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2008 J. Phys.: Condens. Matter 20 294206

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# Pseudo-atomic orbitals as basis sets for the $O(N)$ DFT code CONQUEST

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Received 11 February 2008, in final form 13 April 2008

Published 24 June 2008

Online at [stacks.iop.org/JPhysCM/20/294206](http://stacks.iop.org/JPhysCM/20/294206)

## Abstract

Various aspects of the implementation of pseudo-atomic orbitals (PAOs) as basis functions for the linear scaling CONQUEST code are presented. Preliminary results for the assignment of a large set of PAOs to a smaller space of support functions are encouraging, and an important related proof on the necessary symmetry of the support functions is shown. Details of the generation and integration schemes for the PAOs are also given.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Methods for  $O(N)$  or linear scaling density functional theory (DFT) calculations [1] were first proposed over 15 years ago, but it is only in the last five years that practical calculations using these methods have begun to appear. The codes now available [2–5] are of two types: those that use basis sets akin to plane waves [6–10], allowing systematic basis-set convergence; and those that use pseudo-atomic orbitals (PAOs) as basis sets [2, 3, 11, 12], for which systematic convergence is usually not possible. An important feature of our own CONQUEST code [5, 13, 14] is that both types of basis are implemented, and this means that rapid, though semi-quantitative calculations can be performed for exploratory purposes, but precise calculations are also possible. Our purpose here is to discuss several issues concerning PAO basis sets in  $O(N)$  DFT, some of which appear not to have been adequately addressed before.

Linear scaling methods all depend on Kohn's 'near-sightedness principle' [15], which says that quantum coherence is spatially localized. This can be expressed as a

property of the Kohn–Sham density matrix  $\rho(\mathbf{r}, \mathbf{r}')$ , defined as:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_n f_n \psi_n(\mathbf{r}) \psi_n(\mathbf{r}')^*, \quad (1)$$

where  $\psi_n(\mathbf{r})$  is the  $n$ th Kohn–Sham eigenfunction and  $f_n$  is its occupation number. Localization of coherence is expressed by the statement that:

$$\rho(\mathbf{r}, \mathbf{r}') \rightarrow 0 \quad \text{as } |\mathbf{r} - \mathbf{r}'| \rightarrow \infty. \quad (2)$$

This principle is exploited in CONQUEST and in some other codes by expressing the DFT total energy  $E_{\text{tot}}$  in terms of  $\rho$ , so that the ground state is determined by minimizing  $E_{\text{tot}}$  with respect to  $\rho$  subject to the conditions that the latter is idempotent and that it yields the correct number of electrons. In practice, we express  $\rho$  in terms of localized orbitals  $\phi_{i\alpha}(\mathbf{r})$ , referred to as 'support functions' in CONQUEST:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i\alpha, j\beta} \phi_{i\alpha}(\mathbf{r}) K_{i\alpha, j\beta} \phi_{j\beta}(\mathbf{r}'). \quad (3)$$

The  $\phi_{i\alpha}(\mathbf{r})$  are confined to spherical 'support regions' centred on the atoms ( $\alpha$ th support function on  $i$ th atom), and the matrix  $K_{i\alpha, j\beta}$  can be regarded as the density matrix in the representation of the non-orthogonal 'basis' of  $\phi_{i\alpha}$ . The ground state is then sought by varying the  $\phi_{i\alpha}(\mathbf{r})$  and the matrix  $K_{i\alpha, j\beta}$ , subject to idempotency and correct electron

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number. The heart of the CONQUEST idea is thus that the support functions  $\phi_{i\alpha}$ , while in one sense playing the role of basis functions, are flexible functions, which should themselves be represented in terms of basis functions.

The systematically improvable basis set used to represent the support functions in CONQUEST consists of  $B$ -splines (blip functions) [6], which are a type of finite-element basis. The blip grid spacing is associated with a plane-wave cutoff, as explained in detail elsewhere, and we approach the basis-set limit as we refine this spacing, in exactly the same way as basis-set convergence is obtained in plane-wave methods. This blip basis has been treated in detail in earlier papers, and the focus of the present work is on the PAO basis sets that can also be used to represent the support functions in CONQUEST.

Each PAO consists of a radial function  $R_l(r)$  multiplied by a spherical harmonic  $Y_l^m$ . To achieve reasonable accuracy, we must use multiple-zeta basis sets, in which there is more than a single radial function for each  $l$ . For a given multiple-zeta PAO basis, there is more than one way of defining the support functions. At one extreme, one can define the support functions and PAOs to be the same thing. If we do this, the support functions have no flexibility at all, but we obtain the best ground state possible with the given PAO basis. At the other extreme, one can try to work with the smallest possible set of support functions, each one being represented as a linear combination of PAOs [3, 16–18]. The search for the ground state then involves variation of the coefficients in these linear combinations. There are potentially major advantages in working in this way, because it allows the dimension of the matrix  $K_{i\alpha,j\beta}$  to be greatly reduced, but the ground state will then be less well approximated. We shall present illustrative calculations that shed light on this trade-off.

A question that is closely related to this is that of the symmetry of support functions. In cases where atoms are at high-symmetry sites, the point-group symmetry may impose conditions on the irreducible representations that can appear in the support functions, and this in turn can place constraints on the relationships between support functions and PAOs. We shall present a theory that formulates these constraints, and we shall explore the consequences of disregarding them.

The other issue examined here concerns the choice of PAO basis functions. It is well known that there are different approaches to the construction of these functions, some of which may be better than others. We shall report some evidence that the approach adopted in the SIESTA code may be particularly effective. Finally, we comment briefly on the techniques used for calculating matrix elements between numerical PAOs. The techniques used in CONQUEST are quite close to those employed in SIESTA, but we note a point of difference that may be of interest.

