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Numerical atomic orbitals for linear-scaling calculations

Javier Junquera,[1] Óscar Paz,[1] Daniel Sánchez-Portal,[2,3] and Emilio Artacho[4]
[1]*Departamento de Física de la Materia Condensada, C-III, Universidad Autónoma, 28049 Madrid, Spain*
[2]*Department of Physics and Materials Research Laboratory, University of Illinois, Urbana Illinois 61801*
[3]*Departamento de Física de Materiales and DIPC, Facultad de Química, UPV/EHU, Apdo. 1072 E-20080 San Sebastián, Spain*
[4]*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom*
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The performance of basis sets made of numerical atomic orbitals is explored in density-functional calculations of solids and molecules. With the aim of optimizing basis quality while maintaining strict localization of the orbitals, as needed for linear-scaling calculations, several schemes have been tried. The best performance is obtained for the basis sets generated according to a new scheme presented here, a flexibilization of previous proposals. Strict localization is maintained while ensuring the continuity of the basis-function derivative at the cutoff radius. The basis sets are tested versus converged plane-wave calculations on a significant variety of systems, including covalent, ionic, and metallic. Satisfactory convergence is obtained for reasonably small basis sizes, with a clear improvement over previous schemes. The transferability of the obtained basis sets is tested in several cases and it is found to be satisfactory as well.

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I. INTRODUCTION

In order to make intelligent use of the increasing power of computers for the first-principles simulation of ever larger and more complex systems, it is important to develop and tune linear-scaling methods, where the computational load scales only linearly with the number of atoms in the simulation cell. The present status of these methods and their applications can be found in several reviews.[1–3] Essential for linear scaling is locality, and basis sets made of localized wave functions represent a very sensible basis choice. It is not only the scaling that matters, however, the prefactor being also important for practical calculations. The prefactor depends significantly on two aspects of the basis: (i) the number of basis functions per atom, and (ii) the size of the localization regions of these functions.

Atomic orbitals offer efficient basis sets since, even though their localization ranges are larger than those of some other methods,[4] the number of basis functions needed is usually quite small. The price to pay for this efficiency is the lack of systematics for convergence. Unlike with plane-wave[5] or real-space-grid[6] related methods, there is no unique way of increasing the size of the basis, and the rate of convergence depends on the way the basis is enlarged. This fact poses no fundamental difficulties, it just means that some effort is needed in the preparation of unbiased basis sets, in analogy to the extra work required to prepare pseudopotentials to describe the effect of core electrons.

Maximum efficiency is achieved by choosing atomic orbitals that allow convergence with small localization ranges *and* few orbitals. It is a challenge again comparable to the one faced by the pseudopotential community, where transferability *and* softness are sought.[7] For atomic wave functions the optimization freedom is in the radial shape. Gaussian-type orbitals have been proposed for linear scaling,[8–10] connecting with the tradition of quantum chemistry.[11,12] These bases are, however, quite rigid for the mentioned optimization, imposing either many Gaussians or large localization ranges.

Numerical atomic orbitals (NAO's) are more flexible in this respect. Different ideas have been proposed in the literature, originally within tight-binding contexts concentrating on minimal (single ζ) bases. They are obtained by finding the eigenfunctions of the isolated atoms confined within spherical potential wells of different shapes,[13–15] or directly modifying the eigenfunctions of the atoms.[16] These schemes give strictly localized orbitals, i.e., orbitals that are strictly zero beyond given cutoff radii r_c. A first extension towards more complete basis sets was proposed using the excited states of the confined atoms,[17] but the quite delocalized character of many excited states made this approach inefficient unless very stringent confinement potentials were used.[18]

For multiple ζ, a better scheme was proposed based on the split-valence idea of quantum chemistry,[11,12] but adapted to strictly localized NAO's.[19] In the same work, a systematic way was proposed to generate polarization orbitals suited for these basis sets. The scheme of Ref. 19 has proven to be quite efficient, systematic, and reasonable for a large variety of systems (for short reviews, see Refs. 19 and 20).

In this work we go beyond previous methodologies because of two main reasons: (i) It is always desirable to obtain the highest possible accuracy given the computational resources available, and (ii) it is important to know and show what is the degree of convergence attainable by NAO basis sets of reasonable sizes.

We explore these issues by variationally optimizing basis sets for a variety of condensed systems. The parameters defining the orbitals are allowed to vary freely to minimize the total energy of these systems. This energy is then compared with that of converged plane-wave calculations for exactly the same systems, including same density functional and pseudopotentials. The optimal basis sets are then tested monitoring structural, and elastic properties of the systems.

The transferability of the basis sets optimized for particular systems is then checked by transferring them to other systems and testing the same energetical, structural, and elastic parameters. Finally, the effect of localizing the orbitals tighter than what they variationally choose is explored on a demanding system.

