Large scale and linear scaling DFT with the CONQUEST code

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We survey the underlying theory behind the large-scale and linear scaling DFT code, CONQUEST, which shows excellent parallel scaling and can be applied to thousands of atoms with exact solutions, and millions of atoms with linear scaling. We give details of the representation of the density matrix and the approach to finding the electronic ground state, and discuss the implementation of molecular dynamics with linear scaling. We give an overview of the performance of the code, focussing in particular on the parallel scaling, and provide examples of recent developments and applications.

I. INTRODUCTION

As computing power has increased and methods have become more sophisticated, so computational modelling of materials systems has taken its place alongside experiment and theory in science. Electronic structure methods give insight into bonding and electronic properties of systems, and density functional theory (DFT) is now the de facto method used in fields as diverse as physics, chemistry, earth sciences, materials science and biochemistry [1].

However, almost all DFT calculations are focussed on a relatively small system size, of a few hundred atoms (while feasible, calculations involving more than a thousand atoms are still considered expensive). This size limitation mainly comes from the cost and scaling of standard DFT implementations (asymptotically, the computer time required scales with the cube of the number of atoms in the system, while the memory scales with the square of the number of atoms).

The use of increasingly large numbers of computational cores is one route to larger scale DFT calculations. Indeed, high-performance computing centres have recently scaled to tens of thousands and hundreds of thousands of cores, and exascale computing is scheduled to arrive in the next few years. However, efficient use of systems of this size requires care to ensure that the parallel scaling of any given code remains efficient as the number of cores becomes large. A real-space formulation, and the use of local basis functions to represent the Kohn-Sham (KS) eigenstates, can help with the parallel efficiency of the code, and enables calculations on larger systems, often with several thousand atoms [2–10]. Moreover, there is no inherent reason why DFT implementations should scale with the cube of the system size; in fact, with local basis functions, DFT can be formulated in a linear scaling approach [11, 12].

The use of a few hundred atoms in a calculation potentially introduces many approximations, and in some cases errors. There are systems where larger scale calculations are necessary to model the properties correctly. Features
with dimensions of nanometres or more, or features with strain fields over nanometres, will be seriously restricted by a small calculation as the strain will not be fully relaxed. Dilute alloys can change their properties if the concentration is incorrect (for instance the metal-insulator transition in doped silicon occurs at around $2 \times 10^{19}$ dopants per cubic centimetre, or one dopant per 50,000 silicon atoms). Calculations on biomolecules often use a small quantum mechanical (QM) region embedded into a larger forcefield (MM) region, and it has been shown that the size and choice of the QM region affects the results strongly, with sizes of at least 500 atoms being required. While there are accurate forcefields available, and new approaches to the fitting of forcefields are being developed, simulations requiring electronic structure or bond making and breaking must use DFT or a related approach.

**Conquest** is a large-scale and linear scaling DFT code which is designed to scale efficiently in parallel, and to be applicable to systems with thousands of atoms with full diagonalisation for the ground state, and to systems with millions of atoms with a linear scaling solution of the ground state. It has recently been released under an open-source MIT licence, and in this paper we describe the approach to implementation of the code and recent applications. We first describe the approaches to representing the density matrix, and finding the electronic ground state, and then consider how to eigenvectors can be calculated for systems large enough to require linear scaling. We also discuss the implementation of exact exchange with linear scaling. We then turn to the movement of atoms, considering in particular the calculation of stress, and the implementation of molecular dynamics, both with reference to linear scaling. After presenting the performance of Conquest for various systems, we then illustrate several applications with many thousands of atoms, before concluding.

## II. Methods: Electronic Structure

### A. Pseudopotentials and pseudo-atomic orbitals

The default pseudopotential format used in Conquest is the optimised norm-conserving Vanderbilt pseudopotential (ONCVSP) developed by Hamann from Vanderbilt’s approach. This approach has been used to generate two libraries covering move of the periodic table: PseudoDojo and SG15. Both of these libraries give very good values using the Delta comparison to all-electron results, with PseudoDojo showing an accuracy comparable to the best PAW results (when using a fully-converged plane wave basis set).

This approach to pseudopotential generation is focused on accuracy, and as a consequence includes semi-core states for many elements beyond the third row of the periodic table, as well as partial core corrections in many cases. The spacing of the real-space integration grid required for these pseudopotentials may be finer than other approaches would give. Conquest is also compatible with pseudopotentials in the Troullier-Martins form as generated by Siesta, which are less stringent, and thus less expensive.

As is common for local orbital approaches, we use a neutral atom approach, where the local part of the pseudopotential and a (neutral) atomic density cancel each other out at large distances from the atom; among other things, this removes the need for an Ewald sum for the ion-ion energies. However, it has been shown that the resulting potential can be deep, and require a fine integration grid for convergence. To alleviate this problem, we have implemented the neutral atom projector approach, and will report detailed testing in a future publication.

Conquest can use pseudo-atomic orbitals (PAOs) as basis functions to represent the support functions, while the valence orbitals also serve to generate the atomic density. We generate the PAOs by solving the Schrödinger equation for an isolated, confined atom with a pseudopotential. The basis sets are formed from valence orbitals (with a given number of functions (zetas) for each angular momentum, each with its own confinement) and polarisation functions (typically with $l_v + 1$ where $l_v$ is the angular momentum of the highest occupied state, and a given, different number of functions to the valence states).

The confinement is equivalent to a hard wall, and can be applied either as a radial cutoff, or an energy shift for the orbital. The default basis sets in Conquest are generated either with the same radial cutoffs for all shells, or the same energy shifts. For the energy shifts, we use a tight confinement (a shift of 2eV) and a loose confinement (shift of 0.02 eV) to generate two zeta functions, with a third generated when needed using the average radius of the first two. The radial confinement is found as the average of the radii for all valence functions with the large or small confinement, with the third radius again found as an average. Semi-core states only use one function with a loose confinement (in this case the orbital is strongly confined so that even a very small energy shift gives good results).

We have tested our default basis sets (single zeta with polarisation, SZP, double zeta with polarisation, DZP, and triple zeta with triple polarisation, TZTP) against converged plane wave calculations using the same pseudopotentials. We used a wide variety of systems: elemental semiconductors (C, Si, Ge); oxides (SiO$_2$ in both α-quartz and stishovite phases, MgO, SrTiO$_3$, PbTiO$_3$ and MgSiO$_3$); non-magnetic bcc Fe; and weakly bonded systems (ice XI and BN sheets). In all cases, we showed that the TZTP basis sets reproduced the converged plane wave results with excellent accuracy.
B. Representing the density matrix

Conquest uses the density matrix as the fundamental description of the system being modelling (in contrast to the wavefunctions as is common in many DFT codes). The density matrix is represented in terms of support functions\[23, 24\], \(\phi_{i\alpha}(r)\), and can be written:

\[
\rho(r,r') = \sum_{i\alpha,j\beta} \phi_{i\alpha}(r) K_{i\alpha,j\beta} \phi_{j\beta}(r')
\]  
(1)

(Note that the density matrix can easily be written in terms of the wavefunctions, when these are available, or found by linear scaling optimisation, as described in Section II C.)

The support functions are local functions which move with the atoms, and are strictly localised within a sphere. They are used to form the Hamiltonian and overlap matrices as well as the density matrix:

\[
H_{i\alpha,j\beta} = \int dr \phi_{i\alpha}(r) \hat{H} \phi_{j\beta}(r)
\]  
(2)

The support functions themselves are defined either as primitive PAOs (in a one-to-one mapping), or are represented in terms of one of two basis sets: the PAOs; and blip functions\[25\]. We write:

\[
\phi_{i\alpha}(r) = \sum_s b_{i\alpha s} \theta_s(r)
\]  
(3)

where the basis functions \(\theta_s(r)\) (either pseudo-atomic orbitals or cubic B-splines) are discussed further below.

1. Multi-site support functions

Since the primitive PAOs are localized around the atoms, we can use them as support functions without any modifications, and a large PAO basis set gives high accuracy, as shown in Sec. II A. However, the computational cost of calculations scales with the cubic of the number of support functions. For large-scale calculations, we need to reduce the number of support functions as far as possible. We note that there is a strong link between the basis set chosen and the number of support functions that can be used\[26\].

Multi-site support functions (MSSFs)\[27, 28\] offer one way to reduce the number of support functions. The MSSFs are constructed as linear-combination functions of the PAOs not only on a target atom, but also on its neighbouring atoms, defined by a cutoff radius \(r_{MS}\),

\[
\phi_{i\alpha}(r) = \sum_{k} \sum_{\mu \in k} C_{i\alpha, k\mu} \chi_{k\mu}(r),
\]  
(4)

where \(\chi_{k\mu}\) is a PAO on atom \(k\), \(\alpha\) is the index of the support functions of atom \(i\), \(\mu\) is the index of the PAOs of its neighbouring atoms \(k\) (including \(i\) itself), and \(C_{i\alpha, k\mu}\) are the linear combination coefficients. Since the MSSFs are no longer atomic orbitals but local molecular orbital (MO)-like functions, the number of MSSFs can be equal to that of a minimal basis.