Since we examine here a set of loosely related issues, it will be convenient to present the material concerned with these issues in three separate sections, in each of which we summarize the theory followed immediately by the results of our tests. We note that the present contribution to the proceedings of the CECAM workshop ‘Linear scaling *ab initio* calculations: applications and future directions’ is a report of work in progress, and in some cases the calculations are

intended only to be illustrative. We plan to publish a fuller report on the issues discussed here in due course.

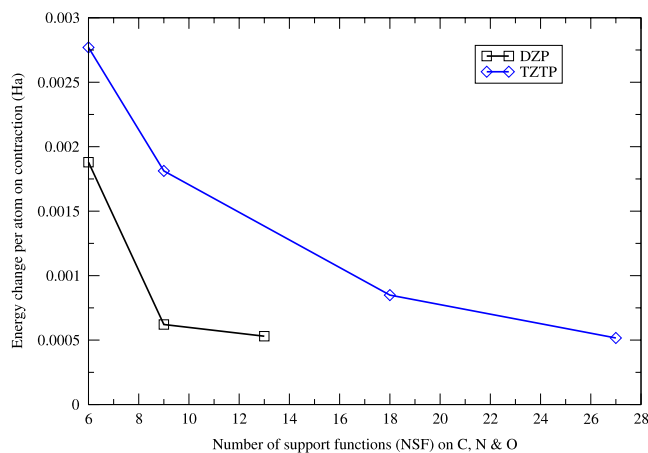
## 2. Support functions and PAOs

The support functions in CONQUEST can be represented in terms of PAOs:

$$\phi_{i\alpha}(\mathbf{r}) = \sum_{lm\zeta} c_{i\alpha}^{lm\zeta} R_{l\zeta}(r) Y_l^m(\hat{\mathbf{r}}), \quad (4)$$

where multiple radial functions (multiple zetas) are possible. In order to form matrix elements (for the overlap and Hamiltonian matrices) integrals between PAOs must be formed; this procedure is summarized in appendix A, with the emphasis on differences to other, similar schemes. The question of generation of radial functions is addressed in section 4. Here, we are concerned with the manner in which PAOs are assigned to support functions; the term *contraction* is used when there are *fewer* support functions than PAOs, and thus multiple PAOs contribute to each support function. This section will present results on the effects of contraction.

There are two extremes in this process: on the one hand, having the smallest number of support functions consistent with the local symmetry; on the other hand, having the same number of support functions as PAOs and each support function represented by one PAO (though, as will be shown below, taking linear combinations of the support functions on-site does not change the density matrix). The first is desirable for efficiency, as the effort required both for linear scaling and exact diagonalization solutions will scale with the cube of the number of support functions on each site. However, restricting the space of the support functions will inevitably raise the energy of the system as variational freedom is lost; thus for best accuracy, the second is desirable. Inevitably, some compromise between performance and accuracy must be chosen. We present here demonstration calculations on the total energy of glycine when contracting the PAO functions into a smaller set of support functions (while obeying the symmetry constraints discussed in section 3). Two basis sets are used: double zeta plus polarization (DZP: 13 PAOs for C, N and O, and 5 PAOs for H) and triple zeta plus triple polarization (TZTP: 27 PAOs for C, N and O, and 12 PAOs for H). In both cases, the hydrogen atoms are contracted into four support functions, while different contractions are used for C, N and O (6 and 9 for DZP and 6, 9 and 18 for TZTP); results for contracting just the orbitals on hydrogen while leaving C, N and O uncontracted were also obtained. The energy relative to the uncontracted energy is shown in figure 1. A number of important observations can be made. First, the more contracted a basis (i.e. the fewer support functions) that is used, the larger the energy shift. This is entirely reasonable (more contraction implies less variational freedom), and it is reassuring to see that the magnitude of the energy shift is in the millihartree per atom range. Second, if the PAO basis contains polarization functions (generally angular momentum functions up to  $l = 2$ ), then with nine support functions extremely good convergence can be achieved (within  $\sim 1$  mHa/atom). These preliminary calculations are encouraging, and a full investigation will be presented in a future publication.



**Figure 1.** Effects of contraction of PAOs on energy of glycine. Basis sets with double zeta plus polarization (DZP) and triple zeta plus triple polarization (TZTP) are contracted. Energy differences per atom are given relative to uncontracted result.

### 3. Symmetry constraints

It often happens that atoms are at sites of point-group symmetry. In this case, it is an important principle that the space spanned by the support functions at such a site must decompose into complete irreducible representations of the point group. A formal proof of this principle is given in appendix B. The practical importance of this is that if the principle is not respected then symmetry will generally be broken in an unphysical way, as will now be demonstrated.

One particular example would be carbon or silicon in the diamond structure. Here, the support functions should break down into irreducible representations of the tetrahedral point group. Let us consider the symmetries of different pseudo-atomic orbitals: s-functions are  $A_1$ ; p-functions are  $T_2$ ; the d-functions split into E ( $x^2 - y^2$ ,  $3z^2 - r^2$ ) and  $T_2$  ( $xy$ ,  $yz$  and  $zx$ ). If we consider only one-to-one SF-PAO assignment (i.e. no contraction) and a single function per angular momentum channel, then it is safe to work with four SFs (using only s, p PAOs); six SFs (using s, p and the  $E_g$  d PAOs); seven SFs (using s, p, and  $T_{2g}$  d PAOs); nine SFs (using s, p and all d PAOs). The extension to multiple functions per angular momentum is trivial. Considering contraction (i.e. less SFs than PAOs), then PAOs of the same *symmetry* can be mixed in the same SFs (e.g. p and  $T_2$  d, or different functions for the same angular momentum), as shown in table 1. Working with other combinations is dangerous, and can lead to symmetry breaking (e.g. forces whose directions break the symmetry) though energy may be lowered on addition of basis functions. In particular, though chemical intuition might suggest choosing four support functions (to reflect tetrahedral symmetry) this would lead to symmetry breaking if d PAOs were used in the basis set.