II. METHOD

The calculations presented below were all done using density-functional theory[21,22] (DFT) in its local-density[23] approximation (LDA). Core electrons were replaced by norm-conserving pseudopotentials[7] in their fully separable form.[24] The nonlocal partial-core exchange-correlation correction[25] was included for Cu to improve the description of the core-valence interactions.

Periodic boundary conditions were used for all systems. Molecules were treated in a supercell scheme allowing enough empty space between molecules to make intermolecular interactions negligible. For solid systems, integrations over the Brillouin zone were replaced by converged sums over selected $\vec{k}$ sets.[26]

Thus far the approximations are exactly the same for the two different sets of calculations performed in this work: based on NAO's and on plane-waves (PW's). The calculations using NAO's were performed with the SIESTA method, described elsewhere.[18,27] Besides the basis itself, the only additional approximation with respect to PW's is the replacement of some integrals in real space by sums in a finite three-dimensional (3D) real-space grid, controlled by one single parameter, the energy cutoff for the grid.[27] This cutoff, which refers to the fineness of the grid, was converged for all systems studied here (200 Ry for all except for Si and H_2, for which 80 and 100 Ry respectively, were used). Similarly, the PW calculations were done for converged PW cutoffs.[28]

Cohesive curves for the solids were obtained by fitting calculated energy values for different unit-cell volumes to cubic, quartic, and Murnaghan-like[29] curves, a procedure giving values to the lattice parameter, the bulk modulus and the cohesive energy of each system. The bulk moduli given by the Murnaghan and quartic fits deviate from each other by around 3%, the Murnaghan values being the lowest and the ones shown in the tables. The deviations between Murnaghan and cubic fits are of the order of 7%. The other cohesive parameters do not change appreciably with the fits.

The atomic-energy reference for the cohesive energy was taken from the atomic calculations within the same DFT and pseudopotentials, always converged in the basis set. They are hence the same reference for NAO's and for PW's, the difference in cohesive energies between the two accounting for the difference in the total energy of the solid. The isolated-atom calculations included spin polarization.

III. BASIS OF NUMERICAL ATOMIC ORBITALS

The starting point of the atomic orbitals that conform the basis sets used here is the solution of Kohn-Sham's Hamiltonian for the isolated pseudoatoms, solved in a radial grid, with the same approximations as for the solid or molecule (the same exchange-correlation functional and pseudopotential). A strict localization of the basis functions is ensured either by imposing a boundary condition, by adding a confining (divergent) potential, or by multiplying the free-atom orbital by a cutting function. We describe in the following three main features of a basis set of atomic orbitals: size, range, and radial shape.

A. Size: Number of orbitals per atom

Following the nomenclature of quantum chemistry, we establish a hierarchy of basis sets, from single ζ to multiple ζ with polarization and diffuse orbitals, covering from quick calculations of low quality to highly converged ones, as converged as the finest calculations in quantum chemistry. A single ζ (also called minimal) basis set (SZ in the following) has one single radial function per angular momentum channel, and only for those angular momenta with substantial electronic population in the valence of the free atom.

Radial flexibilization is obtained by adding a second function per channel: double ζ (DZ). Several schemes have been proposed to generate this second function. In quantum chemistry, the *split valence*[11,30] scheme is widely used: starting from the expansion in Gaussians of one atomic orbital, the most contracted Gaussians are used to define the first orbital of the double ζ and the most extended ones for the second. Another proposal defines the second ζ as the derivative of the first one with respect to occupation.[31] For strictly localized functions there was a first proposal[17] of using the excited states of the confined atoms, but it would work only for tight confinement. An extension of the split valence idea of quantum chemistry to strictly localized NAO's was proposed in Ref. 19 and has been used quite successfully in a variety of systems. It consists of suplementing each basis orbital with a new basis function that reproduces exactly the tail of the original orbital from a given matching radius r_m outwards. The inner part goes smoothly towards the origin as $r^l(a-br^2)$, where a and b are chosen to ensure continuity of the function and its derivative at r_m. We follow this scheme in this work, which generalizes to multiple ζ trivially by adding more functions generated with the same procedure.

Angular flexibility is obtained by adding shells of higher angular momentum. Ways to generate these so-called polarization orbitals have been described in the literature, both for Gaussians[11,12] and for NAO's.[19] In this work, however, they will be obtained variationally, as the rest, within the flexibilities described below.

B. Range: Cutoff radii of orbitals

Strictly localized orbitals (zero beyond a cutoff radius) are used in order to obtain sparse Hamiltonian and overlap matrices for linear scaling. The traditional alternative to this is based on neglecting interactions when they fall below a tolerance or when the atoms are beyond some scope of neighbors. For long ranges or low tolerances both schemes are essentially equivalent. They differ in their behavior at shorter ranges, where the strict-localization approach has the advantage of remaining in the Hilbert space spanned by the basis, remaining variational, and avoiding numerical instabilities no matter how short the range becomes.

