PRELIMINARY CALCULATIONS

All PP-PW calculations have been performed using CASTEP software [2] which implements both LDA and GGA formalisms within a plane wave basis set and the pseudopotential approximation [2].

For comparison we have used three different types of PP's to describe the Si and O ions:

- The USP proposed by Vanderbilt (V) [1]
- The norm-conserving pseudopotential (NCP) as proposed by Kleinman and Bylander (KB) [3]
- An hybrid approximation composed of an NCP(KB) for Si and an USP(V) for O, hereafter denoted as MIX.

For all of the PP's adopted a check for the dependence the total energy of α-quartz (at its experimentally determined structure) the kinetic energy cut-off (E_c) of the PW basis set was performed. The E_c for which the convengence (to within 0.01 eV/atom) has been obtained are:

- USP(V): 400 eV
- NCP(KB): 1000 eV
- MIX: 400 eV

PW basis sets based on these cut-offs were then used in the unconstrained optimisation of the cell and internal coordinates of α-quartz. If not explicity

indicated the following criteria were adopted for PP-PW calculations (note that in parentheses we indicate the corresponding keywords in the .rundat input file of CASTEP [4]). The accuracy for the electronic structure optimisation was 1×10^{-6} eV/atom (EPSIL). The forces on the ions have been obtained by using the Hellmann-Feynmann theorem, and these have been used to relax the ions to equilibrium using the BFGS algorithm. The relaxation has been continued until both the RMS forces (RMSF_TOL) and the RMS atomic displacement (DISP_TOL) on all of the atoms were less than 0.005 eVÅ^{-1} and 0.0005 Å, respectively. In addition, optimisation has been continued until the change of the total energy between successive configurations was less than 1×10^{-6} eV/atom (ETOT_TOL). In order to take into account the Pulay stress during the cell optimization total energies were corrected using the finite-basis set correction method developed by Francis and Payne [5]. The cell relaxation has been continued until the RMS stress (RMS_STR) was less than 0.05 GPa. For α-quartz and α-alumina, 2 and 6 k-points, respectively, were adopted for sampling the Brillouin zone. For LDA calculations the default FFT grid as defined by the Cerius2 interface has been adopted, for GGA calculations a finer FFT grid has been used, defined as $NGX(Y,Z) = 0.32615L\sqrt{E_c}$, where L is the length of the real-space lattice vector [4].

For reference, all-electron (AE) Gaussian-type functions (GTF) calculations were also performed with the CRYSTAL98 code [6], using both LDA and GGA formalisms, which will be denoted as AE-LDA and AE-GGA, respectively. The adopted basis set was Si[6−21G(d)] (with the outermost exponents α(sp) $= 0.13$ and α(d) $= 0.5$ bohr^{-2}) and O[6-31G(d)] (with the outermost exponents α(sp) $= 0.27$ and α(d) $= 0.6$ bohr^{-2}). In a recent study using very sophisticated Gaussian basis sets we have demonstrated that this choice gives excellent geometries and energetics [7]. For Al an 85-11(d) basis set was adopted, as it has been developed previously for high accuracy simulations of zeolites [9, 10]. The details of the energy convergence and geometry optimisation for all of these calculations have been reported elsewhere [7 − 10].

3. α-QUARTZ CALCULATIONS USING USPs
FROM THE CASTEP-MSI LIBRARY

In Table I experimental data and previously published results of DFT first principles calculations on α-quartz have been gathered [11 − 21]. Although not an exhaustive collation of the computated data on α-quartz this is indicative of the current state of the art for PP-PW calculations. Most

TABLE I   DFT first principles theoretical calculations on α-Quartz. Review of published data. Structural data: unit-cell constants, volume, fractional atomic coordinates, average Si—O bond length (in Å), Si—O—Si bond angle (in deg). Computational details: kinetic energy cut-off, pseudopotential, number of k-points

	Expt.[c]	Expt.[c]	LDA	LDA	LDA	LDA	LDA	LDA	LDA	LDA	AE-PW-LDA	AE-LDA
a(Å)	4.914	4.902	4.913	4.89	4.876	4.954	4.892	4.920	4.84	4.899	4.844	4.840
c(Å)	5.406	5.400	5.405	5.49	5.405	5.441	5.389	5.412	5.41	5.383	5.347	5.394
V(Å³)	113.1	112.5	113.0	113.7	111.3	115.6	111.7	113.5	109.8	111.9	108.6	109.4
Si(x)	0.4700	0.4680	0.4638	0.469	0.4654	0.4750	0.4664			0.4695	0.460	0.4628
O(x)	0.4131	0.4124	0.4081	0.418	0.4125	0.4151	0.4129			0.4147	0.409	0.4049
O(y)	0.2677	0.2712	0.2758	0.274	0.2745	0.2584	0.2730			0.2670	0.280	0.2808
O(z)	0.1189	0.1163	0.1215	0.118	0.1143	0.1264	0.1152			0.1199	0.108	0.1065
Si—O(av.)	1.610	1.613	1.621	1.612	1.611	1.607	1.610		1.614	1.602	1.614	1.626
Si—O—Si	143.5	142.4	141.8	143.8	141.8	146.3	142.2		140.2	144.1	139.2	137.5
E_c(eV) PP [a,b]			NC(T)	870. NC(TM)	340. US(V)	1600. NC(T)	400. US(V)	700. NC(TM)	544. NC(H)	396. US(V)		
k–p.					3	6		4	2	14	6	7 [d]
Ref.	[11]	[11]	[12]	[13]	[14]	[15]	[16]	[17]	[18]	[19]	[20]	