As an example of the problems which can arise, we calculate the magnitude and direction of forces on the hydrogen atoms in an isolated methane molecule with perfect tetrahedral bond angles; the bond lengths have been optimized with a DZP basis without contraction, leaving residual forces

**Table 1.** Symmetry-preserving assignment of PAOs to support functions for a DZP basis (two s, six p and five d-functions) in a system with tetrahedral symmetry, for different numbers of support functions (NSF). Note that the support functions to which each set of PAOs is assigned are given as a number or a range; n/a indicates that the PAO is *not* assigned to a support function. The d-functions are split by symmetry.

NSF	s	p	$d_{xy,yz,zx}$	$d_{x^2-y^2,3z^2-r^2}$
4	1	2-4	2-4	n/a
6	1	2-4	2-4	5-6
7	1	2-4	5-7	n/a
9	1	2-4	5-7	8-9
9	1	2-7	2-7	8-9
10	1-2	3-5	6-8	9-10
10	1-2	3-8	3-8	9-10
12	1	2-7	8-10	11-12
13	1-2	3-8	9-11	12-13

of  $0.011 \text{ eV } \text{\AA}^{-1}$  along the tetrahedral directions. The basis has thirteen functions for carbon and five for hydrogen. As the methane molecule obeys tetrahedral symmetry, we would expect there to be three sets of PAOs corresponding to three different irreducible representations: s-functions (equivalent to  $A_1$ ); p-functions and three d-functions (equivalent to  $T_2$ ); and two d-functions (equivalent to E). As the methane molecule does not preserve inversion symmetry, the parity of p- and d-functions does not split  $T_2$ ; however, the functions must have the correct relative signs (so  $p_x$  is paired with  $-d_{yz}$ ,  $p_y$  is paired with  $-d_{zx}$  and  $p_z$  is paired with  $+d_{xy}$ ).

While CONQUEST can optimize the coefficients of contracted basis sets, it cannot optimize the coefficients of basis sets with only a subgroup of d-functions (e.g. just the  $T_2$  functions), so the testing of symmetry-breaking assignments has generally been done without optimization. The key test for symmetry here is whether the forces remain symmetrical, along the tetrahedral directions. Results are shown in table 2 where ‘angle’ is defined as the average of the angles between forces and the tetrahedral directions and ‘force’ is the magnitude of the force. What is immediately clear is that our conclusion above about irreducible representations is borne out: having specific subsets of the d-functions (6a, 7a) does not break symmetry, while assigning the wrong d-functions to the wrong number of support functions (6c, 7b) breaks symmetry, as does putting d-functions into a set of support functions which does not allow spanning of the space (4b, 5). Assigning the  $T_2$  d-functions to the same support functions as the p-functions does not break symmetry, provided the correct signs of the coefficients are chosen (4c, 6b).

The results of optimization of the support function coefficients are shown in the final two columns of table 2, only for selected assignments. It is possible to optimize the coefficients so that we combine these PAOs without breaking the local symmetry (4c, 6b), but not for improper assignments (4b, 5, 6c, 7a); in particular, five support functions result in different angles and magnitudes for the forces (indicated with a star). The behaviour under optimization is complex, with multiple minima. However, starting from 6a or 4a (symmetry correct in PAO assignment to support functions but not all d-functions assigned) and optimizing generates solutions which

**Table 2.** Forces found for assignment of PAOs to support functions *without* optimization and *after* optimization for methane with DZP basis; optimization was only performed for situations where all functions could be considered. The angle refers to the average angle between forces on hydrogen and bond lengths (should be zero). PAO assignments to SFs are either symmetry breaking (SB) or symmetry conserving (SC), and use the same format as in table 1. The star for five support functions indicates that the angles between forces and tetrahedral directions differ from bond to bond. See text for details.

NSF	Symm	s	p	d(T <sub>2</sub> )	d(E)	Force	Angle	Force (Opt)	Angle (Opt)
4a	SC	1	2-4	n/a	n/a	0.63	0.00	—	—
4b	SB	1	2-4	2-4	1	2.50	8.31	—	—
4c	SC	1	2-4	2-4	n/a	2.55	0.00	0.01	0.00
5	SB	1	2-4	5	5	1.10	1.82*	—	—
6a	SC	1	2-4	n/a	5-6	1.09	0.00	0.01	0.00
6b	SC	1	2-4	2-4	5-6	2.55	0.00	0.02	0.00
6c	SB	1	2-4	5-6	n/a	1.13	0.24	—	—
7a	SC	1	2-4	5-7	n/a	1.15	0.00	—	—
7b	SB	1	2-4	n/a	5-7	1.11	0.24	—	—
10	SC	1-2	3-8	n/a	9-10	0.05	0.00	0.02	0.00

both give the correct symmetry and mix the T<sub>2</sub> d-functions with p-functions spontaneously. The overall conclusion of this section is that care needs to be exercised when choosing the assignment of PAOs to support functions, so as to obey local symmetries.

#### 4. Construction of PAOs

The problem of how to generate radial functions to act as a good basis has almost as many solutions as there are codes, though these can be divided into different broad categories; we highlight the following codes: SIESTA [2, 19–21]; OpenMX [3, 17, 22]; PLATO [12]; DMOL<sup>3</sup> [23, 24]. The approaches taken to generate basis functions, and the codes which use them, are:

- Confinement (SIESTA: single energy shift chosen to give different confinement for different  $l$ , split norm for multiple zeta).
- Eigenvalues (OpenMX: the isolated atom is confined for solution, including pseudo-potentials).
- Ionization state (PLATO, DMOL<sup>3</sup>).
- Polarization by increased angular momentum (OpenMX, PLATO, DMOL<sup>3</sup>).
- Polarization by applied electric field (SIESTA).
- Hydrogenic or Rydberg states (DMOL<sup>3</sup>).