For the bases made of strictly localized orbitals, the problem is finding a balanced and systematic way of defining all the different cutoff radii, since both the accuracy and the computational efficiency in the calculations depend on them. A scheme was proposed[19] in which all radii were defined by one single parameter, the energy shift, i.e., the energy raise suffered by the orbital when confined. In this work, however, we step back from that systematic approach and allow the cutoff radii to vary freely in the optimization procedure (up to a maximum value of 8 a.u.).

C. Shape

Within the pseudopotential framework it is important to keep the consistency between the pseudopotential and the form of the pseudoatomic orbitals in the core region. This is done by using as basis orbitals the solutions of the same pseudopotential in the free atom. The shape of the orbitals at larger radii depends on the cutoff radius (see above) and on the way the localization is enforced. The first proposal[13] used an infinite square-well potential (see Fig. 1). It has been widely and successfully used for minimal bases within the *ab initio* tight-binding scheme of Sankey and collaborators[13] using the FIREBALL program, but also for more flexible bases using the methodology of SIESTA.

This scheme has the disadvantage, however, of generating orbitals with a discontinuous derivative at r_c as seen in Fig. 1. This discontinuity is more pronounced for smaller r_c's and tends to disappear for long enough values of this cutoff. It does remain, however, appreciable for sensible values of r_c for those orbitals that would be very wide in the free atom. It is surprising how small an effect such a kink produces in the total energy of condensed systems (see below). It is, nevertheless, a problem for forces and stresses, especially if they are calculated using a (coarse) finite three-dimensional grid.

Another problem of this scheme is related to its defining the basis considering the free atoms. Free atoms can present extremely extended orbitals, their extension being, besides problematic, of no practical use for the calculation in condensed systems: the electrons far away from the atom can be described by the basis functions of other atoms.

Both problems can be addressed simultaneously by adding a soft confinement potential to the atomic Hamiltonian used to generate the basis orbitals: it smooths the kink and contracts the orbital as variationally suited. Two soft confinement potentials have been proposed in the literature (Fig. 1), both of the form $V(r)=V_o r^n$, one for $n=2$ (Ref. 14) and the other for $n=6$.[15] They present their own inconveniences, however. First, there is no radius at which the orbitals become strictly zero, they have to be neglected at some point. Second, these confinement potentials affect the core region spoiling its adaptation to the pseudopotential.

This last problem affects a more traditional scheme as well, namely, the one based on the radial scaling of the orbitals by suitable scale factors. In addition to very basic bonding arguments,[32] it is soundly based on restoring virial's theorem for finite bases, in the case of Coulombic potentials (all-electron calculations).[33] The pseudopotentials limit its applicability, allowing only for extremely small deviations from unity ($\sim 1\%$) in the scale factors obtained variationally (with the exception of hydrogen that can contract up to 25%).[34]

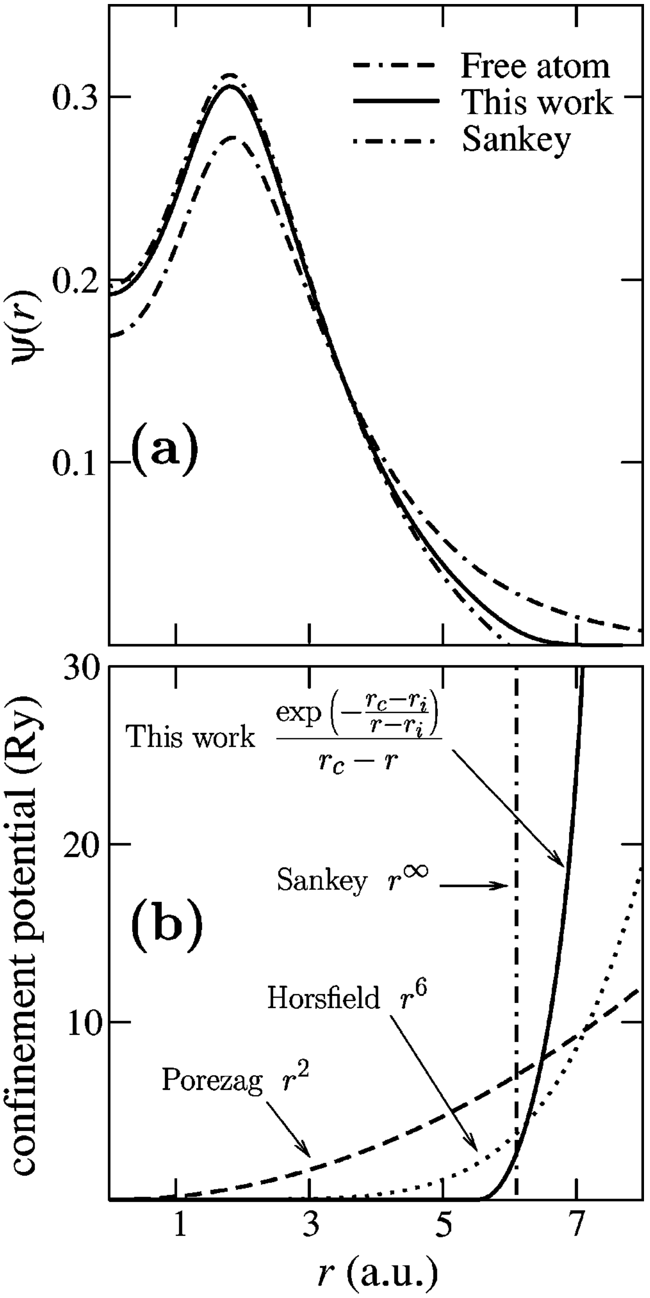

FIG. 1. Shape of the $3s$ orbital of Mg in MgO for the different confinement schemes (a) and corresponding potentials (b).