In Conquest, two methods have been implemented to determine the linear-combination coefficients of the MSSFs. One of the methods is the local-filter-diagonalisation (LFD) method proposed by Rayson and Briddon \[5, 27, 29\], and the other is numerical optimisation\[28\], which will be explained in Sec. II C. In the LFD method, the linear-combination coefficients are obtained by projecting molecular orbital coefficients from a subspace defined by a cluster onto trial vectors which are localized around the target atom. Since the MSSFs will depend on the charge density of the system, which will in turn depend on the MSSFs, the linear-combination coefficients need to be determined self-consistently\[27\]. \(r_{MS}\) should be equal or smaller than the subspace region in the LFD method \(r_{LFD}\).

The accuracy of the MSSFs depends on \(r_{MS}\). In Fig. I we see that the deviation from the full, unrestricted primitive PAO result decreases exponentially not only in a gapped system (bulk Si) but also in a metallic system (bulk Al). The number of MSSFs per atom is four, while that of the TZP PAOs is 17 in both Si and Al, giving a four-fold reduction in number and a significant speed-up. An example of the computational time with the MSSFs is demonstrated in Sec. IV A.
2. On-site support functions

When using a linear scaling solver, as described in Sec. II C, we require a sparse approximation to the inverse overlap matrix to act as a metric\cite{30}. We have found that multiple zeta basis sets, and multi-site support functions, are not compatible with our standard linear-scaling method for finding this inverse overlap (Hotelling’s method). The reasons for this failure are not yet clear, and under investigation, but are most likely to arise from the assumed sparsity pattern of the matrix, and the starting value used. As a result, we have been limited in the basis sets that can be used for linear scaling. Blip functions, which will be discussed in the next section, offer an route to an accurate linear scaling basis set; however, PAOs are often convenient and efficient, and a restriction to SZ or SZP PAO basis sets is limiting.

We have found recently, however, that an adaptation of the MSSF approach allows linear scaling solution for a sparse inverse overlap matrix while retaining accurate basis sets: on-site support functions. We restrict the PAOs forming the support functions for an atom \( i \) to its own PAOs; however, we must be careful to respect any symmetry of the atomic lattice, so that the space spanned by the support functions of the atoms decomposes into complete irreducible representations of the symmetry group\cite{26}. The simplest way to ensure that this is respected is to increase the number of support functions such that it encompasses all angular momenta of the PAOs (e.g. for PAOs including \( l = 0 \to 2 \) we would need 9 SFs, while for PAOs only including \( l = 0 \) and \( l = 2 \) we would need 6 SFs).

This approach bears some similarity to the polarised atomic orbital method\cite{31, 32} though that method imposes no restrictions on the number of functions, and uses a different approach to find the orbital coefficients. In our approach we use the LFD method described in the previous section, using a trial vector which is extended to include the polarisation orbitals. We find that the resulting support functions can be inverted efficiently (interestingly, it is often more efficient than a simple SZP PAO basis set).

When using OSSF with linear scaling, we are still investigating the most efficient approach for finding the ground state; this involves optimising the density matrix, the OSSF coefficients and the charge density. Introducing self-consistency between the OSSF coefficients and the charge density is straightforward, but in a naive loop would add considerably to the computational time. Optimising the energy with respect to the OSSF coefficients is also straightforward, but the most efficient approach (i.e. when to update which parts of the optimisation) requires further research.

The basis sets found using OSSF are significantly better than the simple SZP PAO basis set, as shown in Fig. 2. Here we see that, for a slightly disturbed eight atom bulk silicon cell, as the LFD range is progressively increase, so the rate of convergence of the density matrix optimisation improves. The quality of the resulting inverse overlap matrix is also improved, and the resulting energy and forces on the atoms are significantly better with the OSSF basis sets. We show results for different basis sets in Table I: primitive PAOs (SZP, DZP and TZTP); MSSF for different ranges; and OSSF. The MSSF and OSSF calculations do not update the SF coefficients after finding self-consistency; for MSSF, the LFD range is set to 15 bohr throughout.

As seen in Fig. 2 it is evident that the OSSF give a significant improvement to the performance of the linear
FIG. 2: Convergence of linear scaling density matrix optimisation for different basis sets: SZP; and OSSF with different LFD ranges. The system considered is an eight atom bulk silicon cell, slightly disturbed from the perfect crystal structure.

| Basis     | Energy (Ha) | Force (Ha/bohr) | Time relative to TZTP |
|-----------|-------------|-----------------|-----------------------|
| SZP       | -33.692     | -0.00171        | 0.12                  |
| DZP       | -33.808     | -0.00150        | 0.55                  |
| TZTP      | -33.814     | -0.00146        | 1.00                  |
| MSSF 5 bohr | -33.776     | -0.00155        | 1.16                  |
| MSSF 8 bohr | -33.801     | -0.00144        | 1.12                  |
| MSSF 10 bohr | -33.796     | -0.00141        | 1.23                  |
| MSSF 12 bohr | -33.807     | -0.00145        | 1.23                  |
| OSSF 5 bohr | -33.620     | -0.00163        | 0.83                  |
| OSSF 8 bohr | -33.790     | -0.00142        | 0.95                  |
| OSSF 10 bohr | -33.788     | -0.00143        | 0.87                  |
| OSSF 12 bohr | -33.796     | -0.00143        | 1.16                  |
| OSSF O(N) 8 bohr | -33.605 | -0.00174        | 7.11                  |
| OSSF O(N) 10 bohr | -33.784 | -0.00154        | 6.24                  |
| OSSF O(N) 12 bohr | -33.782 | -0.00154        | 4.86                  |
| OSSF O(N) 15 bohr | -33.792 | -0.00154        | 4.19                  |

TABLE I: Comparison of different basis sets for an eight atom bulk silicon cell, slightly disturbed from the perfect crystal structure. Primitive basis sets have 9, 13 and 27 support functions, respectively; MSSF have 4 support functions and a LFD range of 15 bohr; OSSF have 9 support functions. MSSF and OSSF are not updated after the initial calculation of the coefficients.

scaling solver, and are comparable to the MSSF for the accuracy of forces and the timing. Most notably, we see that with the OSSF found with the LFD radius set to 15 bohr, the linear scaling solver is only 4 times slower than exact diagonalisation with the full TZTP basis set, and 8 times slower than the DZP basis set. This performance difference is expected for such a small system where linear scaling solvers are less efficient than exact solvers. However, it suggests that the choice of basis functions is important in implementing linear scaling. We note that the quality of both OSSF and MSSF basis sets would be improved by optimisation of the coefficients, as described in Sec. II C 3, but even with these simple approximations, good performance is achieved.
3. Blip functions

While PAOs are a convenient basis set, they do not permit systematic convergence of the energy with respect to the basis: while adding extra basis functions will increase the size of the variational space, there are two parameters which offer different degrees of freedom (maximum angular momentum, and number of radial functions, or zetas, per angular momentum channel), and there are no guarantees of how adding to each parameter will change the energy.

The blip functions [25], which are piecewise continuous cubic splines defined on a cubic grid that moves with the atoms, are a basis set that can be systematically converged. The blip grid spacing corresponds directly to a plane wave cutoff, allowing the basis set to be improved systematically (of course, the support functions are confined within a radius, but it has been shown that the total energy converges variationally and rapidly with this radius [25, 33]). The most efficient procedure for initialisation and optimisation of the blip coefficients along with the charge density, and for linear scaling approaches to finding the density matrix, is the subject of on-going research.

C. Solving for the ground state

The ground state electronic structure in CONQUEST is defined by three related quantities: the support functions; the density matrix; and self-consistency between the charge density and the Kohn-Sham potential. The self-consistency procedure is a standard part of DFT and related codes [34], and we implement the Pulay approach [35] which works efficiently.

While the overall search for the ground state could be considered as an optimisation in a space formed by both the support function coefficients and the density matrix elements, it is easier to consider how the density matrix is found for a given set of support functions, and then to discuss methods for optimising the energy with respect to the support function coefficients. We consider first the two approaches to solving for the density matrix: exact diagonalisation, which scales cubically but makes no approximations; and linear scaling, which imposes a range on the density matrix.

1. Density matrix: exact diagonalisation

We perform diagonalisation of the Hamiltonian using ScaLAPACK [36], and are also investigating the use of ELPA [37] (which uses the same interface, and may scale better to large numbers of processes).