CONQUEST can read SIESTA basis files directly, and also has a stand-alone code for PAO generation based on the PLATO PAO code. This can produce PAOs for different ionization states of the atom, for different eigenvalues and different confinement radii. The code reads pseudo-potentials in the FHI (Fritz-Haber Institute) format [25, 26] (which is compatible with the open source plane-wave code ABINIT [27, 28] and can be generated by the open source OPIUM code [29]).

Figure 2 shows the energy difference per atom relative to a converged plane-wave result calculated using both the local density approximation (LDA) and the PBE (Perdew-Burke-Emzerhof) generalized gradient approximation (GGA) functional for two amino acids: glycine and alanine. Two different methods for generating PAO basis sets were used (both are described above in section 4): the SIESTA package, up to DZP; and increasing eigenstates, up to TZTP. Various

conclusions can be drawn from these preliminary calculations: first, convergence is independent of functional and details of bonding (the convergence is similar for both amino acids); second, the SIESTA basis sets (which are generated based on heuristically optimized ideas) are more efficient than the eigenstate basis sets (which are simply generated for the same cutoff); third, that good convergence towards the full result is seen, but would probably require  $f$ -functions and/or hydrogenic functions for full convergence. A full investigation of the effects on convergence of different basis sets will be presented in a future publication.

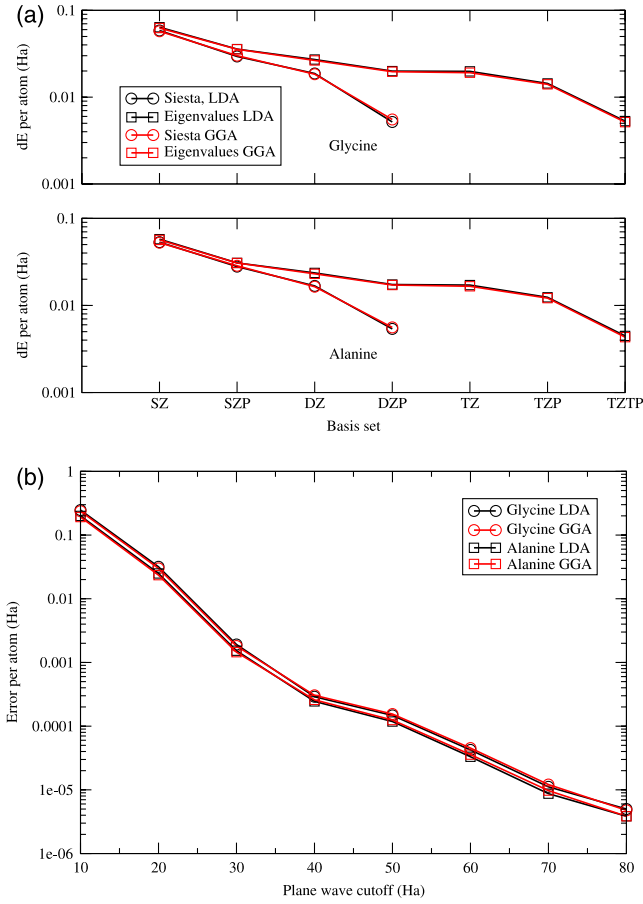
#### 5. Discussion

Details of the implementation of PAOs as a basis set within the linear scaling code CONQUEST have been presented, along with the different schemes for generating multiple radial functions for each angular momentum value. An important restriction on the size and nature of the set of support functions was derived: if there is a local point-group symmetry about an atom, then the support functions must decompose into irreducible representations of the point group. The importance of this was illustrated for the methane molecule and the tetrahedral point group.

Various calculations were presented. Preliminary results on the convergence of total energy with basis-set size for glycine and alanine indicated that good convergence relative to plane-wave results is possible. The contraction of PAOs into a smaller support function basis for glycine resulted in shifts of the  $\sim 1$  mHa/atom result, while providing substantial increase in efficiency; nominally the speed-up should be the cube of the ratio of the number of basis functions in the two cases, though practical tests show that actual performance gains may be only up to half this (depending on implementation, system size, etc). The assignment of PAOs to symmetry-preserving and symmetry-breaking support function sets showed that great care must be taken to maintain local symmetry for support functions.

While this paper has been concerned with PAOs as a basis set in the CONQUEST code, we recall that the blip functions, which are also available, form a systematically convergent basis set. These two basis sets allow different types of





**Figure 2.** (a) Convergence with basis for SIESTA PAOs and eigenvalue-based PAOs for glycine (top) and alanine (bottom). Energy differences per atom are relative to converged plane-wave result. (b) Convergence with plane-wave cutoff for comparison.

calculations to be performed: fast, qualitative calculations with a minimal basis of PAOs (non-self-consistent calculations add further speed); quantitative calculations using a full PAO basis (possibly with contraction onto a smaller but symmetry-preserving support function basis set); and systematically converged calculations with blip functions (in a small support function basis). This gives CONQUEST enormous flexibility in exploring new systems quickly as well as accurately pursuing specific aspects of known problems. A full exploration of the convergence of both PAOs and blips will be presented in a future publication.

## Acknowledgments

DRB is supported by the Royal Society. VB is supported by the IRC in Nanotechnology. This work is partly supported by Grant-in-Aid for Scientific Research from the MEXT, Japan.

## Appendix A. Matrix elements of PAOs

In this section, the scheme used for evaluation of integrals between PAOs is described. Naturally, it has many points of contact with other PAO-based schemes, such as PLATO [12] and

SIESTA [2]; we will therefore only present points of difference with these existing schemes.