An alternative scheme to avoid the kink has also been proposed:[16] Instead of modifying the potential, it directly modifies the orbitals of the atom. Following ideas of previous mixed-basis schemes[37] the atomic orbital is multiplied by $1-\exp[-\alpha(r-r_c)^2]$ for $r<r_c$ and zero otherwise.[16] In Ref. 16 it is the hard confined wave function which is then modified, while in Ref. 37 it is the free atom wave function. We follow Ref. 37. This method is tested in the next section. This scheme does provide strict localization beyond r_c, but introduces a different problem: for large α and small r_c a bump appears in the orbital close to r_c, which becomes a discontinuity in the wave function in the limit of infinite α (Ref. 37) (this is not the case in Ref. 16).

In this work we propose a new soft confinement potential avoiding the mentioned deficiencies. It is shown in Fig. 1. It is flat (zero) in the core region, starts off at some internal radius r_i with all derivatives continuous, and diverges at r_c ensuring the strict localization there. It is

$$V(r)=V_{\mathrm{o}}\frac{e^{-(r_c-r_i)/(r-r_i)}}{r_c-r}. \tag{1}$$

In the following the different schemes are compared, their defining parameters being allowed to change variationally.

Finally, the shape of an orbital is also changed by the ionic character of the atom. Orbitals in cations tend to shrink, and they swell in anions. Introducing a δQ in the basis-generating free-atom calculations gives orbitals better adapted to ionic situations in the condensed systems.

IV. OPTIMIZATION PROCEDURE

Given a system and a basis size, the range and shape of the orbitals are defined by a set of parameters as described above. The parameters are described in the following. Per atomic species there is a global δQ, an extra charge (positive or negative) added to the atom at the time of solving the atomic DFT problem for obtaining the basis orbitals (see below).

Confinement is imposed separately for each angular momentum shell, with its corresponding parameters that depend on the scheme used. Hard confinement implies one parameter per shell (r_c), and our soft confinement implies three (r_c, r_i, and V_{o}). One parameter (V_{o}) is needed only in the r^n-confinement schemes,[14,15] and two parameters in the scheme of Elsaesser *et al.*[37] (r_c and the width of the cutting function). Finally, for each ζ beyond the first, there is a matching radius as mentioned above.[19]

The values of these parameters are defined variationally, according to the following procedure:

(i) Given a set of parameters, the Kohn-Sham Hamiltonian (including the pseudopotential) is solved for the isolated atom, in the presence of the confining potential and the extra charge δQ. (In the case of the scheme of Elsaesser *et al.*,[37] there is no confining potential, but an *a posteriori* modification of the solution wave functions.) This is done for all the relevant l shells of all the different atomic species. The multiple zetas are built from the former using the matching procedure described above,[19] according to the r_m's within the set of parameters. This procedure gives a basis set for each set of parameter values.

(ii) Given the basis set, a full DFT calculation is performed of the system for which the basis is to be optimized, normally a condensed system, solid or molecule. The Kohn-Sham total energy of this system becomes then a function of that set of parameters. Note that neither the extra charge nor the confinement potentials are added to the Kohn-Sham Hamiltonian of the system, they were just used to define the basis. The total-energy calculations are performed for given structural parameters of the studied system. We have chosen to work with experimental structures. This choice is, however, of no great importance since the basis sets are supposed to be transferable enough to render any bias negligible. This is certainly the case at the DZP level, not so much for minimal bases. See the section on transferability below.

TABLE I. Comparison of different confinement schemes on the cohesive properties of MgO, for SZ and DZP basis sets. The generalization of the different schemes to DZP is done as explained in the text. Unconfined refers to using the unconfined pseudoatomic orbitals as basis. *a*, *B*, and E_c stand for lattice parameter, bulk modulus, and cohesive energy, respectively. The PW calculations were performed with identical approximations as the NAO ones except for the basis. Experimental values were taken from Ref. 40.