	Expt.[c]	Expt.[c]	GGA	GGA	AE-PW-GGA	AE-GGA
a(Å)	4.914	4.902	4.97	5.027	4.990	4.958
c(Å)	5.406	5.400	5.52	5.509	5.484	5.433
V(Å³)	113.1	112.5	118.1	120.6	118.5	115.7
Si(x)	0.4700	0.4680		0.4814	0.474	0.4650
O(x)	0.4131	0.4124		0.4165	0.413	0.4100
O(y)	0.2677	0.2712		0.2460	0.261	0.2777
O(z)	0.1189	0.1163		0.1364	0.123	0.1087
Si—O(av.)	1.610	1.613	1.623	1.615	1.627	1.644
Si—O—Si	143.5	142.4	145.5	149.1	144.8	139.5
E_c(eV) PP [a,b]			1600. NC(T)	396. US(V)		
k–p.			6	14	6	7 [d]
Ref.	[11]	[11]	[15]	[19]	[20]	

[a] NC = Norm-conserving, US = Ultra-soft; [b] T = Teter, TM = Trouiller-Martins, V = Vanderbilt, H = Hamann; [c] 269 K and 13 K, respectively; [d] Present work.

studies have used LDA functionals [12–21] while a few more recent studies have also adopted the GGA formalism [18–20]. Some studies have reported results using USPs [14, 19]. For comparison, all-electron GTF [21] and linear-augmented plane-wave (LAPW) data [20] have been included. This data provides a reference point for the discussions below.

Considering initially the AE-GTF results we note the following general features:

(1) AE-LDA lattice parameters are slightly underestimated with respect to experimental data, whereas Si—O bond lengths are longer and Si—O—Si angles are smaller.

(2) AE-GGA tends to overstimate the cell parameters, in part because Si—O bonds are slightly longer (1.64 rather than 1.62 Å). The Si—O—Si angles are similar to those computed within the LDA.

Details of the structure computed using the standard USPs from the CASTEP-MSI library are summarized in Tables II and III for the LDA and GGA functionals respectively. The LDA data should be comparable to that of Liu et al. [14] (see Tab. I) as we have used very similar computational conditions. However, the agreement with Liu's data is rather poor; the Si—O bond length is underestimated by about 0.02 Å and the Si—O—Si bond angle overestimated by about 5 degrees. As can be seen from Table II the computed data are relatively insensitive to variations in the k-space sampling and kinetic energy cut-off and thus the choice of pseudopotential is the most likely source of these differences. Comparing the PW-LDA data to the AE-LDA data only accentuates the differences as the Liu data is already underestimating bond lengths and overestimating bond angles. We note that

TABLE II   PW-LDA/USP$_{MSI}$ theoretical calculations on α-Quartz. Effect of the energy cutoff and of the number of k-points for sampling the Brillouin zone. See Table I for other details

E_c	340.(2)[a]	340.(4)[a]	340.(8)[a]	400.[b]	500.[b]	600.[b]	600.[c]
$a(Å)$	4.9190	4.9077	4.9249	4.8784	4.8721	4.8759	4.8771
$c(Å)$	5.4208	5.4081	5.4185	5.3707	5.3694	5.3710	5.3701
$V(Å^3)$	113.6	112.8	113.8	110.7	110.4	110.6	110.6
Si(x)	0.4766	0.4751	0.4769	0.4710	0.4709	0.4710	0.4710
O(x)	0.4167	0.4165	0.4171	0.4149	0.4150	0.4151	0.4153
O(y)	0.2550	0.2578	0.2545	0.2647	0.2651	0.2647	0.2647
O(z)	0.1302	0.1280	0.1307	0.1222	0.1220	0.1223	0.1223
Si—O(av.)	1.592	1.591	1.592	1.591	1.590	1.591	1.591
Si—O—Si	147.8	147.1	148.1	145.0	144.9	145.0	145.0

[a] FFT grid = fine, in parentheses number of k-points.
[b] Tol. = default.
[c] FFT grid = fine; k-points = 4.

TABLE III   PW-GGA/USP$_{MSI}$ theoretical calculations on α-Quartz. Effect of the energy cutoff and of the number of k-points for sampling the Brillouin zone. See Table I for other details

E_c	340.[a]	400.[b]	400.	500.[b]
a(Å)	4.9626	4.9842	4.9861	4.9821
c(Å)	5.4722	5.4862	5.4664	5.4683
V(Å^3)	116.7	118.0	117.7	117.5
Si(x)	0.4879	0.4901	0.4901	0.4907
O(x)	0.4198	0.4208	0.4197	0.4196
O(y)	0.2339	0.2299	0.2288	0.2277
O(z)	0.1477	0.1512	0.1517	0.1526
Si—O(av.)	1.585	1.587	1.586	1.586
Si—O—Si	152.9	153.8	153.5	153.6

[a] k-points = 8.
[b] FFT grid = default.

the PW-LDA data generated here are in reasonable agreement with the recent results published by Demuth *et al.* [19] presumably because the computational conditions used are very similar.

Calculations performed with the GGA for these pseudopotentials are reported in Table III. One expects the semi-local treatment of the electron exchange interaction to result in a slight increase in the bond length and this is observed in the AE data. In contrast, in the PW-GGA calculations based on these psuedopotentials we observe a further contraction of the Si—O bond length.