Since we apply periodic boundary conditions to our simulation cell, the Brillouin zone must be sampled appropriately; we have implemented the Monkhorst-Pack [38] sampling method as a default approach to Brillouin zone sampling, but any arbitrary set of k-points can be used. (At present we do not account for the symmetry of the simulation cell beyond time-reversal symmetry, as the code is designed for large-scale simulations which are unlikely to show significant symmetries.)

The Kohn-Sham eigenstates are represented in terms of the support functions, with the density matrix found as:

\[
|\psi_{nk}\rangle = \sum_{i\alpha} c_{i\alpha}^{nk} |\phi_{i\alpha}\rangle
\]

\[
K_{i\alpha,j\beta} = \sum_{nk} f_{nk} u_k^{nk} c_{i\alpha}^{nk} c_{j\beta}^{nk}^* \quad \text{(5)}
\]

where the weight of each k-point is given as \(w_k\) and the occupancy of the eigenstate is \(f_{nk}\) (which is found using a simple Fermi-Dirac distribution, or the Methfessel-Paxton [39] approach). The diagonalisation at each k-point can be assigned to a sub-group of processes, enabling a calculation using many k-points to be sped up significantly.

2. Density matrix: linear scaling

To achieve linear scaling in computational time with the system size, we restrict the range of the density matrix elements, where the band energy is defined as \(E_{\text{band}} = 2 \text{Tr}[KH]\). When this approach is coupled with strictly local basis functions, all matrices are sparse, and all matrix operations scale linearly with system size.

During the optimisation, we must constrain the electron number (a relatively straightforward task [23]), and also the idempotency of the density matrix (a much more complex task in a variational context). We follow the LNV
TABLE II: Lattice constants \( a_0 \) of bulk Si calculated with MSSF with ranges \( r_{MS} \) of 5.0, 8.0 and 17.0 bohr, and percent deviations (\%D) from \( a_0 \) calculated with the primitive TZDP PAOs.

| \( r_{MS} \) | \( a_0 \)     | \%D |
|------------|---------------|-----|
|            | LFD opt       |     |
| 5.0        | 5.447         | 1.0 | 0.2 |
| 8.0        | 5.403         | 0.2 | 0.1 |
| 17.0       | 5.393         | 0.0 | 0.0 |
| TZDP       | 5.395         |     |

This drives the density matrix, \( K \), towards idempotency (strictly it is driven towards weak idempotency, where the eigenvalues lie between zero and one, but may not be exactly zero and one). If, as above, we write \( E = \text{Tr}[K H] \) then we can use the gradient \( \partial E / \partial L_{i\alpha,j\beta} \) to minimise the energy with respect to the density matrix, and the density matrix \( K \) will be driven towards idempotency as the minimisation proceeds.

The initial density matrix is generated from the Hamiltonian, using an iterative procedure based on a generalisation of the McWeeny transform\[42, 43\]. We use an approximate, sparse inverse overlap matrix as the metric for the optimisation, found using the iterative Hotelling method. As discussed in Sec. II B, this has certain consequences for the basis sets that can be used, but both OSSF and blip basis sets show promise for accurate, linear scaling calculations.

### 3. Optimising support functions

As mentioned in Sec. II B, we can construct support functions by taking linear combinations of PAOs (MSSFs or OSSFs) or blips. The linear combination coefficients can be optimised numerically by minimizing the DFT total energy with respect to the coefficients\[28\]. For MSSFs and OSSFs, the coefficients obtained by the LFD method generally form good initial values for the numerical optimisation. The initial blip coefficients are found as a best fit to PAOs. In this section, we demonstrate optimisation of SF coefficients for the MSSFs, though the formalism is identical for the other approaches. We note that these optimisation processes are liable to ill-conditioning, which can be mitigated\[44\].

Figure 3 shows the energy-volume (E-V) curves of bulk Si\[28\] calculated with simple LFD (filled symbols) and optimisation of the MSSF coefficients (open symbols). The number of MSSFs per atom is four, while that of the primitive TZDP (3s3p2d) PAOs is 22. Table II summarises the lattice constant \( a_0 \) obtained by fitting the E-V curves with Birch-Murnaghan equation. The results are improved, i.e., becoming closer to the results of the primitive PAOs, by the numerical optimisation in all cases. When \( r_{MS} \) is large, e.g. 17.0 bohr, since the MSSFs found with LFD method accurate results, the change from numerical optimisation is small. When \( r_{MS} \) is 8.0 bohr, the difference with and without the numerical optimisation is significantly larger, but both LFD and the numerical optimisation show reasonable accuracy. On the other hand, when \( r_{MS} \) is as small as 5.0 bohr, the result with the LFD method is not accurate, with a 1\% deviation from the full TZDP result, but we find significant improvement of the accuracy from numerical optimisation, reducing the percentage deviation to 0.2\%.

### D. Electronic structure for large systems

Linear scaling, or \( \mathcal{O}(N) \), calculations which work with the density matrix implicitly integrate over energy and produce only the sum of the occupied eigenvalues and not any of the Kohn-Sham eigenstates of the system. However, we often want to know the individual eigenstates to analyze the electronic structure of the system, though generally within a relatively small energy range. These can be found efficiently from the converged ground-state Hamiltonian by using the Sakurai-Sugiura (SS) method\[45\]. The SS method\[46, 47\] is an efficient interior eigenproblem solver for large sparse matrices using contour integrals in the complex plane, which provides the eigenvalues and eigenvectors in a finite eigenvalue range with high parallel efficiency. We first optimise the electronic Hamiltonian with the \( \mathcal{O}(N) \) method in CONQUEST, and then obtain the eigenstates of the Hamiltonian in a finite energy window with a one-shot approach\[40, 41\] where we write the density matrix \( K \) in terms of an auxiliary density matrix \( L \), using the McWeeny transform:

\[
K = 3LSL - 2LSLSL
\]
FIG. 3: Energy-volume curves of bulk Si, demonstrating the effect of optimising MSSF coefficients after the initial LFD process. Symbols correspond to the calculated energies by primitive TZDP PAOs and MSSF with multi-site ranges ($r_{MS}$) 17.0, 8.0 and 5.0 bohr, using the LFD method (filled symbols) and numerical optimisation (open symbols). The local filter diagonalization range $r_{LFD}$ was set to be equal to $r_{MS}$. (Adapted from Ref. 28 with permission from the PCCP Owner Societies.)

FIG. 4: Electronic density distributions (blue) of the Ge hut clusters (light gray) on the Si(001) (dark gray) (totally 23,737 atoms) around the Fermi level. (Reprinted with permission from J. Chem. Theory Comput. 13, 4146 (2017). Copyright (2017) American Chemical Society.)

SS calculation. Here we demonstrate the usefulness of the combination of the $O(N)$ and SS methods by showing two examples.

The first example is the energy-specific electron-density distribution in a hut-shaped Ge cluster on Si(001) surface consisting of 23,737 atoms (the physical system is described in more detail in Sec. V A). Figure 4 shows the electron density distribution in the energy range [-0.01 eV: + 0.02 eV] around the Fermi level, obtained by calculating the Kohn-Sham eigenvectors in this range with the SS method. The calculation for the eigenvalues and eigenvectors required 146 seconds using 64 nodes of the K supercomputer. We also calculated the eigenstates in the same energy range for a larger Ge/Si(001) system, consisting of 194,573 atoms, in 2,399 seconds using 6,400 nodes.