	SZ			DZP		
Basis scheme	a (Å)	B (GPa)	E_c (eV)	a (Å)	B (GPa)	E_c (eV)
Unconfined	4.25	119	6.49			
Sankey	4.17	222	10.89	4.12	165	11.82
Elsaesser	4.16	228	11.12	4.12	163	11.84
Porezag	4.18	196	11.17	4.09	183	11.83
Horsfield	4.15	221	11.26	4.11	168	11.86
This work	4.15	226	11.32	4.10	167	11.87
PW				4.10	168	11.90
Expt.				4.21	152	10.3

(iii) The previous two steps are built in as a function into a minimization algorithm. As a robust and simple minimization method not requiring the evaluation of derivatives, we have chosen the downhill simplex method.[38] We have not dedicated special efforts to maximizing the efficiency of the minimization procedure since the systems used for basis optimization typically involve a small number of atoms and the total-energy calculations are quick. The possible improvement in the minimization efficiency is therefore of no relevance to the present study.

We have no argument to discard the existence of several local minima in the energy function. For the systems studied here there may be sets of parameters giving better bases than the ones we obtain. We systematically tested their robustness by restarting new simplex optimizations from the already optimized sets. More systematic searches for absolute minima, however, would require much more expensive techniques, which would not be justified at this point. We have thus satisfied ourselves with the ones obtained, that show good and consistent convergence characteristics. The values obtained for the parameters in the optimizations described below can be obtained from the authors.[39]

V. RESULTS

A. Comparison of different confinement schemes

Table I shows the performance for MgO of the different schemes described above for constructing localized atomic orbitals. The basis sets of both magnesium and oxygen were variationally optimized for all the schemes. Mg was chosen because the 3*s* orbital is very extended in the atom and both the kink and the confinement effects due to other orbitals are very pronounced. Results are shown for a SZ (single *s* and *p*

TABLE II. Basis comparisons for bulk Si. a, B, and E_c stand for lattice parameter (in Å), bulk modulus (in GPa), and cohesive energy (in eV), respectively. SZ, DZ, and TZ stand for single ζ, double ζ, and triple ζ. P stands for polarized, DP for doubly polarized. LAPW results were taken from Ref. 41, and the experimental values from Ref. 42.

	SZ	DZ	TZ	SZP	DZP	TZP	TZDP	PW	LAPW	Expt.
a	5.52	5.49	5.48	5.43	5.40	5.39	5.39	5.38	5.41	5.43
B	85	87	85	97	97	97	97	96	96	98.8
E_c	4.70	4.83	4.85	5.21	5.31	5.32	5.34	5.37	5.28	4.63

channels for both species) and a DZP basis (double s and p channels plus a single d channel). Figure 1 shows the shape of the optimal $3s$ orbital for the different schemes, and the shape of the confining potentials.

The following conclusions can be drawn from the results: (i) Within the variational freedom offered here, the $3s$ orbital of Mg wants to be confined to a radius of around 6.5 bohr, irrespective of scheme, which is extremely short for the free atom. This confinement produces a pronounced kink in the hard scheme. (ii) The total energy is relatively insensitive to the scheme used to generate the basis orbitals, as long as there is effective confinement. (iii) The basis made of unconfined atomic orbitals is substantially worse than any of the others. (iv) The pronounced kink obtained in Sankey's hard confinement scheme is not substantially affecting the total energy as compared with the other schemes. It does perturb, however, by introducing inconvenient noise in the energy variation with volume and other external parameters, and especially in the derivatives of the energy. (v) The scheme proposed in this work is variationally slightly better than the other ones, but not significantly. Its main advantage is the avoidance of known problems. In the remainder of the paper, the confinement proposed in this work will be used unless otherwise specified.

B. Basis convergence

Table II shows how NAO bases converge for bulk silicon. This is done by comparing different basis sizes, each of them optimized. The results are compared to converged (50 Ry) PW results (converged basis limit) keeping the rest of the calculation identical. Figure 2(a) shows the cohesion curves for this system.

Even though the main point of this work is testing the convergence of NAO basis sets independently of other issues, we consider it interesting to gauge the relevance of the errors introduced by the basis by comparing them with other typical errors that appear in these calculations. The NAO and PW results are thus compared to all-electron LDA results[49] to compare basis errors with the ones produced by the pseudopotentials. Experiment gives then reference to the error comitted by the underlying LDA.

The comparisons above are made with respect to the converged-basis limit, for which we used PW's up to very high cutoffs. It is important to distinguish this limit from the PW calculations at lower cutoffs, as used in many computations. To illustrate this point, Fig. 2(b) compares the energy convergence for PW's and for NAO's. Even though the convergence of NAO results is *a priori* not systematic with the way the basis is enlarged, the sequence of bases presented in the figure shows a nice convergence of total energy with respect to basis size (the number of basis functions per atom are shown in parentheses in the figure): the convergence rate is similar to the one of PW's (DZP has three times more orbitals than SZ, and a similar factor is found for their equivalents in PW's). For the particular case of Si, Fig. 2 shows that the polarization orbitals ($3d$ shell) are very important for convergence, more than the doubling of the basis. This fact is observed from the stabilization of SZP with respect to SZ, which is much larger than for DZ.