In making the relatively fine comparisons of structures detailed above one must address the issue of how structural optimisation is performed. In particular, previous studies differ in their treatment of the Pulay component of the stress. Often the optimal lattice parameters and internal atomic coordinates are determined based on minimization of the total energy at fixed volume and an equation of state fitted to a few calculated points to determine the equilibrium volume. As we have optimised the structure with respect to cell and internal degrees of freedom simultaneously we have checked the cell optimisation by mapping out the potential energy surface (PES) around the computed minimum within the PW-GGA formalism. The corresponding results are shown in Table IV. Data were collected on a 3 × 3 grid changing the equilibrium lattice parameters by ± 2.5% and fully relaxing the internal coordinates for each cell at each point. These results show that the computed cell parameters correspond to a true minimun on the PES. We note that these variations in the cell produce variations in the Si—O bond length and angle comparable to the errors with respect the AE results and, despite the rather small variations involved, correspond to a

TABLE IV   PW-GGA/USP$_{MSI}$ theoretical calculations on α-Quartz. Study of the PES around the minimum obtained at $E_c = 400.$ eV, by changing the size of the cell by a $\pm 2.5\%$ factor[a, b]

$a\backslash c$	5.3490	5.4862	5.6234
Total energy (eV)			
4.8597	-2973.3653041	-2973.3973236	-2973.3826690
4.9842	-2973.4287257	-2973.4546214	-2973.4164505
5.1087	-2973.4042987	-2973.3520768	-2973.2094325
Geometrical features (Å, deg.): Si—O av. (Si—O—Si)			
4.8597	1.585(145.4)	1.584(148.2)	1.585(151.4)
4.9842	1.585(150.9)	1.586(154.3)	1.594(155.9)
5.1087	1.598(155.7)	1.604(156.7)	1.614(157.8)

[a] Geometry initial guess: opt. PW-GGA/USP$_{MSI}$ $E_c = 400.$ (see Tab. III).
[b] FFT grid = default.

TABLE V   PP-PW theoretical calculations on α-Quartz by using different kind of pseudo-potentials from MSI library. See Table I for other details

PP	US(V)		NC(KB)		MIX	
Method	LDA	GGA	LDA	GGA	LDA	GGA
a(Å)	4.8784	4.9861	4.8698	4.9935	4.8992	5.0139
c(Å)	5.3707	5.4664	5.3594	5.4702	5.3887	5.5057
V(Å^3)	110.7	117.7	110.1	118.1	112.0	119.9
Si(x)	0.4710	0.4901	0.4674	0.4845	0.4679	0.4848
O(x)	0.4149	0.4197	0.4125	0.4188	0.4129	0.4179
O(y)	0.2647	0.2277	0.2713	0.2410	0.2703	0.2398
O(z)	0.1222	0.1517	0.1161	0.1412	0.1171	0.1420
Si—O (av.)	1.591	1.586	1.602	1.597	1.609	1.605
Si—O—Si	145.0	153.5	142.4	151.3	142.8	151.2

large variation in the total energy (~ 0.2 eV per cell). It is thus unlikely that the observed discrepancies in bond lengths and angles are the result of incomplete optimisation.

Having eliminated other sources of the observed discrepancy we turn to the effects of the choice of pseudopotential. Table V documents the variation of the structure with the different choices of pseudopotential documented above. For all of the PPs and methods adopted, Si—O bonds are shorter and Si—O—Si angles are larger than those computed in AE calculations (see Tab. I). In addition the Si—O bond lengths computed using the LDA functional are longer than those using the GGA. This is in contrast to all AE calculations and to one's intuition about the role of semi-local exchange.

As we are interested in simulating microporous siliceous materials, we have optimised a few all-silica zeolites: sodalite (SOD), chabazite (CHA) and edingtonite (EDI), at the PW-GGA level. In Table VI we report the

TABLE VI   Comparison between PW-GGA and AE-GTF[a] HF and B3-LYP calculations on silica polymorphs. Optimized structural data and relative stability with respect to α-quartz are reported.[b] See text for acronyms

System	Method	a	c	α	$\langle Si{-}O \rangle$	$\langle Si{-}O{-}Si \rangle$	ΔE
α-QUA	PW-GGA	4.986	5.466		1.586	153.5	0.0
	AE-HF	4.953	5.427		1.614	144.8	0.0
	AE-B3LYP	4.955	5.428		1.636	141.0	0.0
SOD	PW-GGA	8.818			1.583	160.1	− 3.2
	AE-HF	8.887			1.613	153.7	4.6
	AE-B3LYP	8.845			1.628	147.7	5.4
CHA	PW-GGA	9.164		94.2	1.587	149.3	1.3
	AE-HF	9.319		94.7	1.613	149.3	6.3
	AE-B3LYP	9.373		94.8	1.629	148.2	6.8
EDI	PW-GGA	6.814	6.361		1.587	155.0	5.2
	AE-HF	6.917	6.453		1.611	155.4	11.6
	AE-B3LYP	7.000	6.492		1.631	154.4	11.6

[a] AE-GTF results from Refs. [7, 9, 10].
[b] Cell parameters in Å and deg; Average bond distances and angles in Å and deg; Relative stability to α-QUA in kJ/mol.

optimal structures and relative stabilities and compare them to data from the literature [7–10]. With these pseudopotentials the PW-GGA Si—O bond lengths are systematically shorter than AE values while angles are in reasonable agreement. Unlike α-QUA, for which the cell size was over-estimated we find that for these microporous structures the errors in bond distances yield cell parameters smaller than the AE data. Experimentally, for both high-density and low-density silica frameworks the observed most stable polimorph is α-QUA, followed by high-density and low-density silica frameworks respectively [22, 23]. In agreement with the experimental findings, the AE-GGA stability ranking is: α-QUA > SOD > CHA > EDI, giving α-QUA as the most stable structure. In contrast to this the PW-GGA calculations find the sodalite framework to be significantly more stable than α-quartz (Tab. VI).