The second example is the density of states (DOS) of a DNA system in water, which consists of 3,439 atoms. The DOS calculated with MSSF (see Sec. II B 1) (4,774 functions) and primitive PAOs (27,883 functions), and their difference are shown in Fig. 5. The DOS from the MSSF is very close to the full primitive PAO DOS in occupied states, and unoccupied states near Fermi level, while the DOS in the unoccupied states far from Fermi level are quite different. This is because the MSSFs are determined by optimising the occupied states with a small number of support functions, and the accuracy of the MSSFs for unoccupied states often becomes poor. To improve this poor description, we can use the SS method. First, we optimise the electronic density of the target system using MSSF, and we re-construct the electronic Hamiltonian using the primitive PAOs with the optimised density. Then we use the SS method to obtain the eigenstates. Thus, we can obtain the DOS even in unoccupied states far from Fermi level quite accurately, as shown in Fig. 5.
E. Exact exchange

Exact exchange (EXX) correction to the original Kohn-Sham formulation of DFT, leading to the class of hybrid exchange-correlation functionals, has become very popular, since in the vast majority of cases, it improves the overall reliability of the DFT predictions. Depending on the implementation — mainly basis set and boundary conditions — orbital dependence is introduced to the KS-DFT formalism via the EXX energy standard expression:

$$E_x = -\frac{1}{4} \int \mathrm{d}r \rho(r', r) \rho(r', r) \frac{1}{|r - r'|} = -\sum_{n,m} \int \mathrm{d}r \psi^*_m(r) \psi^*_n(r) \psi_n(r) \psi_m(r'),$$

(8)

where \( \{ \psi_n \} \) is the set of \( N \) occupied KS states, can bring the computational cost to a prohibitive level more rapidly than pure LDA/GGA DFT when increasing the system size. Within the framework of CONQUEST, where the density matrix of Eq. 8 are expanded onto a set of \( M \) localized and real basis functions, the exchange energy reads: \( E_x = -\text{Tr} \{ KX \} \), with the exchange matrix \( X \) elements given by:

$$X_{i\alpha,j\beta} = \sum_{k\mu,l\nu} \int \mathrm{d}r \rho_{i\alpha,k\mu}(r) K_{k\mu,l\nu} \rho_{l\nu,j\beta}(r') = \sum_{k\mu,l\nu} \int \mathrm{d}r \psi^*_i(r) \psi^*_k(r) K_{k\mu,l\nu} \psi_l(r) \psi_m(r').$$

(9)

As a result, calculation of \( X \) requires to evaluate at most \( M^4 \) electron repulsion integrals (ERIs) defined by the integrand of Eq. 9. The first equality in the equation above outlines the fact that evaluating an ERI is similar to computing the Hartree energy, with in place of the full electronic density, localized pair densities \( \rho_{i\alpha,k\mu}, \rho_{l\nu,j\beta} \) coupled by the density matrix elements \( K_{k\mu,l\nu} \). Consequently, ERI calculation can be performed by solving a Poisson equation into a predefined local cell. Note that, contrary to the Hartree energy, solution of this equation should be free of periodic boundary conditions.

When dealing with a numerical basis set such as the PAOs, several options to compute the ERIs are available, with for instance the semi-analytic solution given by Toyoda and Ozaki\[48, 49\] combining fast-spherical Bessel transform for the radial integration and a more traditional analytic method for the spherical harmonic part. Another approach is based on the experience of Gaussian-type orbital (GTO) ERI solvers.\[51, 52\] In that case, the PAO-ERIs are transformed into a set of contracted GTO-ERIs which are then calculated analytically.\[51, 52\] Instead, we use a route which circumvents the calculation of the ERIs and works for any smooth finite-range functions, which is particularly well suited for \( O(N) \) approaches based on the pseudopotential approximation. The key part is to perform the sum over the index \( l\nu \) before solving for the Coulomb potential of the pair densities; this simple re-ordering increases the efficiency of the procedure markedly. For this, we introduce the contraction functions, \( \Phi_{k\mu}(r') \), as:

$$\Phi_{k\mu}(r') = \sum_{l\nu} K_{k\mu,l\nu}(r') \phi_{l\nu}(r')$$

(10)
It should be noted that the domain over which these functions are defined requires some care. The sum over \( l \nu \) need only include those support functions \( \phi_{l \nu} \) overlapping with \( \phi_{j \beta} \), as \( \Phi_{k \mu} \) will be multiplied by this function. Contracted densities are then defined as

\[
\bar{\rho}_{k \mu, j \beta}(r') = \Phi_{k \mu}(r') \phi_{j \beta}(r'),
\]

and the resulting Coulomb potential,

\[
\bar{v}_{k \mu, j \beta}(r) = \int dr' \frac{\bar{\rho}_{k \mu, j \beta}(r')}{|r - r'|},
\]

is calculated by solving Poisson’s equation. Once the potential has been found, a further contraction over \( k \mu \) is performed to create,

\[
\Omega_{j \beta}(r) = \sum_{k} \bar{v}_{k \mu, j \beta}(r) \phi_{k \mu}(r),
\]

where, again, the sum over support functions \( k \mu \) need only include those functions which overlap with functions \( i \alpha \). The exchange matrix elements are then calculated by numerical integration:

\[
X_{i \alpha, j \beta} = \int dr \phi_{i \alpha}(r) \Omega_{j \beta}(r).
\]

The process —from Eq. 10 to (14)— by which the EXX is calculated in CONQUEST, will be referred to as the contraction reduction integral (CRI). The set of function \( \Omega_{j \beta} \) is effectively defined by the density matrix range, and the need for \( j \beta \) to overlap with atoms \( l \nu \), which naturally control the number of functions entering in the sums of Eqs. 11 and 13. Note that the calculation time can be reduced by imposing a range condition \( (R_X) \) on the exchange matrix. This is related to the sparsity property of \( \rho(r, r') \) and the truncation of all the operators involved in the Hamiltonian.

![FIG. 6: Comparison of CPU times necessary to compute EXX in isolated water clusters as a function of number atoms (N) using explicit ERI calculation and the CRI method. Ideal N^4 and N^3 scalings are given by plain lines.](image)

Practical tests on the efficiency of this approach algorithm were carried out on a set of isolated water clusters \( (\text{H}_2\text{O})_n \) \( (n \leq 20) \) with fused cubes structures. Calculations of exchange energy were performed after the KS density matrix had been converged using the standard self-consistent-field (SCF) method. As a result, the timings presented below for exact exchange (EXX) energy can be compared to a single SCF cycle as found in hybrid-DFT calculation. For this demonstration, SZP PAO orbitals have been used for hydrogen and oxygen with cutoff radii of 4.7 and 3.8 au, respectively. We emphasize that the main conclusions of this work can be easily extended to more flexible basis sets, as long as the support functions are localized. The CPU times used for the computation of EXX are reported in Fig. 6 as a function of the number of atoms using: (i) the explicit evaluation of the full set of ERI, (ii) the CRI approach, and (iii) the CRI approach with partial storage of the PAO on the grids. Comparing the formal scalings obtained for the CRI methods against the full ERI approach, it becomes clear that the former reduces the quartic scaling to cubic with respect to the size of the system.

At this point we should emphasise that exchange energy values obtained with the three schemes are fully identical, their accuracies being only dependent on the Poisson solver used to evaluate the pair potential in Eq. 12. Among the
FIG. 7: Variation of the CPU time with respect to the range $R_X$ (in a.u.) for the calculation of EXX in isolated water clusters using the CRI method.

Various numerical methods, one can choose to evaluate the Coulomb potential in reciprocal or real space. Whereas the former is the most appropriate for periodic neutral systems —when the positively charged nuclei compensate exactly the electronic charge density— it becomes less reliable for isolated and/or charged systems. Several schemes have been developed to tackle this problem. Alternatives based on the discrete variable representation (DVR) of Eq. 12 which avoids the direct resolution of the Poisson equation have been proposed. The density is generally expanded in a direct product of one-dimensional localized real-space basis functions as for instance, interpolating scaling functions (ISF). After extended comparisons between the DVR-ISF developed by Genovese et al. and corrected FFT-based schemes, we found that systematic convergence of the ERI is obtained with a better accuracy and at a lower cost using the real space Poisson solver.

FIG. 8: Convergence of the EXX energy with respect to the exchange range $R_X$ for the cluster $(\text{H}_2\text{O})_{20}$. Error is given with respect to the exact calculation.

As shown in Fig. 7 if a finite range $R_X$ is introduced within the CRI algorithm, the CPU time can be significantly reduced, allowing linear scaling to be achieved for clusters with more than 36 atoms (with $R_X = 7.0$ au). Computational resources further decrease with shorter EXX ranges, along with faster onset of the linear-scaling regime. The EXX accuracy with respect to the range of the exchange matrix is shown in Fig. 8 for the cluster $(\text{H}_2\text{O})_{20}$ presenting the “boxkite” structure. After somewhat erratic behavior at low values, it is found that an accuracy below 0.5 mHa is reached for $R_X \geq 8$. Even though the non-local nature of the EXX interaction may need some special care when introducing a cutoff radius on $X$ elements, it is reasonable to believe that the CRI implementation, along with a judicious choice of convergence parameters, is opening the way to exact exchange calculations on 100,000+ atoms with CONQUEST for a fair efficiency/accuracy ratio.
III. METHODS: MOVING ATOMS

A. Forces and stresses

Forces have been available in Conquest for some time, as described elsewhere\cite{70,71}, with the force being the exact differential of the energy, including Pulay forces where appropriate.

Calculation of the stress tensor has recently been implemented within the current release of Conquest. The definition of the stress tensor is standard\cite{2}:

\[
\sigma_{\alpha\beta} = \frac{\partial E}{\partial \epsilon_{\alpha\beta}} = \frac{\partial E}{\partial r_{\alpha}} r_{\beta}
\]

where \(\alpha\) and \(\beta\) are Cartesian directions indices, and the second equality holds for most contributions to the stress. In this case, the first term is the force, so most contributions to the stress tensor can be calculated at the same time the forces are calculated. There are a few exceptions to this, however, but they are easily evaluated\cite{2,72}.