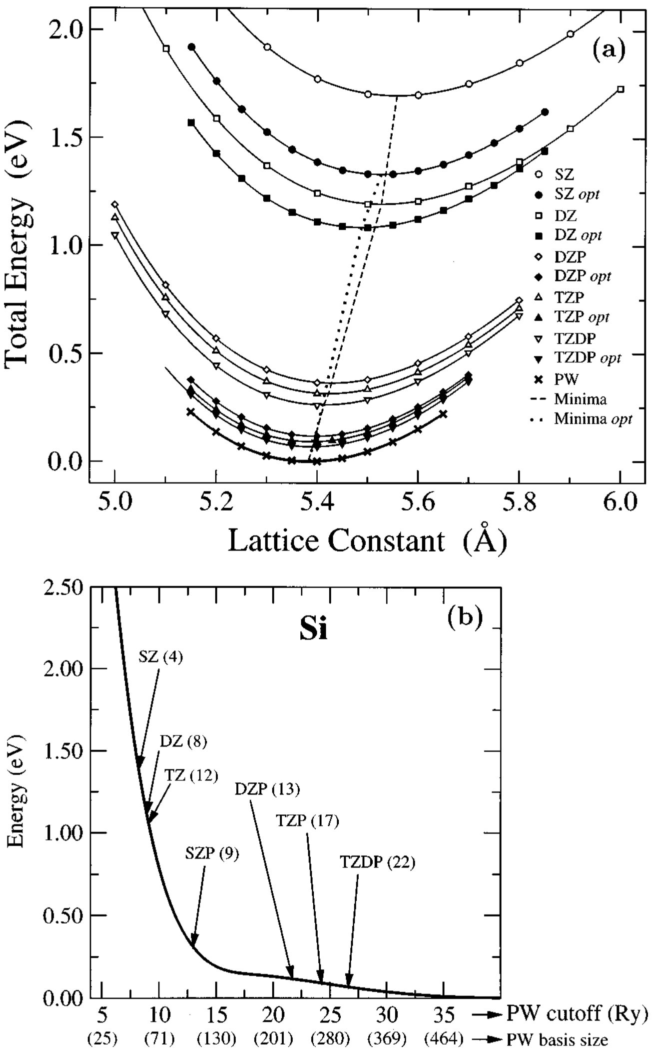

FIG. 2. Convergence of NAO basis sets for bulk Si. (a) Cohesive curve for different basis sets. The lowest curve shows the PW results, filled symbols the NAO bases of this work (opt), and open symbols the NAO bases following Ref. 19. Basis labels are like in Table II. (b) Comparison of NAO convergence with PW convergence. In parentheses is the number of basis functions per atom.

Figure 2 shows that an atomic basis at the DZP level requires ten times less functions than its (energetically) equivalent PW basis, being Si the easiest system for PW's.

TABLE III. Equivalent PW cutoff (E_{cut}) to optimal DZP bases for different systems. Comparison of number of basis functions per atom for both bases. For the molecules, a cubic unit cell of 10 Å of side was used.

System	No. funct. DZP	No. funct. PW	E_{cut} (Ry)
H_2	5	11296	34
O_2	13	45442	86
Si	13	227	22
Diamond	13	284	59
α-quartz	13	923	76

For other systems the ratio is much larger, as shown in Table III.

It is important to stress that deviations smaller than the ones due to the pseudopotential or the DFT used are obtained with a relatively modest basis size as DZP. This fact is clear in Table II for Si, and in Table IV for other systems. Table IV summarizes the cohesion results for a variety of solids of different chemical kind. They are obtained with optimal DZP basis sets. It can be observed that DZP offers results in good agreement with converged-basis numbers, showing the convergence of properties other than the total energy. The deviations are similar or smaller than those introduced by LDA or by the pseudopotential.[47]

TABLE IV. Basis comparisons for different solids. a, B, and E_c stand for lattice parameter (in Å), bulk modulus (in GPa), and cohesive energy (in eV), respectively.

		Exp	LAPW	Other PW	PW	DZP
Au	a	4.08[a]	4.05[b]	4.07[c]	4.05	4.07
	B	173[a]	198[b]	190[c]	191	188
	E_c	3.81[a]	-	-	4.19	4.03
MgO	a	4.21[d]	4.26[e]	-	4.10	4.11
	B	152[d]	147[e]	-	168	167
	E_c	10.30[d]	10.40[e]	-	11.90	11.87
C	a	3.57[a]	3.54[f]	3.54[g]	3.53	3.54
	B	442[a]	470[f]	436[g]	466	453
	E_c	7.37[a]	10.13[f]	8.96[g]	8.90	8.81
Si	a	5.43[a]	5.41[h]	5.38[g]	5.38	5.40
	B	99[a]	96[h]	94[g]	96	97
	E_c	4.63[a]	5.28[h]	5.34[g]	5.37	5.31
Na	a	4.23[a]	4.05[i]	3.98[g]	3.95	3.98
	B	6.9[a]	9.2[i]	8.7[g]	8.8	9.2
	E_c	1.11[a]	1.44[j]	1.28[g]	1.22	1.22
Cu	a	3.60[a]	3.52[b]	3.56[g]	-	3.57
	B	138[a]	192[b]	172[g]	-	165
	E_c	3.50[a]	4.29[k]	4.24[g]	-	4.37
Pb	a	4.95[a]	-	4.88	-	4.88
	B	43[a]	-	54	-	64
	E_c	2.04[a]	-	3.77	-	3.51