In summary, the analysis of the data collated here demonstrates that in using the standard, CASTEP-MSI, ultrasoft pseudopotentials to study silica polymorphs:

- Si—O bonds are too short,
- Si—O—Si angles are too large (most notably in α-QUA),
- the wrong order of stability of microporous silica polimorphs with respect to α-QUA is predicted.

The insensitivity of this data to other computational parameters indicates that there is a serious problem with the USPs. We have therefore constructed a new set of pseudopotentials for studying these systems.

4. CONSTRUCTION AND TESTING OF NEW USPs

The form and construction of USPs has been discussed in detail by Vanderbilt [1]. Here we give sufficient details to establish the principles upon which the new pseudopotentials are based. As a starting point we establish a core radii (r_c) with the criteria that the core radii do not overlap for reasonable contractions of the unit cell [14].

In the silica system where Si is tetracoordinated the nearest neighbor distance between Si and O is about 3.0 a.u. However, the cutoff radii adopted in the CASTEP-MSI library are 1.8 a.u. and 1.3 a.u. for Si and O respectively, resulting in an overlap between core regions even under ambient conditions. We have adopted smaller core radii for Si and would therefore expect this pseudopotential to be more transferable to related systems.

4.1. The Silicon Pseudopotential

The silicon pseudopotential was generated from the ionized $3s^2 3p^1$ reference configuration. Nonlocal projectors in s and p channels were introduced with one reference energy for each channel which was taken to be the atomic eigenvalue. The cutoff radius for both s and p valence functions and for the local potential were taken to be 1.4 and 1.0 a.u., respectively. The cutoff r_{inner} was chosen to be 0.8 a.u. for all angular momenta. In order to improve transferability, several attempts were made to create an USP for silicon with these radii and two reference energies for each channel. Unfortunately such an USP is unstable leading to ghost states during the fitting of the atomic solution.

4.2. The Oxygen Pseudopotential

The oxygen USP in the CASTEP-MSI library was generated using an unusual choice of reference energies. Typically, in order to span the band energies in a solid state calculation one selects the eigenvalue of the bound electronic state and a nearby energy (say 0.5 Ry higher) to use as reference states. In the distributed potential this is not the case and as the two reference energies for both the s- and p-projectors are set equal to the s and p bound state eigenvalues. A new potential has been generated utilising the same neutral $2s^2 2p^4$ electronic configuration but with s- and p-channels treated as non-local components with reference energies set to the appropriate bound state eigenvalue and the eigenvalue plus 0.5 Ry. We used a core cutoff radius of 1.3 a.u. for both s and p valence wave functions and 1.0 a.u. for the local potential. The L dependent r_{inner} radii used for

pseudizing the localized core-region charge augmentation function $Q_{ij}(r)$ were chosen to be 0.7 a.u. for all angular momenta.

It is worth noting that despite what we believe to be a significantly better method of construction the new O-USP generated here, when used in conjunction with the CASTEP-MSI Si-USP, gives similar results to those reported above using the original O-USP. This confirms that the discrepancies documented above are mainly due to faults in the Si-USP.

4.3. Testing the New Si and O Pseudopotentials

The structure and energetics of α-quartz and sodalite computed using the new pseudopotentials are summarissed in Tables VII–IX.

In comparing the present results with both the literature and the previous ones, there is an important aspect to take into account. The pseudopotentials of the CASTEP-MSI library are constructed from the AE-LDA atomic solution. It has become a common practice to use such LDA-pseudopotentials even when treating the valence electrons within the GGA approximation. This is a possible source of errors in the PW-GGA calculations reported above. Indeed, the new Si-USP based on an AE-LDA atomic solution, gives excellent results at LDA level, but results for a GGA valence treatment are still poor. Adopting GGA pseudopotentials based on fully self-consistent GGA all-electron atomic calculations give results in much better agreement with the AE-GGA calculations as shown in Table VII. This correction results in a lengthening of the Si—O bond and a decrease of the Si—O—Si angle can be observed, even if the Si—O—Si angle is still very large. The GGA Si—O bonds are now longer than LDA

TABLE VII PW-LDA and PW-GGA calculations on α-Quartz. Comparison among the USP_{MSI} and the present USP's generated by using either the LDA or the GGA atomic solution. See Table I for other details

PP	USP_{MSI}		USP_{LDA}		USP_{GGA}
method	LDA	GGA	LDA	GGA	GGA
$a(\text{Å})$	4.8784	4.9861	4.9215	5.0040	5.0684
$c(\text{Å})$	5.3707	5.4664	5.4046	5.4985	5.5866
$V(\text{Å}^3)$	110.7	117.7	113.4	119.2	124.3
$Si(x)$	0.4710	0.4901	0.4709	0.4844	0.4835
$O(x)$	0.4149	0.4197	0.4134	0.4173	0.4157
$O(y)$	0.2647	0.2277	0.2661	0.2412	0.2438
$O(z)$	0.1222	0.1517	0.1197	0.1405	0.1375
Si—O (av.)	1.591	1.586	1.610	1.604	1.631
Si—O—Si	145.0	153.5	143.8	150.7	149.5

TABLE VIII   PW theoretical calculations on α-Quartz by using different USP's. See Table I for other details

USP	MSI[a]	V_{LDA}[b]	V_{GGA}[c]	CH1[d]	CH2[e]
$a(\text{Å})$	4.9861	5.0040	5.0684	5.0138	4.9797
$c(\text{Å})$	5.4664	5.4985	5.5866	5.5048	5.4631
$V(\text{Å}^3)$	113.4	119.2	124.3	119.8	117.32
Si(x)	0.4901	0.4844	0.4835	0.4844	0.4847
O(x)	0.4197	0.4173	0.4157	0.4172	0.4186
O(y)	0.2277	0.2412	0.2438	0.2413	0.2396
O(z)	0.1517	0.1405	0.1375	0.1402	0.1427
Si—O (av.)	1.586	1.604	1.631	1.607	1.593
Si—O—Si	153.5	150.7	149.5	150.6	151.6

[a] USP from the CASTEP-MSI library.
[b] USP generated here (AE-LDA atomic solution).
[c] USP generated here (AE-GGA atomic solution).
[d] As V_{LDA} but with two projectors in the p channel.
[e] As V_{LDA} but with lloc = 2.