The original formulation of stress within DFT is traced back to the pioneering work of Nielsen and Martin\cite{73,74}, where a formulation for the stress was expressed for the first time in the framework of the local-density approximation (LDA) and later derived in more detail\cite{75,76}. We have chosen to omit the factor of \(\frac{1}{\Omega}\) in eq. \ref{eq:stress} since it averages the total stress over the macroscopic simulation cell and in a case where the volume \(\Omega\) is not well defined would give spurious results. Note that pressure, as calculated at present, uses the volume of the simulation cell for the purpose of conversion and if there is vacuum in any direction the pressure should not be considered accurate. For this reason Conquest internally uses values of stress to optimise simulation cells.

Stress is an extremely useful quantity: it is used to optimise simulation cell parameters, though this requires care to converge both the integration grid spacing, and numbers of k-points. Additionally, it is used in the NPT ensemble for molecular dynamics.

Our implementation of stress is valid for both exact diagonalisation and linear scaling solvers. However, we have found that the stress converges extremely slowly with respect to density matrix truncation. Figure 9 shows the convergence of force (i.e. energy differences), total energy and stress with density matrix truncation for three different elemental semiconductors with very different gaps: carbon, silicon and germanium. Calculations were performed on the diamond structure (with a small perturbation in the case of the force calculation) at the optimal lattice parameter found using exact diagonalisation, with integration grid cutoffs equivalent to 400 Ha and an \(8 \times 8 \times 8\) \(\Gamma\)-centred Monkhorst-Pack grid. To aid comparison between exact diagonalisation and linear scaling calculations, we used the simplest basis set, i.e. single zeta, though this does not change the final results significantly. The plots show the difference between the \(O(N)\) and full diagonalisation results. The full diagonalisation results for the stresses were all less than 0.001 Ha (and less than 0.1 GPa when converted to a pressure). For the forces, the full diagonalisation results were 0.036 Ha/bohr for C, 0.016 Ha/bohr for Si and 0.014 Ha/bohr for Ge. The total energies were -47.891 Ha for C, -33.611 Ha for Si and -39.589 Ha for Ge.

![Convergence of forces, total energy, and stress](image)

**FIG. 9**: Convergence of: (a) forces; (b) total energy; and (c) stress (note that stress is in Ha, and is not normalised by the simulation cell volume). These plots demonstrate the convergence of \(O(N)\) calculations against a reference of exact diagonalisation, so zero on the \(y\)-axis represents exact convergence to the diagonalisation reference.

The spatial decay of the density matrix is not analytically described for complex materials, but can be shown to decay approximately exponentially with gap\cite{77,78}:

\[
\rho(r, r') \propto \exp(-\gamma |r - r'|)
\]

We can see in Fig. 9 that the rates of convergence of the different materials with density matrix truncation decrease with decreasing gap size, as expected. It is notable that the initial errors are largest for the stresses, and that
significant differences in the stress remain even at very large density matrix ranges. We will investigate this fully in a future publication, but we are confident that this comes from the implicit dependence of energy on density matrix truncation range, which should be included in a stress calculation as it will change as the unit cell is changed; however, an analytic form for this stress is not available.

B. Structure optimisation

Structural optimisation can be performed using a variety of standard approaches: the L-BFGS algorithm for atomic optimisation; conjugate gradients for atomic and simulation cell optimisation; and quenched molecular dynamics (both in a simple form, and using the FIRE algorithm). We note that some form of preconditioning will become increasingly important as system sizes increase, and we are planning to implement some recently proposed preconditioners.

C. Molecular dynamics

Since the calculated forces are accurate and we can treat large systems, it is reasonable to expect that we can perform reliable molecular dynamics of large complex systems using CONQUEST. Unfortunately, it is not so easy to realize reliable MD simulations with the linear-scaling DFT technique, or with MSSF. We have two key issues here. First, the calculation time for each MD step should be small enough to reach a meaningful simulation time. Second, density matrix should be sufficiently accurate to produce reliable MD simulations. During structure optimization, we can refine the accuracy step by step, without significant penalty. In many cases, we need a rather high accuracy only in the late stages of structure optimization. On the other hand, for MD simulations, we need to calculate the density matrix accurately at every step to ensure that the correct trajectory is followed. The accuracy of the density matrix depends on the tolerance to which it is optimised. Here, the optimized quantities are the auxiliary density matrix $L$ for linear-scaling MD simulations of a 64-atom silicon crystalline system with different tolerances on the optimisation.

First, the calculation time for each MD step should be small enough to reach a meaningful simulation time. Second, the density matrix depends on the tolerance to which it is optimised. Here, the optimized quantities are the auxiliary density matrix $L$, which should be constant in reliable NVE-MD simulations. The results show that we need a very strict tolerance for stable MD simulations. Note that, if we use McWeeny initialization at the beginning of the simulations, the time evolution of $E_{BO}$, which should be constant in reliable NVE-MD simulations. The results show that we need a very strict tolerance for stable MD simulations. Note that, if we use McWeeny initialization at every MD step (shown by solid line in Fig. 10), $E_{BO}$ is almost constant even if we use a rough tolerance. But, this leads to a high computational cost at each iteration.

To solve this problem, CONQUEST uses the XLBOMD method, with the DMM method. The extended Lagrangian used in CONQUEST is:

$$\mathcal{L}^{XBO} = \mathcal{L}^{BO} (R, \dot{R}) + \frac{1}{2} \mu \text{Tr} [\dot{\mathbf{X}}^2] - \frac{1}{2} \mu \omega^2 \text{Tr} [(LS-X)^2],$$  

where $S$ is the overlap matrix and $X$ is a sparse matrix associated with $LS$ rather than $L$ to maintain the orthogonal metric. $\mu$ is the fictitious electronic mass and $\omega$ is the curvature of the electronic harmonic potential. If we take the limit $\mu \to 0$, $\mathcal{L}^{XBO}$ becomes $\mathcal{L}^{BO}$ and we have equations of motion for nuclear positions and $X$, and for $X$:

$$\ddot{\mathbf{X}} = \omega^2 (LS - \mathbf{X}),$$  

If we apply the Verlet scheme to calculate $X$, we have

$$X(t + \delta t) = 2X(t) - X(t - \delta t) + \delta t^2 \omega^2 [L(t)S(t) - X(t)],$$

i.e. the trajectory of $X(t)$ is time-reversible, and evolves in a harmonic potential centred on the ground-state density $L(t)S(t)$. The matrix $XS^{-1}$ is then used as the initial guess for the $L$-matrix.

If we use this method, the total energy $E_{BO}$ is stable and the MD trajectories do not strongly depend on the tolerance or the range $R_L$ in the $O(N)$ calculations. Figure 11 shows the variation of the total energy $E_{BO}$ with...
FIG. 10: Time evolution of Born-Oppenheimer total energy ($E_{BO}$) obtained by McWeeny initialization at every step (solid line) and by reusing the $L$ matrix from the previous step for different tolerances (symbols). Symbols indicate tolerances of $1.6 \times 10^{-5}$ (circles), $1.6 \times 10^{-7}$ (squares), and $1.6 \times 10^{-9}$ (triangles). Reprinted with permission from J. Chem. Theor. Comput. 10, 5419 (2014). Copyright (2014) American Chemical Society.

Simulation time for different values of $R_L$. The fluctuations in the energy are smaller for larger $R_L$, but even with $R_L = 13$ bohr, the energy drift in $E_{BO}$ is very small, meaning that the MD simulation is stable.

In practice, the $X$-matrix sometimes moves away from the harmonic centre over time, increasing the number of SCF iterations required to reach the ground state over the course of a simulation. To remove this instability, the dissipative term, $a \sum_{m=0}^{M} c_m X(t - m\delta t)$, is included\cite{87}. In principle, this dissipation term may break the time-reversible symmetry, but it is made to have a minimal effect and it is found that the MD simulations with the term is stable.

Using this XLBOMD + DMM method, we can also treat the canonical ensemble and perform constant temperature (NVT) MD simulations, for example, using the Nosé-Hoover chain (NHC) method\cite{88}. The detailed explanation of the integration scheme used for the canonical ensemble is provided in Sec. A 2 a. Figure 12 shows the time evolution of the temperature, the constant of motion for the NHC method, and the DFT potential energy $V_{BO}$, in NVT-MD simulations of the same crystalline 64-atom silicon system at 300K, with and without XLBOMD method. We find that temperatures are stable and close to 300K in both simulations. However, we again observe the problem of drift in the constant of motion when we do not use the XLBOMD method, while there are no such problems in the XLBOMD+DMM simulations. More importantly, the profile of $V_{BO}$ is completely different between the usual DMM and XLBOMD+DMM MD simulations. CONQUEST can also perform NVT simulations using the SVR thermostat\cite{89}, which is extremely efficient and provides excellent conservation of the constant of motion, as described in Sec. A 2 d.