[a] C. Kittel, Ref. 42.
[b] A. Khein, D. J. Singh, and C. J. Umrigar, Ref. 43.
[c] B. D. Yu and M. Scheffler, Ref. 44.
[d] F. Finocchi, J. Goniakowski, and C. Noguera, Ref. 40.
[e] J. Goniakowski and C. Noguera, Ref. 45.
[f] N. A. W. Holzwarth *et al.,* Ref. 46.
[g] M. Fuchs, M. Bockstedte, E. Pehlke, and M. Scheffler, Ref. 47.
[h] C. Filippi, D. J. Singh, and C. J. Umrigar, Ref. 41.
[i] J. P. Perdew *et al.*, Ref. 48.
[j] M. Sigalas *et al.*, Ref. 49.
[k] P. H. T. Philipsen and E. J. Baerends, Ref. 50.

TABLE V. Transferability of basis sets. ‘‘Transf.’’ stands for the DZP basis transferred from other systems, while ‘‘Opt.’’ refers to the DZP basis optimized for the particular system. For MgO the basis was transferred from bulk Mg and an H_2O molecule, for graphite the basis was transferred from diamond, and for H_2O it was taken from H_2 and O_2. a, B, and E_c stand for lattice parameter, bulk modulus, and cohesive energy, respectively. ΔE stands for the energy difference per atom between graphite and a graphene plane. E_b is the binding energy of the molecule.

System	Basis	Properties		
MgO		a (Å)	B (GPa)	E_c (eV)
	Transf.	4.13	157	11.81
	Opt.	4.10	167	11.87
	PW	4.10	168	11.90
	Expt.	4.21	152	10.30
Graphite		a (Å)	c (Å)	ΔE (meV)
	Transf.	2.456	6.50	38
	PW[a]	2.457	6.72	24
	Expt.[b]	2.456	6.674	23[c]
H_2O		$d_{\text{O-H}}$ (Å)	$\theta_{\text{H-O-H}}$ (deg)	E_b (eV)
	Transf.	0.975	105.0	12.73
	Opt.	0.972	104.5	12.94
	PW	0.967	105.1	13.10
	LAPW[d]	0.968	103.9	11.05
	Expt.[e]	0.958	104.5	10.08

[a] M. C. Schabel and J. L. Martins, Ref. 51.
[b] Y. Baskin and L. Mayer, Ref. 52.
[c] L. A. Girifalco and R. A. Ladd, Ref. 53.
[d] P. Serena, A. Baratoff, and J. M. Soler, Ref. 54.
[e] G. Herzberg, Ref. 55.

VI. TRANSFERABILITY

To what extent do optimal bases keep their performance when transferred to different systems than the ones they were optimized for? This is an important question, since if the performance does not suffer significantly, one can hope to tabulate basis sets per species, to be used for whatever system. If the transferability is not satisfactory, a new basis set should then be obtained variationally for each system to be studied. Of course the transferability increases with basis size, since the basis has more flexibility to adapt to different environments. In this work we limit ourselves to try it on DZP bases for a few representative systems.

Satisfactory transferability has been obtained when checking in MgO the basis set optimized for Mg bulk and O in a water molecule. Similarly, the basis for O has been tested in H_2O and O_2, and the basis for C in graphite and diamond.

TABLE VI. Performance of the basis of Si and O as optimized in c-Si and in a water molecule, respectively, for the structural parameters of α-quartz.

	Expt.[a]	PW[b]	PW[c]	PW[d]	PW[e]	DZP
a (Å)	4.92	4.84	4.89	4.81	4.88	4.85
c (Å)	5.41	5.41	5.38	5.32	5.40	5.38
$d^1_{\text{Si-O}}$ (Å)	1.605	1.611	1.60	1.605		1.611
$d^2_{\text{Si-O}}$ (Å)	1.614	1.617	1.60	1.605		1.611
$\alpha_{\text{Si-O-Si}}$ (deg)	143.7	140.2		139.0		140.0

[a] L. Levien, C. T. Prewitt, and D. J. Weidner, Ref. 56.

[b] D. R. Hamann, Ref. 57.

[c] P. Sautet (unpublished) using ultrasoft pseudopotentials, Ref. 58.

[d] G.-M. Rignanese *et al.*, Ref. 59.

[e] F. Liu *et al.*, using ultrasoft pseudopotentials (Ref. 60).