The overlap between PAO functions separated by a vector  $\mathbf{R}$  can be written:

$$S(\mathbf{R}) = \int \phi_1^*(\mathbf{r})\phi_2(\mathbf{r} - \mathbf{R}) d^3\mathbf{r}. \quad (\text{A.1})$$

However, this convolution is rather awkward; it can be shown (following some algebraic manipulation) that it reduces to:

$$S(\mathbf{R}) = \sum_{l_1=-l_2}^{l_1+l_2} \sum_{m=-l}^{m=l} \int d\Omega_k ((-1)^{m_1} Y_{l_1-m_1}(\hat{\mathbf{k}}) Y_{l_2 m_2}(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{k}})) \times \left( \int k^2 dk \phi_1'(k) \phi_2'(k) j_l(kR) \right) (8(i^{l_1})^* (i^{l_2}) (i^l)^*) \times Y_{lm}^*(\hat{\mathbf{R}}), \quad (\text{A.2})$$

where

$$\phi_1'(k) = \int r^2 dr j_{l_1}(kR) f_1(r). \quad (\text{A.3})$$

The integral between PAO functions and non-local pseudo-potential projector functions uses an identical form to this. The kinetic energy integrals only require the addition of a factor of  $k^2$  within the integral.

Bessel functions up to twice the maximum value of  $l$  are required (which at the moment is set to  $l = 3$ , but is trivially extended). Rayleigh's formula is used for analytic evaluation:

$$j_n(x) = (-1)^n \left( \frac{1}{x} \frac{d}{dx} \right)^n \left( \frac{\sin(x)}{x} \right). \quad (\text{A.4})$$

Bessel functions of order one or higher tend to zero at the origin. For the high orders, Rayleigh's formula relies on cancellation of large numbers, so near the origin a series expansion can become necessary:

$$j_n(x) = 2^n x^n \sum_{s=0}^{\infty} \frac{(-1)^s (s+n)!}{s!(2s+2n+1)!} x^{2s}. \quad (\text{A.5})$$

Real PAOs in CONQUEST are defined as:

$$\phi(\mathbf{r}) = \begin{cases} f(r) C_{lm} P_m^l(\cos\theta) \cos(m\phi), & m \geq 0 \\ f(r) C_{lm} P_m^l(\cos\theta) \sin(m\phi), & m < 0 \end{cases} \quad (\text{A.6})$$

with the normalization constants found by integrating over  $\phi$  and  $\theta$ :

$$C_{lm} = \sqrt{\frac{2l+1(l-m)!}{2\pi(l+m)!}}. \quad (\text{A.7})$$

Integrals over solid angles are reduced to Wigner 3- $j$  symbols (we note that this is one major difference to the SIESTA implementation, where the integrals are performed using Gaussian quadrature). This gives:

$$I_{\Omega} = \int d\Omega Y_{l_1 m_1}(\Omega) Y_{l_2 m_2}(\Omega) Y_{l_3 m_3}(\Omega) = 4\pi \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{(4\pi)^3}} \times \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \quad (\text{A.8})$$

where

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{l_1-l_2-l_3} (-1)^{l_3-m_3} \frac{s_{l_3 m_1 m_2}^{l_1 l_2}}{\sqrt{2l_3+1}}, \quad (\text{A.9})$$

and  $s_{l_3 m_1 m_2}^{l_1 l_2}$  is a vector coupling coefficient.

This yields an easily extended, efficient implementation of pseudo-atomic orbitals in terms of radial functions and spherical harmonics.

## Appendix B. Support functions and irreducible representations

We stated in section 3 an important theorem that applies to the support functions at an atomic site, when the electronic ground state of the system is invariant under the operations of a point group at that site. The theorem states that this invariance can only be preserved if the space spanned by the support functions at the atomic site decomposes into complete irreducible representations of the point group. We sketch here a formal proof of this theorem. The correctness of the theorem does not depend on the basis sets used to represent the support functions, but we will assume here that a PAO basis is used. The PAO basis on each site consists of complete irreducible representations of the rotational point group.

### B.1. General ideas

The statement that the electronic ground state is invariant under an operation  $S$  is interpreted here as meaning that the density matrix  $\rho(\mathbf{r}, \mathbf{r}')$  is invariant under this operation. As before, we denote by  $\phi_{i\alpha}(\mathbf{r})$  the  $\alpha$ th support function on atom  $i$ , and we denote by  $\phi_{i\alpha}^S(\mathbf{r})$  the function into which  $\phi_{i\alpha}(\mathbf{r})$  is transformed by the action of  $S$ . Then, with  $\rho(\mathbf{r}, \mathbf{r}')$  given by:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i\alpha, j\beta} \phi_{i\alpha}(\mathbf{r}) K_{i\alpha, j\beta} \phi_{j\beta}(\mathbf{r}'), \quad (\text{B.1})$$

the application of  $S$  produces the transformed density matrix  $\rho^S(\mathbf{r}, \mathbf{r}')$  given by:

$$\rho^S(\mathbf{r}, \mathbf{r}') = \sum_{i\alpha, j\beta} \phi_{i\alpha}^S(\mathbf{r}) K_{i\alpha, j\beta} \phi_{j\beta}^S(\mathbf{r}'). \quad (\text{B.2})$$

Invariance under  $S$  requires that:

$$\rho^S(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}, \mathbf{r}'). \quad (\text{B.3})$$

The strategy of our proof will be to demonstrate that if the space spanned by the support functions at the atomic site does not decompose into complete irreducible representations then there must exist functions  $\psi(\mathbf{r})$  such that:

$$\int d\mathbf{r}' \rho(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') = 0 \quad \text{and} \quad (\text{B.4})$$

$$\int d\mathbf{r}' \rho^S(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') \neq 0,$$

which implies that  $\rho^S(\mathbf{r}, \mathbf{r}') \neq \rho(\mathbf{r}, \mathbf{r}')$ . The proof will indicate how such functions  $\psi(\mathbf{r})$  can be found; indeed, this is the key

aim of this section. Before coming to the proof itself, we will establish notation, note an important invariance property with respect to on-site linear combinations, and indicate the structure of the proof. After these preliminaries, we shall then outline the main points of the proof.