TABLE IX   PW-GGA theoretical calculations on α-QUA and SOD. Comparison among the USP$_{MSI}$ and the present USP's generated by using either the LDA or the GGA atomic solution[a]

System	USP	a	c	$\langle Si-O \rangle$	$\langle Si-O-Si \rangle$	ΔE
α-QUA	USP$_{MSI}$	4.986	5.466	1.586	153.5	0.00
	USP$_{LDA}$	5.004	5.498	1.605	150.7	0.00
	USP$_{GGA}$	5.068	5.587	1.631	149.5	0.00
SOD	USP$_{MSI}$	8.818		1.583	160.1	−3.22
	USP$_{LDA}$	8.916		1.601	159.8	0.14
	USP$_{GGA}$	9.056		1.627	159.4	0.66

[a] Cell parameters in Å and deg; Average bond distances and angles in Å and deg; Relative stability to α-QUA in kJ/mol.

ones showing the same trend observed for AE calculations. Nevertheless, in the GGA case, the combination of longer Si—O bonds and larger Si—O—Si angles yields bigger cells. These results are in agreement with data published recently by Hafner and co-workers using the VASP software [19] which are displayed in Table I. The remaining differences between the two sets of data are likely to be due to the different electronic configuration adopted as reference states in the AE atomic calculations, as in Ref. [19] a neutral reference configuration was adopted for the Si-USP.

In Table VIII the sensitivity of the calculations to details of the pseudopotential construction are documented. Potentials within the GGA are used in which either two projectors in the p channel are used (CH1) or the local potential is chosen so that the logarithmic derivative is correct at the second valence eigenvalue (CH2). Notice that in both cases the LDA atomic solution was adopted for creating the USPs. Adding two projectors

in the p channel (CH1) does not yield any improvement while CH2 tends to yield shorter Si—O bonds and larger Si—O—Si angle which is reminiscent of the data generated from the CASTEP-MSI pseudopotentials.

In Table VI it was shown that for crystalline microporous siliceous materials the CASTEP-MSI USP's do not give the right order of stability with respect to α-quartz. The relative stability with respect to sodalite, only, is documented in Table IX. The new USP's produce the correct order of stability although the energy difference between α-quartz and sodalite is significantly less than that computed in AE-GTF calculations (see Tab. VI).

4.4. Aluminum Pseudopotential

As we are interested in studying aluminosilicate systems, such as zeolites, we examined the performance of the Al-USP distributed in the CASTEP-MSI library. This potential was constructed in a similar way to the Si-USP with a core radius of 2.0 a.u. In zeolites the average Al—O distance is around 3.34 a.u., which is very close to the sum of the cutoff radii of the Al and O USPs leading to almost overlapping core regions under ambient conditions. Therefore, in order to increase the reliability of the potentials, the Al r_c was reduced to 1.7 a.u. The new USP was constructed using essentially the same conditions adopted for silicon (see above). The neutral $3s^2 3p^1$ reference configuration was used with nonlocal projectors in s and p channels and a single reference energy for each channel taken to be the atomic eigenvalue. The cutoff radius for both s and p valence functions and for the local potential were taken to be 1.7 and 1.3 a.u., respectively. The cutoff r_{inner} was chosen to be 1.1 for all angular momenta. As for the Si and O potentials, two versions of the new Al-USP were generated based on LDA and GGA all-electron atomic solutions.

As a test case α-alumina was adopted. In Table X PW-GGA results are reported in comparison with a few available data. The new Al-USP gives results in good agreement with experimental [24] and with the AE calculations. The new USP generated from a AE-GGA atomic solution follows the same trend observed in the silicates – the unit cell volume is larger, and the Al—O bonds longer than predicted by the LDA. This trend is in agreement with the AE results.

4.5. Other Pseudopotentials – H, C, N

As the need to base GGA calculations on potentials generated from GGA atomic solutions is very clear a number of other psedopotentials were regenerated from the fully self-consistent GGA all-electron atom calculations but using computational conditions essentially the same as those

TABLE X   Test of the new USP for Al. Comparison among different theoretical calculations on α-Alumina

Method	Expt.	LDA	LDA	AE-HF	AE-HF$_{PZ}$	AE-HF$_{PW91}$	GGA	GGA	GGA	AE-GGA
a(Å)	5.1293	5.123	5.091	5.1170	5.0391	5.0026	5.0732	5.1090	5.2070	5.1484
α(deg)	55.29	55.20	55.33	55.31	55.38	55.44	55.17	55.28	55.36	55.31
Al(u)	0.3521	0.3522	0.3538	0.3521	0.3520	0.3525	0.3521	0.3528	0.3527	0.3516
O(v)	0.5562	0.5562	0.5555	0.5562	0.5555	0.5554	0.5576	0.5569	0.5557	0.5568
Al—O(1)				1.850	1.827	1.815	1.830	1.842	1.883	1.864
Al—O(2)				1.966	1.933	1.921	1.952	1.971	2.005	1.976
E$_c$(eV)		1100.					400.	400.	400.	
PP		NC(TM)					US$_{MSI}$[a]	US$_{LDA}$[b]	US$_{GGA}$[c]	
k – p.		8					6	6	6	4[d]
Ref.	[24]	[25]	[26]	[27]	[27]	[27]				

[a] Al-USP from MSI library.
[b] New Al-USP generated with the AE-LDA atomic solution.
[c] New Al-USP generated with the AE-GGA atomic solution.
[d] Present work.

existing in the CASTEP-MSI library. New H, C, N were generated in this way and are documented in the Appendix. The H-USP was generated with parameters suggested by C. Pickard (see `http://www.cse.clrc.ac.uk/Software/CASTEP/H_00.usp`).