Since the stress tensors can be also calculated using CONQUEST with the DMM method, as shown in Sec. III A, it is also possible to include the degrees of freedom of the unit cell for NPT simulations with a given pressure, using the Parrinello-Rahman equations of motion\cite{90}. CONQUEST uses the Martyna-Tobias-Tuckerman-Klein modification\cite{91}, coupling the constant pressure equations of motion to a Nosé-Hoover chain thermostat to recover the NPT ensemble. The integration scheme used in the NPT ensemble is also explained in Sec. A 2 b.

This scheme is tested on a bulk crystalline silicon system containing 1,000 atoms, and the $O(N)$ method for finding the electronic ground state, as shown in Fig. 13. A minimal basis set (SZ) was employed, together with a grid cutoff of 100 Ha and the PBE exchange-correlation functional. The extended-Lagrangian scheme described above was used, with a velocity Verlet integrator for the $X$ matrix and 5th order dissipation. The system was equilibrated using a Berendsen-type weak coupling thermostat and barostat, at a temperature of 300 K and pressure of 0.1 GPa. The cell volume was allowed to vary, but constrained to be cubic. An integration time step of 0.5 fs was used, with a 5th-order Yoshida-Suzuki integration scheme, and thermostat and barostat coupling time periods of 15 fs and 160 fs respectively. An ad hoc drag was applied to the barostat, reducing the velocities of the cell and its Nosé-Hoover thermostats by 5% each time-step. This was found to improve the stability, preventing the amplification of “ringing”
FIG. 11: Variation of $E_{BO}$ during the NVE MD simulation of crystalline Si, with $R_L = 13$ bohr (top), 16 bohr (middle), and 20 bohr (bottom). Reprinted with permission from J. Chem. Theor. Comput. 10, 5419 (2014). Copyright (2014) American Chemical Society.
procedure (one iteration was needed for $\varepsilon = 10^{-5}$; three iterations for $\varepsilon = 10^{-6}$), it breaks the time-reversal symmetry in the propagation of the electronic degrees of freedom. This broken time-reversibility of the electronic degrees of freedom behaves like a heat sink for the physical system, albeit controlled by the thermostatting algorithm.

In the conventional BOMD formalism, the potential energy rapidly decreased owing to the broken time symmetry (figure 1(c)); it resulted in a rapid decrease in the forces acting on atoms (not shown), which prohibits physically meaningful MD simulations. In the extended Lagrangian BOMD formalism, the potential energy kept physically relevant values (figure 1(c)). This is because the initial value used for the density matrix is obtained in a time-reversible way (see equation (19)).

To assess the feasibility and stability of our integration scheme, we performed NVT simulations on bulk silicon for 50 ps at three different temperatures: 300, 600, and 900 K. The time evolution of the conserved quantity and the potential energy for the simulations is shown in figure 2. To evaluate the energy fluctuations, we calculated the mean

FIG. 2: Time evolution of the conserved quantity (black) and the potential energy (green) obtained from NVT simulations on bulk silicon at 300 K (a), 600 K (b), and 900 K (c) in the framework of the extended Lagrangian BOMD formalism in combination with the DMM method.

FIG. 1: Comparison between conventional and extended Lagrangian BOMD simulations (crystalline silicon) in the canonical ensemble. (a) Time evolution of temperature during conventional (dashed red) and extended Lagrangian (black) BOMD simulations. (b) Time evolution of the extended energy during conventional (red: $\varepsilon = 10^{-5}$; blue $\varepsilon = 10^{-6}$) and extended Lagrangian (black) BOMD simulations. (c) Time evolution of the potential energy during conventional (red: $\varepsilon = 10^{-5}$; blue: $\varepsilon = 10^{-6}$) and extended Lagrangian (black) BOMD simulations.

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of the barostat, with a minimal impact on energy conservation.

It can be seen that in order to achieve good energy conservation, the L-tolerance lower than $10^{-5}$, with a significant drift in the conserved quantity occurring at looser tolerances; without the XL-BOMD scheme, the tolerance required would be much tighter. We note that the NPT integrator is considerably more sensitive to the time step due to coupling between the thermostat and barostat degrees of freedom, and that in this case a time step of 1.0 fs also resulted in a significant energy drift, though we are seeking to alleviate this sensitivity.
FIG. 13: NPT molecular dynamics on 1000 atom bulk silicon system. The three lines demonstrate the effect of varying the tolerance applied to the optimisation of the energy with respect to the density matrix during the $O(N)$ solution ("L-tolerance").

IV. PERFORMANCE

Here we demonstrate the performance of CONQUEST showing two examples, one for the MSSFs with diagonalisation and another for the $O(N)$ calculations.

A. Performance of MSSF

A recent study on the graphene/Rh(111) interface [10] showcases both the accuracy and efficiency of the MSSFs. This study used large basis sets of PAOs contracted to a minimal size using the MSSF formalism, i.e., 15 and 22 PAOs of rhodium and carbon atoms are contracted to 6 and 4 MSSFs, respectively. In Ref. [10] it was demonstrated that the PAOs and MSSFs show comparable accuracy with plane-waves for the electronic and atomic structure of graphene/Rh(111), as shown in Fig. 14. The accuracy of PAOs has been further investigated in Ref. [92].

This study then demonstrates the great reduction in computational effort by using MSSFs. Table III shows the computational times of a SCF step for the graphene/Rh(111) systems consisting of 1544 and 3088 atoms (shown in Fig.15). MSSF clearly require more computational time for matrix construction than the PAOs, which comes from the calculations of the linear combination coefficients, as explained in Sec. II. On the other hand, the time to diagonalise the electronic Hamiltonian is reduced significantly by using MSSFs, because diagonalisation time scales cubically with the number of support functions. For the 1,544-atom system, the total time, i.e., the summation time of matrix construction and diagonalisation, is reduced by a factor of $\approx 3$, from 1,256.9 seconds to 439.6 seconds. For the 3,088-atom systems, when using 108 processes, the total time is reduced by a factor of $\approx 18$, from 37,803.5 seconds to 2,156.3 seconds, which indicates that the use of MSSFs becomes more efficient as systems become larger. Comparing the time for the matrix construction for the 1,544 atoms with 432 MPI processes and that for the 3,088 atoms with 864 MPI processes, i.e., when both the system size and the number of processes are doubled, the times are very close to each other, which indicates the construction of the MSSFs is $O(N)$ and parallelized ideally.
FIG. 14: Density of states of m14 graphene/Rh(111) calculated with plane-waves (black), PAOs (green) and MSSFs (blue). The red line in the lower panel represents the difference between the DOS calculated with PAOs and MSSFs. Reproduced from Ref. [10] with permission. Copyright IOP Publishing. All rights reserved.

FIG. 15: Atomic structure of graphene/Rh(111) system (3,088 atoms).

B. Performance of $O(N)$ calculations on massively parallel computers

The performance of CONQUEST on the Japanese, Fujitsu-made K-computer is of real significance [93]. This computer once topped the TOP500 list [94] (June and November 2011) and 8 years later still features on the list in 20th place (November 2019) due to its impressive peak performance of 11,280.4 TFlops/s from its 705,024 physical cores. CONQUEST was found to display almost ideal parallel efficiency, as shown in Fig. 16, utilising up to 200,000 physical cores on systems up to 2 million atoms [6]. Using the crystalline silicon systems as a benchmark, it was demonstrated that in the $O(N)$ mode of operation that both strong scaling (the wall time for a fixed number of atoms, increasing the physical core count) and weak scaling (the wall time for a fixed number of atoms/physical core, increasing the number of atoms) performs very well. Specifically, for strong scaling it is found that performance is good should the number of atoms/core be $\geq 4$ but for weak scaling, the performance is close to perfect for any given number of atoms per core all they way up to 2,000,000 atoms [6]. Strong scaling has also been tested on the UK national supercomputer ARCHER, a Cray XC30 MPP system (Figure 16a). This demonstrates also the high efficiency of the code until about 4-atoms/core. When testing the scalability of the $O(N)$ algorithm itself (Figure 16b), we see that we achieve near-perfect linear scaling with system size even in the range of 2560-24565 atoms.

|                | 1544 atoms | 3088 atoms | 432 | 432 | 108 | 108 | 864 |
|----------------|------------|------------|-----|-----|-----|-----|-----|
| No. of MPI process |            |            |     |     |     |     |     |
| PAO MSSF | 64.3 | 400.4 | 155.7 | 1455.4 | 405.9 |
| diagonalisation | 1192.5 | 39.2 | 37647.7 | 700.8 | 165.9 |
| total$^a$ | 1256.9 | 439.6 | 37803.5 | 2156.3 | 571.8 |

$^a$Summation of matrix construction and diagonalisation.