### B.2. Notation

To simplify the notation, we require that the atomic sites are labelled in such a way that the site at which the point-group symmetry is studied is the site  $i = 1$ . The support functions  $\phi_{1\alpha}(\mathbf{r})$  on this site span a space  $\Sigma$ , called the ‘local support space’. The question at issue is whether the function  $\phi_{1\alpha}^S(\mathbf{r})$  into which  $\phi_{1\alpha}(\mathbf{r})$  is transformed by the action of  $S$  is or is not contained in  $\Sigma$ . If there is any  $\phi_{1\alpha}(\mathbf{r})$  and any  $S$  for which  $\phi_{1\alpha}^S(\mathbf{r}) \notin \Sigma$ , then the local support space is not invariant under the operations of the point group. In such a case, we denote by  $\bar{\Sigma}^S$  the space spanned by all the support functions  $\phi_{1\alpha}(\mathbf{r})$  on site  $i = 1$ , together with all the functions  $\phi_{1\alpha}^S(\mathbf{r})$  into which they are transformed by  $S$ . We call  $\bar{\Sigma}^S$  the ‘extended local support space’. The basic theorem then states that if  $\bar{\Sigma}^S \neq \Sigma$ , it follows that  $\rho^S(\mathbf{r}, \mathbf{r}') \neq \rho(\mathbf{r}, \mathbf{r}')$ .

### B.3. On-site linear combinations

The proof to be presented below uses the fact that the ground-state density matrix is unaffected if we define new support functions on each atomic site as linear combinations of the old support functions on that site. We mean by this that if  $\phi_{i\alpha}$  and  $\tilde{\phi}_{i\alpha}(\mathbf{r})$  are old and new support functions on site  $i$ , related by a non-singular linear transformation:

$$\phi_{i\alpha}(\mathbf{r}) = \sum_{\beta} L_{\alpha\beta}^{(i)} \tilde{\phi}_{i\beta}(\mathbf{r}), \quad (\text{B.5})$$

then:

$$\begin{aligned} \rho(\mathbf{r}, \mathbf{r}') &= \sum_{i\alpha, j\beta} \phi_{i\alpha}(\mathbf{r}) K_{i\alpha, j\beta} \phi_{j\beta}(\mathbf{r}') \\ &= \sum_{i\alpha, j\beta} \tilde{\phi}_{i\alpha}(\mathbf{r}) \tilde{K}_{i\alpha, j\beta} \tilde{\phi}_{j\beta}(\mathbf{r}'), \end{aligned} \quad (\text{B.6})$$

where:

$$\tilde{K}_{i\alpha, j\beta} = \sum_{\gamma, \delta} L_{\gamma\alpha}^{(i)} K_{i\gamma, j\delta} L_{\delta\beta}^{(j)}. \quad (\text{B.7})$$

This emphasizes the fact that the density matrix is essentially determined by the local support space on every atomic site, rather than by the choice of the individual support functions on every site.

### B.4. Structure of the proof

The proof to be presented below consists of three main parts, which are as follows:

- (i) If the local support space is not invariant under the action of  $S$ , so that  $\bar{\Sigma}^S \neq \Sigma$ , then the dimension  $\bar{\nu}^S$  of  $\bar{\Sigma}^S$  exceeds the dimension  $\nu$  of  $\Sigma$ . We write  $\bar{\nu}^S = \nu + \lambda$ , where  $1 \leq \lambda \leq \nu$ . We shall show that if  $\bar{\Sigma}^S \neq \Sigma$  then, by using the freedom to redefine the support functions by taking on-site linear combinations, we can always ensure

that  $\phi_{1\alpha}^S(\mathbf{r}) \notin \Sigma$  for  $1 \leq \alpha \leq \lambda$ , while  $\phi_{1\alpha}^S(\mathbf{r}) \in \Sigma$  for  $\lambda < \alpha \leq \nu$ . In other words, we can always choose the support functions on site  $i = 1$  so that for only the first  $\lambda$  of the support functions  $\phi_{1\alpha}(\mathbf{r})$  do the transformed functions  $\phi_{1\alpha}^S(\mathbf{r})$  fail to belong to  $\Sigma$ . (This linear transformation makes notation considerably simpler throughout the proof.)

- (ii) We shall then show that with  $\bar{\Sigma}^S \neq \Sigma$ , and with the support functions  $\phi_{1\alpha}(\mathbf{r})$  chosen in the way we have just described, it is always possible to find functions  $\psi(\mathbf{r})$  having the following four properties:

$$\int d\mathbf{r}' \phi_{i\alpha}(\mathbf{r}') \psi(\mathbf{r}') = 0 \quad \text{for all } (i, \alpha) \quad (\text{B.8})$$

$$\int d\mathbf{r}' \phi_{j\beta}^S(\mathbf{r}') \psi(\mathbf{r}') = 0 \quad \text{for } j \neq 1 \text{ and all } \beta \quad (\text{B.9})$$

$$\int d\mathbf{r}' \phi_{1\alpha}^S(\mathbf{r}') \psi(\mathbf{r}') = 0 \quad \text{for all } \alpha > \lambda \quad (\text{B.10})$$

$$\xi_{i\alpha} = \int d\mathbf{r}' \sum_{\beta=1}^{\lambda} K_{i\alpha,1\beta} \phi_{1\beta}^S(\mathbf{r}') \psi(\mathbf{r}') \neq 0$$

for some  $(i, \alpha)$ . (B.11)

These can be summarized as follows:  $\psi$  is orthogonal to *all untransformed* functions;  $\psi$  is orthogonal to the *transformed* functions on sites away from site 1;  $\psi$  is orthogonal to those functions on site 1 which lie within  $\Sigma$ ; and finally, the scalar  $\xi_{i\alpha}$  can be found with a non-zero value for at least one  $i\alpha$  pair from the functions on site 1 lying outside  $\Sigma$ .