5. CONCLUSIONS

New ultra-soft pseudopotentials (USP's) for Si and O suitable for studies of silicate materials have been generated. The performance of the new USP's in density functional calculations on a number of model systems has been documented. A detailed comparison to experimentally observed structures and previous theoretical calculations of structures and energetics has been made. Highly converged all-electron calculations have been used as a benchmark for the quality of the USP's. The new USP's are significantly more reliable and accurate than those previously developed and widely distributed. With the new USP's computed structural parameters follow well established trends with regard to local and gradient corrected treatments of exchange and correlation. The correct order of stability of the α-quartz and sodalite structures is also reproduced although the energy difference is not in quantitative agreement with the all-electron calculations. A new Al USP is also generated and its performance in calculations on α-alumina documented. The importance of consistent treatments of exchange and correlation for core and valence electrons is established and new H, C and N pseudopotentials suitable for GGA calculations are reported.

All of the settings used in creating the new USP's reported here are given in Appendix 1. The new USP's, in a format suitable for CASTEP calculations, may be obtained by sending email to ukcp@dl.ac.uk.

APPENDIX: DETAILS OF THE NEW USP'S

Si_01_V.usp

New USP generated by B. Civalleri (N. M. Harrison)

```
pseudopotential report: version  7.3.2 date 10-26-1999


silicon                      ceperley-alder exchange-corr

z =  14.    zv =   4.    exfact =   0.00000

                             etot  =  -6.93915

index    orbital      occupation     energy

  1        300            2.00         -1.40

  2        310            1.00         -0.86

keyps = 3      ifpcor = 0

rinner =      0.80      for L=    1

rinner =      0.80      for L=    2

rinner =      0.80      for L=    3

  new generation scheme:

  nbeta =  2      kkbeta =  545     rcloc =    1.0000

  ibeta    l     epsilon   rcut

    1       0      -1.40    1.40

    2       1      -0.86    1.40

lloc   =-1  eloc   =   0.000

ifqopt = 2  nqf    = 8  qtryc =  10.000

all electron calculation used koelling-harmon equation

     ***********logarithmic mesh***********
```

Si_01_Vgga.usp

New USP generated by B. Civalleri (N. M. Harrison). The AE-GGA(PW91) solution was used.

```
         pseudopotential report: version  7.3.2 date 10-26-1999
```

```
    silicon                      slater x-alpha exchange-corr

    z =  14.    zv =   4.    exfact =   4.00000

                                etot  =  -6.93013

    index    orbital      occupation    energy

      1        300           2.00        -1.40

      2        310           1.00        -0.86

    keyps = 3     ifpcor = 0

    rinner =      0.80     for L=    1

    rinner =      0.80     for L=    2

    rinner =      0.80     for L=    3

      new generation scheme:

      nbeta = 2      kkbeta =  545      rcloc =     1.0000

      ibeta     l     epsilon   rcut

        1        0      -1.40   1.40

        2        1      -0.86   1.40

    lloc   =-1  eloc   =   0.000

    ifqopt = 3  nqf    = 8  qtryc =  10.000

    all electron calculation used koelling-harmon equation

         ************logarithmic mesh************
```

Al_01_CB.usp

USP generated by B. Civalleri (N. M. Harrison).

```
pseudopotential report: version  7.3.2 date 10-27-1999
```

```
aluminum                      ceperley-alder exchange-corr

z =  13.     zv =   3.     exfact =   0.00000

                               etot  =  -3.89524

index    orbital      occupation     energy

  1        300           2.00         -0.58

  2        310           1.00         -0.20

keyps = 3      ifpcor = 0

rinner =      1.10      for L=    1

rinner =      1.10      for L=    2

rinner =      1.10      for L=    3

   new generation scheme:

   nbeta = 2      kkbeta = 557      rcloc =     1.3000

   ibeta     l      epsilon   rcut

     1        0       -0.58    1.70

     2        1       -0.20    1.70

lloc   =-1  eloc   =   0.000

ifqopt = 3  nqf    = 8  qtryc =  10.000

all electron calculation used koelling-harmon equation

       ***********logarithmic mesh***********
```

Al_01_CBgga.usp

USP generated by B. Civalleri (N. M. Harrison). The AE-GGA(PW91) solution was used.

```
pseudopotential report: version  7.3.2 date 10-27-1999
```

```
aluminum                     slater x-alpha exchange-corr

z =  13.    zv =   3.    exfact =   4.00000

                             etot  =  -3.88039

index     orbital       occupation     energy

  1          300            2.00         -0.57

  2          310            1.00         -0.20

keyps = 3     ifpcor = 0

rinner =      1.10      for L=     1

rinner =      1.10      for L=     2

rinner =      1.10      for L=     3

   new generation scheme:

   nbeta =  2     kkbeta =   557     rcloc =     1.3000

   ibeta    l     epsilon    rcut

     1       0       -0.57    1.70

     2       1       -0.20    1.70

lloc   =-1  eloc   =    0.000

ifqopt = 3  nqf    = 8  qtryc =  10.000

all electron calculation used koelling-harmon equation

      ************logarithmic mesh************
```