TABLE III: Computational time for self-consistent-field calculation step with PAOs and MSSFs for graphene/Rh(111) performed on the supercomputer SGI ICE X in NIMS; data from Ref. [10].
V. APPLICATIONS

There are a multitude of applications to which CONQUEST has been applied. Studies using both exact diagonalisation (with and without the use of MSSFs) and the $O(N)$ mode of operation have all been exploited in large-scale structural relaxations and molecular dynamics. In the solid state, the code has been used to study the properties of nanowires [95, 96], Ge hut clusters on Si (001) surfaces [97], charge transport properties [98], interfaces between graphene with metals [10] and ferroelectric domain morphologies in perovskite oxide heterostructures. The code has also been applied to complex biological systems including hydrated DNA [99, 100] and gramicidin-A [101]. It is the purpose of this section to outline some of these studies and to suggest areas that the code could find new applications.
A. Nanoscale Ge/Si systems

One of the most important targets for large-scale DFT study is nano-structured semiconductors. Among them, Ge/Si systems have many attractive properties as a candidate for next-generation devices. Heteroepitaxy and strained growth in Ge/Si systems can be used as important techniques to control the structures and to explore new favorable properties.

CONQUEST was first applied to study the stability of Ge three-dimensional islands on Si substrate, called hut clusters, made of four equivalent Ge(105) facets. Experimentally, this 3D structure appears when the coverage of Ge atoms becomes large, after the formation of a two-dimensional (2D) structure with defects. Here, CONQUEST calculations were performed with LDA and non-selfconsistent mode using a minimal basis set (SZ), whose accuracy was thoroughly investigated for Ge/Si systems. The stability of the 3D structure in the heteroepitaxy systems is usually determined by the competition between the energy gain of the strain relief by the 3D structure and the energy loss due to the increase of the surface area by the formation of facets in the 3D structures. However, Ge/Si(001) system has a unique property that strained Ge(105) facet is more stable than strained Ge(001) surface even if the increase of the area is considered. Thus, in order to clarify the stability of the 3D structure, it is necessary to include the effects of the edges between the facets and the finite area of the actual facets. For this, we need to treat the actual size of the hut clusters with the Si substrate. Usual DFT methods cannot treat the 3D structure having the similar size with experiments, but it is possible using CONQUEST with structure optimization. In the early study with CONQUEST, the total energy having the same coverage of Ge atoms were compared between the 2D and 3D structures and it was found that 3D structure becomes more stable when the coverage of Ge is larger than 2.7 monolayers. This is close to the minimum coverage showing the transition from 2D to 3D growth in experiments, supporting the high accuracy of the present DFT method.

Further studies considered the stability of a single Ge dimer adsorbed at various sites on the facets. This study aimed to clarify the initial process during the formation of a new facet layer. Experimentally, it is reported that elongated hut clusters tend to grow, under some specific growth condition, by increasing the length of the longer side while keeping the width (shorter side) unchanged. The detailed mechanism underlying the growth of new facet layers is extremely difficult to obtain from experiments, since the complete facet is formed rapidly. We expect large-scale DFT calculations to play a significant role in clarifying these processes. By performing structure optimization for more than 100 different sites for the adsorption site of a single Ge dimer, as shown in Figure 17(c), it was suggested that the top or the edges of the facets are the most preferable sites, and higher positions are more stable than lower ones. This kind of study is now possible with CONQUEST using a parallel supercomputer. The largest system in this study contains about 200,000 atoms, whose structure is shown in Fig. 17(b). Together with the study of double and triple dimer adsorptions, it was concluded that the new layer of facet is very likely to grow from top to bottom.

Recently, CONQUEST was also applied to study Si/Ge and Ge/Si core-shell nanowires, using SZP basis set with self-consistency. Semiconductor nanowires are promising candidates for the next-generation vertical-type transistors, and have been extensively studied both experimentally and theoretically. The core-shell type nanowires have many interesting and attractive properties for next-generation electronics. All of these properties, however, will depend strongly on the size of core and shell. Using CONQUEST with the \( \mathcal{O}(N) \) method, strain distributions were calculated for nanowires with different sizes, shown in Fig. 18(a) up to experimentally accessible sizes. These are hexagonal Si/Ge core-shell nanowires along <110> direction, and with numbers of atoms ranging from 612 to 2,404. The strain distributions in the core region of these nanowires are shown in Fig. 18(b). We can see that the strain is distributed anisotropically, depending on the direction of the bonds, and that large variations of strains exist in the interface and surface regions.

The structure of a more circular Si/Ge core-shell nanowire was also investigated and its band structure were calculated with the Sakurai-Sugiura (SS) method explained in Sec. II D, using the optimized structure and the self-consistent charge density obtained by \( \mathcal{O}(N) \) calculations. The occupied eigenstates near the Fermi level were also calculated and are shown in Fig. 18(c). We can clearly see that the distribution is anisotropic and localized in the Ge-shell region. The effect of arsenic doping and its dependence on the doping sites in the Si nanowires were also recently reported, using a rather high quality basis set (TZTP), with MSSF method.

B. PbTiO\(_3\) films on SrTiO\(_3\) substrates

Studies of the perovskite oxides can also make good use of large-scale electronic structure calculations. CONQUEST can be used to study large supercells of technologically relevant piezoelectric alloys like PbZr\(_x\)Ti\(_{1-x}\)O\(_3\), where approximations designed to circumvent the need for large supercell calculations (like the virtual crystal approximation) are unable to quantify local structural distortions. The study of ferroelectric domains in thin films is another
problem requiring large-scale electronic structure calculations and accurate structural relaxations. Using the MSSF method and a large basis set of PAOs (DZDP), the nature of the ferroelectric flux closure domains in thin PbTiO$_3$ films on SrTiO$_3$ substrates was revealed. Using the initial geometry displayed in figure 19a, we were able to relax the system, to a stringent 0.01 eV/Å force tolerance using quenched molecular dynamics. The force reduction for the first 50 steps is shown in figure 19b. Figure 19c shows the local polarization vector field of a nine unit cell deep film. Such a field is calculated using the relaxed structure, the deviation in displacement from high symmetry sites and the Born effective charge tensors [114].

C. Biological systems

Complex biological systems are one of the most important targets for large scale DFT simulations [115]. Conquest has been already applied to several biological systems, such as hydrated DNA [99, 100], dihydrofolate reductase (DHFR) [116], and the gramicidin A (gA) ion channel [101] systems. In the study of gA system, the optimized structure of the isolated gA molecule, shown in Fig. 20(b), was first calculated for the two previously reported structural models, 1MAG and 1JNO. The electronic structure of the gA molecule was also analyzed and it was concluded that the side chains of gA does not affect the electrostatic potential in the pore of gA. This kind of study of the isolated gA molecule cannot explain the selectivity of the ion permeation in the gA system, and it suggests the importance to simulate the system in the channel environment. We should treat the gA molecule in lipid bilayers sandwiched by bulk water regions, as is shown in Fig. 20(a). Using Conquest, we can perform stable self-consistent DFT calculations of such a complex system made of 17,102 atoms, having a rather irregular charge distribution. Figure 20(c) shows that the density matrix minimization, for a SZP basis set, of this system is robust. It is important to note that, for stability in the self-consistency process, we need to update the charge density as well as the density matrix at each step in the calculation. More detailed information of this large-scale DFT study on the gA system will be reported in the future.

D. Large-scale MD simulations with Conquest

In Sec. VA we introduced energetically stable structures of the perfect epitaxial models for Si/Ge core-shell nanowires. However, it is also important to investigate defects or Si-Ge intermixing at the interface for the actual nanowires. In addition, we sometimes need to clarify the thermodynamic stability or the dynamical processes. In
such cases, molecular dynamics simulations based on DFT (DFT-MD) are useful and important. Using the XLBOMD + DMM method, explained in Sec. 111(c), we are now able to do practical and reliable self-consistent DFT-MD simulations of very large systems. The MD simulations in this section used SZ (NWs, SiO\textsubscript{2}) and SZP (hydrated DNA) basis sets.