- (iii) The proof will conclude with the demonstration that a function  $\psi(\mathbf{r})$  having the foregoing properties also satisfies the conditions:

$$\int d\mathbf{r}' \rho(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') = 0,$$

$$\int d\mathbf{r}' \rho^S(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') \neq 0,$$
(B.12)

from which it follows that  $\rho(\mathbf{r}, \mathbf{r}')$  is not invariant under the action of  $S$ .

### B.5. Main points of the proof

We now outline the three parts of the proof, giving the main points.

*Part 1.* We start by justifying our statement that the *untransformed* support functions  $\phi_{i\alpha}$  on site  $i = 1$  can be chosen so that only for  $1 \leq \alpha \leq \lambda$  do the transformed functions  $\phi_{1\alpha}^S$  lie outside the local support space  $\Sigma$ . (Recall that  $\lambda$  is the dimension of the extended local support space minus the dimension of the local support space.) The basic idea can be seen by considering the case  $\lambda = 1$ . A new function is required to span the extended space  $\bar{\Sigma}^S$ , which we label  $\chi_1$  and choose such that  $\chi_1 \notin \Sigma$ . Let the labelling be chosen so that  $\phi_{11}^S \notin \Sigma$ , and write the transformed function as:

$$\phi_{11}^S(\mathbf{r}) = \sum_{\beta} c_{1\beta} \phi_{1\beta}(\mathbf{r}) + \chi_1(\mathbf{r}). \quad (\text{B.13})$$

Here we choose the coefficients  $c_{1\beta}$  to ensure that  $\chi_1$  is orthogonal to  $\Sigma$ . Then for the other support functions  $\phi_{1\alpha}$  ( $\alpha > 1$ ), let the transformed functions be:

$$\phi_{1\alpha}^S(\mathbf{r}) = \sum_{\beta} c_{\alpha\beta} \phi_{1\beta}(\mathbf{r}) + d_{\alpha} \chi_1(\mathbf{r}). \quad (\text{B.14})$$

But we can use the freedom to take linear combinations on each atomic site to define new support functions  $\tilde{\phi}_{1\alpha}$  so that  $\tilde{\phi}_{11} = \phi_{11}$ , but for  $\alpha > 1$  we take  $\tilde{\phi}_{1\alpha} = \phi_{1\alpha} + f_{\alpha} \phi_{11}$ , with the coefficients  $f_{\alpha}$  chosen so that  $d_{\alpha} + f_{\alpha} = 0$ , which ensures that their transformed versions are:

$$\tilde{\phi}_{1\alpha}^S(\mathbf{r}) = \sum_{\beta} (c_{\alpha\beta} + f_{\alpha} c_{1\beta}) \phi_{1\beta}(\mathbf{r}), \quad (\text{B.15})$$

which all lie within  $\Sigma$ . With these redefined support functions, all the  $\tilde{\phi}_{1\alpha}^S(\mathbf{r})$  lie within  $\Sigma$ , except for the first  $\alpha = 1$ . This concept can clearly be generalized to the case  $\lambda > 1$ , and this justifies our statement.

We assume from now on that the support functions  $\phi_{1\alpha}$  on site  $i = 1$  have been chosen so that only for  $1 \leq \alpha \leq \lambda$  do the transformed functions fail to lie in  $\Sigma$ , and for these the transformed functions are expressed as:

$$\phi_{1\alpha}^S(\mathbf{r}) = \sum_{\beta} c_{\alpha\beta} \phi_{1\beta}(\mathbf{r}) + \chi_{\alpha}(\mathbf{r}), \quad (\text{B.16})$$

where all of the functions  $\chi_{\alpha}(\mathbf{r})$  ( $\alpha = 1, \dots, \lambda$ ) are orthogonal to  $\Sigma$ .

*Part 2.* Here, we show the existence of functions  $\psi(\mathbf{r})$  having the properties given in equations (B.8)–(B.11). In the total space  $\Omega$  spanned by all PAOs in the system, let  $\bar{\Omega}_1$  denote the subspace spanned by all the PAOs on atomic sites  $i \neq 1$ . Then the support functions  $\phi_{1\alpha}$  ( $1 \leq \alpha \leq \nu$ ) and the associated functions  $\chi_{\sigma}$  ( $1 \leq \sigma \leq \lambda$ ) (see equation (B.16)) can each be expressed as a component orthogonal to  $\bar{\Omega}_1$  and a component lying entirely within  $\bar{\Omega}_1$ :

$$\phi_{1\alpha} = \phi_{1\alpha}^{\perp} + \phi_{1\alpha}^{\parallel} \quad (\alpha = 1, \dots, \nu)$$

$$\chi_{\sigma} = \chi_{\sigma}^{\perp} + \chi_{\sigma}^{\parallel} \quad (\sigma = 1, \dots, \lambda).$$
(B.17)

Now let  $T^{\perp}$  denote the space of dimension  $\nu + \lambda$  spanned by all the  $\phi_{1\alpha}^{\perp}$  and all the  $\chi_{\sigma}^{\perp}$ . Within  $T^{\perp}$ , we choose a set of  $\lambda$  linearly independent functions  $\hat{\chi}_{\sigma}$  that are orthogonal to all the  $\phi_{1\alpha}^{\perp}$ . Specifically, we choose the  $\hat{\chi}_{\sigma}$  as a projection of  $\chi_{\sigma}$  onto the subspace of  $T^{\perp}$  that is orthogonal to all the  $\phi_{1\alpha}^{\perp}$ . With this choice, we have  $\langle \chi_{\beta} | \hat{\chi}_{\sigma} \rangle = \langle \hat{\chi}_{\beta} | \hat{\chi}_{\sigma} \rangle$ , which will be useful later. Clearly these functions  $\hat{\chi}_{\sigma}$  are orthogonal to all functions in  $\bar{\Omega}_1$  and are also orthogonal to all of the  $\phi_{1\alpha}$  ( $\alpha = 1, \dots, \nu$ ). If we write  $\psi$  as:

$$\psi(\mathbf{r}) = \sum_{\sigma=1}^{\lambda} h_{\sigma} \hat{\chi}_{\sigma}(\mathbf{r}), \quad (\text{B.18})$$

with arbitrary coefficients  $h_{\sigma}$ , then  $\psi(\mathbf{r})$  satisfies equations (B.8) and (B.9). It also satisfies equation (B.10), since the  $\phi_{1\alpha}^S$  for  $\alpha > \lambda$  are linear combinations of the  $\phi_{1\alpha}$ . So all



that remains is to show that the coefficients  $h_\sigma$  can be chosen so that  $\psi$  also satisfies equation (B.11).