Again, the results show deviations due to the basis that are smaller than the errors introduced by the pseudopotentials and/or the DFT functional. The results are shown in Table V.

Table VI shows the results for the structural parameters of SiO_2 in its α-quartz structure. The DZP numbers have been obtained for a basis that was optimized not for α-quartz itself, but for bulk silicon for the Si basis and for the water molecule for the O basis. SiO_2 was chosen because its being quite sensitive to many approximations and in particular to the basis set. It was hard to converge for previous NAO schemes,[19] giving[61] typically longer Si-O bonds (with deviations of around 1.5% and smaller unit cells (deviations of around 1.5 and 2% for the a and c parameters, respectively). The results of Table VI are very satisfactory, showing (i) the good performance of NAO's, (ii) their transferability in this case, and (iii) the improvement of the basis sets proposed here over previous bases.

VII. LIMITING THE RANGE

In this work we have concentrated on variationally optimized basis sets, allowing the cutoff radii for the different orbitals to vary freely, as long as the orbitals remained strictly localized. This was done in the spirit of exploring the capabilities of the NAO basis sets. Some orbitals demanded reasonably short values of r_c, others chose long ranges. As mentioned earlier, the range of the orbitals is important for the efficiency in the calculations. Therefore further work will be very important to explore the possibility of enforcing smaller ranges in reasonably balanced ways and its effect on the convergence. A systematic study in this direction will be subject of future work, we have limited ourselves here to illustrate the nature of the problem in the particular example of α-quartz.

TABLE VII. Tightening the confinement of the basis in α-quartz.

r_c^{Si} (a.u.)			r_c^{O} (a.u.)			a (Å)	c (Å)	$d^1_{\text{Si-O}}$ (Å)	$d^2_{\text{Si-O}}$ (Å)	$\alpha_{\text{Si-O-Si}}$ (deg)
s	p	d	s	p	d					
8.0	8.0	8.0	8.0	8.0	8.0	4.85	5.38	1.611	1.612	140.0
6.0	6.0	6.0	8.0	8.0	8.0	4.85	5.35	1.607	1.608	140.0
6.0	6.0	6.0	5.0	5.0	5.0	4.74	5.29	1.610	1.610	134.0
6.0	6.0	6.0	4.5	4.5	4.5	4.69	5.26	1.610	1.610	132.0
6.0	6.0	6.0	5.0	6.5	4.0	4.84	5.36	1.607	1.608	139.7
5.6	6.3	4.2	4.0	5.3	2.8	4.81	5.34	1.607	1.610	138.2

The basis has been optimized as before (Si in bulk Si and O in H_2O), but imposing now tighter r_c's. The results are summarized in Table VII. The constraining of Si orbitals to 6.0 a.u. affects the geometry only slightly, whilst the contraction of the O orbitals to 5.0 a.u. implies a substantial contraction of the cell due to the decrease of Si-O-Si angle rather than the shortening of the Si-O bond. Note that, from an atomic perspective, the confinement of Si to 6 a.u. is tighter than the 5 a.u. confinement of O.

Allowing for different r_c's for the different channels we observe that the shrinking of the cell is avoided keeping a long p orbital for O, the s and d remaining comparably shorter, indicating the (expected[19]) different "compressibilities" of the different orbitals.

As a candidate of unifying criterion, we tested a simple way of defining r_c for each channel: Given an optimal orbital $\psi(r)$ as obtained from the unconstrained minimization, a tighter r_c is chosen such that $\psi(r_c)=0.01\ \text{a.u.}^{-3/2}$. With the r_c's of all channels and species obtained in this manner, the basis is reoptimized keeping these r_c's fixed. Even though the energy raise is appreciable (about 70 meV per atom), the geometry retains an acceptable accuracy, the orbitals being quite short, thus allowing quite efficient calculations. Further work is, however, needed to explore in detail this and other possibilities.

VIII. CONCLUSIONS

The variational optimization of NAO basis sets for different systems allows us to draw the following conclusions. (i) The performance of NAO basis sets of modest size as DZP is very satisfactory for the systems tried. For this basis size, the errors due to the basis are comparable or smaller than the errors due to the pseudopotential and LDA. (ii) The bases obtained here represent a substantial improvement over previous NAO basis sets. In particular, the optimization in condensed systems offers better and more efficient bases than purely atomic schemes. (iii) The radial shapes of the orbitals obtained as proposed in this work offer better bases than previous schemes from a variational point of view, albeit not a substantial difference is obtained. (iv) The elimination of the discontinuity in the derivative, while retaining strict localization and leaving the core region untouched as in this work and in Ref. 16 gives bases of better quality from the point of view of the energy, its derivatives, and computational efficiency. (v) The bases obtained showed enough transferability to expect that a basis tabulation would be useful, and that the optimization of the basis for each particular system will not be necessary. Finally, (vi) the selective sensitivity to orbital-range tightening has been shown, making clear the need of further work systematically to control the cutoff radii for improving efficiency without loss of accuracy.

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