O_01_CB.usp

Created by B. Civalleri (N. M. Harrison)

```
pseudopotential report: version  7.3.2 date 10-21-1999


oxygen                    ceperley-alder exchange-corr

z =   8.    zv =   6.    exfact =   0.00000

                          etot  = -31.52093

index    orbital      occupation    energy

  1        200           2.00        -1.74

  2        210           4.00        -0.68

keyps = 3     ifpcor = 0

rinner =      0.70     for L=    1

rinner =      0.70     for L=    2

rinner =      0.70     for L=    3

  new generation scheme:

  nbeta =  4      kkbeta =  519     rcloc =     1.0000

  ibeta    l     epsilon   rcut

   1       0       -1.74   1.30

   2       0        0.50   1.30

   3       1       -0.68   1.30

   4       1        0.50   1.30

lloc   = 2 eloc   =   0.000

ifqopt = 2  nqf    = 8 qtryc =  10.000

all electron calculation used schroedinger equation

     ***********logarithmic mesh***********
```

O_01_CBgga.usp

Created by B. Civalleri (N. M. Harrison). The AE-GGA(PW91) solution was used.

```
pseudopotential report: version  7.3.2 date 10-26-1999
```

```
oxygen                       slater x-alpha exchange-corr

z =   8.    zv =   6.    exfact =   4.00000

                         etot  = -31.63430

index    orbital      occupation     energy

  1        200           2.00        -1.76

  2        210           4.00        -0.67

keyps = 3     ifpcor = 0

rinner =      0.70     for L=    1

rinner =      0.70     for L=    2

rinner =      0.70     for L=    3

  new generation scheme:

  nbeta =  4      kkbeta =  519      rcloc =     1.0000

  ibeta    l     epsilon   rcut

   1       0      -1.76    1.30

   2       0       0.50    1.30

   3       1      -0.67    1.30

   4       1       0.50    1.30

lloc   = 2  eloc   =   0.000

ifqopt = 3  nqf    = 8  qtryc =  10.000

all electron calculation used schroedinger equation

      ************logarithmic mesh************
```

C_01_CBgga.usp

USP generated by B. Civalleri (N. M. Harison) by using the CASTEP-MSI library parameters but based on the AE-GGA(PW91) solution.

```
           pseudopotential report: version  7.3.2 date 11-18-1999


    carbon                       slater x-alpha exchange-corr

    z =   6.     zv =   4.    exfact =   4.00000

                                 etot  = -10.73832

    index     orbital        occupation      energy

      1         200             2.00         -1.01

      2         210             2.00         -0.39

    keyps = 3      ifpcor = 0

    rinner =       1.25      for L=    1

    rinner =       1.25      for L=    2

    rinner =       1.25      for L=    3

      new generation scheme:

      nbeta =  4      kkbeta =  491      rcloc =     1.4000

      ibeta    l      epsilon   rcut

        1        0       -1.01   1.40

        2        0        0.50   1.40

        3        1       -0.39   1.40

        4        1        0.50   1.40

    lloc   = 2  eloc   =   0.000

    ifqopt = 3  nqf     = 8  qtryc =  10.000

    all electron calculation used koelling-harmon equation

          ***********logarithmic mesh***********
```

N_01_CBgga.usp

USP generated by B. Civalleri (N. M. Harrison) by using the CASTEP-MSI library parameters but based on the AE-GGA(PW91) solution.

```
      pseudopotential report: version  7.3.2 date 11-18-1999


   nitrogen                    slater x-alpha exchange-corr

   z =   7.    zv =   5.    exfact =   4.00000

                                  etot  = -19.34483

   index    orbital       occupation     energy

     1        200            2.00        -1.37

     2        210            3.00        -0.53

   keyps = 3     ifpcor = 0

   rinner =       0.80      for L=    1

   rinner =       0.80      for L=    2

   rinner =       0.80      for L=    3

     new generation scheme:

     nbeta =  4      kkbeta =  629      rcloc =     1.4000

     ibeta    l     epsilon   rcut

       1       0      -1.37   1.60

       2       0       1.00   1.60

       3       1      -0.53   1.60

       4       1       1.00   1.60

   lloc  = 2 eloc  =   0.000

   ifqopt = 3  nqf    = 8  qtryc =   9.000

   all electron calculation used koelling-harmon equation

         ************logarithmic mesh************
```

H_01_CBgga.usp

USP generated by B. Civalleri (N. M. Harrison) following suggestions from C. J. Pickard Based on the AE-GGA(PW91) atomic solution.

```
        pseudopotential report: version  7.3.2 date 11-10-1999


    H                              slater x-alpha exchange-corr

    z =   1.    zv =   1.    exfact =   4.00000

                                etot  =  -0.92050

    index    orbital       occupation    energy

      1         100            1.00       -0.48

    keyps = 3     ifpcor = 0

    rinner =       0.60      for L=    1

       new generation scheme:

       nbeta =  2      kkbeta =  353     rcloc =     0.8000

       ibeta     l     epsilon    rcut

         1       0       -0.48    0.80

         2       0        0.50    0.80

    lloc   = 1 eloc    =   0.000

    ifqopt = 3  nqf    = 6  qtryc =   9.000

    all electron calculation used koelling-harmon equation

        ************logarithmic mesh************
```

References

[1] Vanderbilt, D. (1990). "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism", *Phys. Rev. B*, **41**, 7892.

[2] CASTEP 3.9 academic version, licensed under the UKCP-MSI agreement, 1999.

[3] Kleinman, L. and Bylander, D. M. (1982). "Efficacious form for model pseudopotentials", *Phys. Rev. Lett.*, **48**, 1425.

[4] Lindan, P. J. D., The Guide to CASTEP 3.9, Daresbury Laboratory, CLRC, 1999. (see http://www.cse.dl.ac.uk/Activity/UKCP for further details).