To show this, note first that not all  $K_{i\alpha,1\beta}$  can be zero for all  $(i, \alpha)$  and for all  $\beta = 1, \dots, \lambda$ . If they were all zero, then the support functions  $\phi_{1\beta}$  ( $\beta = 1, \dots, \lambda$ ) would not appear in the density matrix at all, and their behaviour under transformation would be irrelevant. So choose an  $i$  and an  $\alpha$  for which there are non-zero elements  $K_{i\alpha,1\beta}$  for at least one  $\beta$  in the range  $1 \leq \beta \leq \lambda$ . Call these  $i^*$  and  $\alpha^*$ , and examine the quantity:

$$\xi_{i^*\alpha^*} = \int d\mathbf{r}' \sum_{\beta=1}^{\lambda} K_{i^*\alpha^*,1\beta} \phi_{1\beta}^S(\mathbf{r}') \psi(\mathbf{r}'). \quad (\text{B.19})$$

But recalling equation (B.16) and noting that  $\psi(\mathbf{r})$  is orthogonal to all  $\phi_{1\alpha}$ , this can be rewritten as:

$$\xi_{i^*\alpha^*} = \int d\mathbf{r}' \sum_{\beta=1}^{\lambda} K_{i^*\alpha^*,1\beta} \chi_\beta(\mathbf{r}') \psi(\mathbf{r}'). \quad (\text{B.20})$$

If we substitute in equation (B.18) then, we find:

$$\xi_{i^*\alpha^*} = \int d\mathbf{r}' \sum_{\beta=1}^{\lambda} K_{i^*\alpha^*,1\beta} \chi_\beta(\mathbf{r}') \sum_{\sigma=1}^{\lambda} h_\sigma \hat{\chi}_\sigma(\mathbf{r}') \quad (\text{B.21})$$

$$= \sum_{\beta=1}^{\lambda} K_{i^*\alpha^*,1\beta} \left( \int d\mathbf{r}' \chi_\beta(\mathbf{r}') \sum_{\sigma=1}^{\lambda} h_\sigma \hat{\chi}_\sigma(\mathbf{r}') \right) \quad (\text{B.22})$$

$$= \sum_{\beta=1}^{\lambda} K_{i^*\alpha^*,1\beta} \left( \sum_{\sigma=1}^{\lambda} h_\sigma \int d\mathbf{r}' \chi_\beta(\mathbf{r}') \hat{\chi}_\sigma(\mathbf{r}') \right). \quad (\text{B.23})$$

Now this has the form of a scalar product  $\xi_{i^*\alpha^*} = \sum_{\beta=1}^{\lambda} k_\beta g_\beta$  of two  $\lambda$ -component vectors. The first vector has components  $k_\beta = K_{i^*\alpha^*,1\beta}$  and the second has components:

$$g_\beta = \sum_{\sigma=1}^{\lambda} h_\sigma \int d\mathbf{r}' \chi_\beta(\mathbf{r}') \hat{\chi}_\sigma(\mathbf{r}') \\ = \sum_{\sigma=1}^{\lambda} h_\sigma \int d\mathbf{r}' \hat{\chi}_\beta(\mathbf{r}') \hat{\chi}_\sigma(\mathbf{r}'). \quad (\text{B.24})$$

It is clear from this that the coefficients  $h_\sigma$  can be chosen to yield any desired set of coefficients  $g_\beta$ , and in particular a set of coefficients for which  $\xi_{i^*\alpha^*}$  is non-zero. This shows that  $\psi$  can be chosen to satisfy equation (B.11).

*Part 3.* For functions  $\psi(\mathbf{r})$  having the properties noted in Part 2, it follows from equation (B.8) that  $\int d\mathbf{r}' \rho(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') = 0$ . But we note also that:

$$\int d\mathbf{r}' \rho^S(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') = \sum_{i\alpha} \phi_{i\alpha}^S(\mathbf{r}) \\ \times \int d\mathbf{r}' \sum_{j\beta} K_{i\alpha,j\beta} \phi_{j\beta}^S(\mathbf{r}') \psi(\mathbf{r}'). \quad (\text{B.25})$$

On the right, all the terms for  $j \neq 1$  vanish, as do the terms  $j = 1$  and  $\beta > \lambda$  (see equations (B.9) and (B.10)),

so we have:

$$\int d\mathbf{r}' \rho^S(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') = \sum_{i\alpha} \phi_{i\alpha}^S(\mathbf{r}) \\ \times \int d\mathbf{r}' \sum_{\beta=1}^{\lambda} K_{i\alpha,1\beta} \phi_{1\beta}^S(\mathbf{r}') \psi(\mathbf{r}') = \sum_{i\alpha} \xi_{i\alpha} \phi_{i\alpha}^S(\mathbf{r}). \quad (\text{B.26})$$

Since not all  $\xi_{i\alpha}$  vanish, and since the  $\phi_{i\alpha}^S(\mathbf{r})$  are linearly independent, we conclude that  $\int d\mathbf{r}' \rho^S(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') \neq 0$ .

This completes the proof that  $\rho(\mathbf{r}, \mathbf{r}') \neq \rho^S(\mathbf{r}, \mathbf{r}')$ . The conclusion is that for the point-group symmetry of the ground state to be preserved, the support functions at the atomic site must form complete irreducible representations.

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