[5] Francis, G. P. and Payne, M. C. (1990). "Finite basis set corrections to total energy pseudopotetial calculations", *J. Phys. Condens. Matter*, **2**, 4395.

[6] Saunders, V. R., Dovesi, R., Roetti, C., Causà, M., Harrison, N. M., Orlando, R. and Zicovich-Wilson, C. M., CRYSTAL-98 User's Manual (Università di Torino, Torino, 1999).

[7] Civalleri, B., Zicovich-Wilson, C. M., Ugliengo, P., Saunders, V. R. and Dovesi, R. (1998). "A periodic *ab initio* study of the structure and relative stability of silica polymorphs", *Chem. Phys. Lett.*, **292**, 394.

[8] Civalleri, B., Casassa, S., Garrone, E., Pisani, C. and Ugliengo, P. (1999). "Quantum mechanical *ab-initio* characterization of a simple periodic model of the silica surface", *J. Phys. Chem. B*, **103**, 2165.

[9] Ugliengo, P., Civalleri, B., Dovesi, R. and Zicovich-Wilson, C. M. (1999). "Periodic B3-LYP calculations of H-edingtonites both alone and interacting with acetylene", *Phys. Chem. Chem. Phys.*, **1**, 545.

[10] Ugliengo, P., Civalleri, B., Zicovich-Wilson, C. M. and Dovesi, R. (2000). "H-chabazite with variable Si/Al ratio: stability and O_bH vibrational frequency computed in a periodic LCAO B3-LYP approach", *Chem. Phys. Lett.*, **318**, 247.

[11] Lager, G. A., Jorgensen, J. D. and Rotella, F. J. (1982). "Crystal structure and thermal expansion of α-quartz SiO_2 at low temperatures", *J. Appl. Phys.*, **53**, 6751.

[12] Allan, D. C. and Teter, M. P. (1987). "Nonlocal Pseudopotential in molecular-dynamical density-functional theory: application to SiO_2", *Phys. Rev. Lett.*, **59**, 1136; Allan, D. C. and Teter, M. P., "Local density approximation total energy calculations for silica and titania structure and defects", *J. Am. Ceram. Soc.*, **73**, 3247.

[13] Chelikowsky, J. R., King, H. E. Jr., Trouiller, N., Martins, J. L. and Glinnermann, J. (1990). "Structural properties of alpha-quartz near the amorphous transition", *Phys. Rev. Lett.*, **65**, 3309.

[14] Liu, F., Garofalini, S. H., King-Smith, D. and Vanderbilt, D. (1994). "First-principles study of crystalline silica", *Phys. Rev. B*, **49**, 12528.

[15] Teter, D. M., Gibbs, G. V., Boisen, M. B. Jr., Allan, D. C. and Teter, M. P. (1995). "First-principles study of several hypothetical silica framework stuctures", *Phys. Rev. B*, **52**, 8064.

[16] Gibbs, G. V., Rosso, K. M., Teter, D. M., Boisen, M. B. Jr. and Bukowiuski, M. S. T. (1999). "Model structures and properties of the electron density distribution for low quartz at pressure: a study of the SiO bond", *J. Mol. Struct.*, **485–486**, 13.

[17] Holm, B. and Ahuja, R. (1999). "*Ab initio* calculation of elastic constants of SiO_2 stishovite and α-quartz", *J. Chem. Phys.*, **111**, 2074.

[18] Hamann, D. R. (1996). "Generalized gradient theory for silica phase transitions", *Phys. Rev. Lett.*, **76**, 660.

[19] Demuth, Th., Jeanvoine, Y., Hafner, J. and Ángyán, J. G. (1999). "Polymorphism in silica studied in the local density and generalized-gradient approximations", *J. Phys. Condens. Matter*, **11**, 3833.

[20] FLAPW (WIEN97); LDA = PW, GGA = PBE; Zupan, A., Blaha, P., Schwarz, K. and Perdew, J. P. (1997). "Pressure-induced phase transition in solid Si, SiO_2, and Fe: performance of local-spin-density and generalized-gradient-approximation density functionals", *Phys. Rev. B*, **58**, 11266.

[21] Catti, M., Civalleri, B. and Ugliengo, P. (2000). "Structure and energetics of SiO_2 polymorphs by quantum-mechanical and semiclassical approaches", *J. Phys. Chem. B*, **104**, 7259.

[22] Petrovic, I., Heaney, P. J. and Navrotsky, A. (1996). "Thermochemistry of the new silica polymorph moganite", *Phys. Chem. Minerals*, **23**, 119.

[23] Petrovic, I., Navrotsky, A., Davis, M. E. and Zones, S. I. (1993). "Thermochemical study of the stability of frameworks in high silica zeolites", *Chem. Mater.*, **5**, 1805.

[24] Brown, A. S., Spackman, M. A. and Hill, R. J. (1993). "The electron distribution in corundum. A study of the utility of merging single-crystal and powder diffraction data", *Acta Cryst. A*, **49**, 513.

[25] Yourdshahyan, Y., Ruberto, C., Bengston, L. and Lundqvist, B. I. (1997). "First-principles calculations on the atomic and electronic structure of κ-Al_2O_3", *Phys. Rev. B*, **56**, 8553.

[26] Manassidis, I. and Gillan, M. J. (1994). "The structure and energetics of alumina surfaces calculated from first principles", *J. Am. Ceram. Soc.*, **77**, 335.

[27] Wander, A., CRYSTAL: HF and HF+DFT *a posteriori* correction, basis set = Al[85-11G(d)] ,O[8-411G(d)]; *unpublished results.*