For the Si/Ge core-shell nanowires with the perfect epitaxial case, DFT-MD simulations of the Si/Ge core-shell nanowires containing 4,788 atoms, whose diameter is 10.4 nm (Si core is 7.2 nm and the thickness of Ge shell part is 1.6 nm), at 900K were recently performed. The DFT-MD simulations confirmed that the structure is stable at least up to 10 pico seconds. This does not guarantee that the perfect epitaxial model is more stable than other structures containing defects or intermixing, but it indicates that the model is at least meta-stable. We also performed the DFT-MD simulations of Si/Ge and Ge/Si core-shell nanowires at 3000K, whose snapshot structures are shown in Fig. 21(a) and (b). We observed that the Ge region melted first in both cases. As linear-scaling DFT-MD simulations on such large systems are now practical, we expect that they can be used to explore possible structures of various
FIG. 19: The results of structural relaxation calculations with Conquest. (a) The initial geometry used to study ferroelectric flux closure domains in PbTiO$_3$ films on SrTiO$_3$ substrates. This example shows a three unit cell deep film with domain period of six unit cells. (b) The evolution the magnitude of maximum force on any atom for the first 50 quenched molecular dynamics steps for three different film configurations. (c) The local polarisation vector field of a 9 unit cell deep PbTiO$_3$ film (2,088 atoms) on a SrTiO$_3$ substrate.

types of defects or intermixing effects at the Si/Ge interfaces by a local heating technique. Such study is now in progress. Furthermore, as we explained in Sec. (d), we can now perform DFT-MD simulations at a constant high temperature and a given high pressure. Structural properties of melt SiO$_2$ (Fig. 21(c)) are now investigated using Conquest.

Of course, complex biomolecules, such as DNA in water, are also an important target for large-scale DFT-MD studies using Conquest. It is noteworthy that free energy calculations based on the blue moon ensemble method are now available with Conquest. We expect a variety of dynamical processes or enzyme reactions in biological systems will be studied with Conquest in the future.

VI. CONCLUSIONS

We have summarised the principles behind the implementation of the Conquest code, which enables it to address large scale DFT simulations, up to around 10,000 atoms, with exact diagonalisation, and significantly larger systems, at least up to millions of atoms, using linear scaling DFT. We showed how support functions can be represented in three ways, leading to a powerful approach for representing the density matrix. We also gave details on approaches to find the electronic structure of large systems, even with linear scaling, and indicated how hybrid DFT methods can be extended to extremely large systems.

We gave details of atomic movement, particularly molecular dynamics, and how the implementation and performance is affected by the use of linear scaling methods. We demonstrated that accurate, linear scaling MD is feasible with reasonable computational time, for standard ensembles (NVE, NVT and NPT, though care is needed with the calculation of stress and linear scaling). We then showed the performance of the MSSF approach, and how it opens up the possibility of exact simulations with many thousands of atoms. We also investigated the parallel performance of the code, both with MSSF and linear scaling, finding excellent performance including perfect scaling for certain
The authors would like to express their gratitude to all the developers and beta testers of Conquest who have contributed to the code over the years. In particular, Professor Mike Gillan initiated and oversaw the development and implementation for many years, and his input was invaluable. We also acknowledge, in alphabetical order, Michiaki Arita, Veronika Brazdova, Rathin Choudhury, Chris Goringe, Eduardo Hernandez, Chathurangi Kumarasinghe, Conn O’Rourke, Alex Sena, Kane Shenton, Umberto Terranova, Milica Todorovic, Lianheng Tong, and Antonio Torralba.

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FIG. 21: Snapshot structures for (a) Ge/Si core-shell and (b) Si/Ge core-shell nanowires at 3000K, (c) melting SiO$_2$ at 3000K and 10GPa. (d) hydrated DNA system (details of the simulation are found in Ref. 100).
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Appendix A: Further details of MD implementation

Here, we explain the details of the integration scheme used in the molecular dynamics, since it is important for the actual implementation, and related to the stability of the molecular dynamics.

1. Microcanonical ensemble

The microcanonical ensemble is generated simply by solving Hamilton's equation of motion for the Hamiltonian,
\[ H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(r_i), \quad (A1) \]

resulting in the following equations of motion:

\[ \dot{r}_i = \frac{p_i}{m_i}, \quad (A2) \]
\[ \dot{p}_i = \frac{\partial U(r_i)}{\partial r_i} = F_i, \quad (A3) \]

These equations are integrated using the velocity Verlet algorithm.

### 2. Non-Hamiltonian molecular dynamics

Hamiltonian dynamics describe systems that are isolated from their surroundings, and in order to generate the canonical and isobaric-isothermal ensembles, the system must be coupled to an external bath (heat for the former and heat and stress in the case of the latter). In the extended system approach, a set of non-Hamiltonian equations of motion including degrees of freedom for a thermostat and/or barostat are posited, and shown to generate the correct statistical ensemble post hoc.

#### a. Canonical (NVT) ensemble

The Nosé-Hoover Hamiltonian\[^{[117, 118]}\] for the canonical ensemble can be written,

\[ H = \sum_i \frac{1}{2} m_i s^2 \dot{r}_i^2 + U(r_i) + \frac{1}{2} Q s^2 - (n_f + 1) k_B T \ln s, \quad (A4) \]

where \( r_i \) and \( \dot{r}_i \) are respectively the position and velocity of particle \( i \), \( U \) is the potential energy (in this case the DFT total energy), \( s \) is a dimensionless quantity that can be interpreted post hoc as a time step scaling factor, \( Q \) is the fictitious mass of the heat bath and \( n_f \) is the number of ionic degrees of freedom. Hamilton’s equations of motion can then be solved to generate the Nosé-Hoover equations of motion. However, Martyna et al. demonstrate that this method does not generate an ergodic trajectory, and propose an alternative formulation with a chain of \( M \) coupled heat thermostats of mass \( Q_k \), each with “position” \( \eta_k \) and conjugate momentum \( p_{\eta_k} \[^{[119]}\] , resulting in the following equations of motion.

\[ \dot{r}_i = \frac{p_i}{m_i}, \quad (A5) \]
\[ \dot{p}_i = -\frac{\partial U(r)}{\partial r_i} - \frac{p_m}{Q_1} p_i \quad (A6) \]
\[ \dot{\eta}_k = \frac{p_{\eta_k}}{Q_k} \quad (A7) \]
\[ \dot{p}_{\eta_k} = \left( \sum_{i=1}^{N} \frac{p_i}{m_i} - n_f k_B T \right) - \frac{p_{\eta_k-1}}{Q_{\eta_k-1}} p_{\eta_k} \quad (A8) \]
\[ \dot{p}_{\eta_k} = \left( \frac{p_{\eta_k-1}^2}{Q_{\eta_k-1}} - k_B T \right) - \frac{p_{\eta_k+1}}{Q_{\eta_k+1}} p_{\eta_k} \quad (A9) \]
\[ \dot{p}_{\eta_M} = \left( \frac{p_{\eta_{M-1}}^2}{Q_{\eta_{M-1}}} - k_B T \right) \quad (A10) \]

These equations are integrated by constructing an appropriate Liouvillian and translated into an algorithm via the Trotter-Suzuki expansion, as described in Hirakawa et al.\[^{[88]}\].
b. Isobaric-isothermal (NPT) ensemble

The Parrinello-Rahman equations of motion [90] extend the constant volume equations of motion to include the degrees of freedom of the unit cell via the extended system approach. CONQUEST uses the Martyna-Tobias-Tuckerman-Klein modification [91], coupling the constant pressure equations of motion to a Nosé-Hoover chain thermostat to recover the NPT ensemble. For an cell unconstrained unit cell, the equation of motion are,

\[
\dot{r}_i = \frac{p_i}{m_i} + \frac{p_g}{W_g} r_i \tag{A11}
\]

\[
\dot{p}_i = F_i - \frac{p_g}{W_g} p_i - \left( \frac{1}{N_f} \right) \frac{\text{Tr}[p_g]}{W_g} r_i - \frac{p_\xi}{Q} p_i \tag{A12}
\]

\[
\dot{h} = \frac{p_g h}{W_g} \tag{A13}
\]

\[
\dot{p}_g = V(P_{\text{int}} - P_{\text{ext}}) + \left[ \frac{1}{N_f} \sum_{i=1}^{N} \frac{p_i^2}{m_i} \right] I - \frac{p_\xi}{Q} p_g \tag{A14}
\]

\[
\dot{\xi} = \frac{p_\xi}{Q} \tag{A15}
\]

\[
\dot{p}_g = \sum_{i=1}^{N} \frac{p_i^2}{m_i} + \frac{1}{W_g} \text{Tr}[p_g^T p_g] - (N_f + d^2)kT, \tag{A16}
\]

where \(r_i, p_i\) and \(m_i\) are respectively the position, momentum and mass of particle \(i\), \(\xi, p_\xi\) and \(Q\) are the position, momentum and mass of the thermostat and \(h, p_g\) and \(W_g\) are the matrix of lattice vectors, their velocities and the barostat mass. For simplicity, only a single Nosé-Hoover thermostat is included, but in CONQUEST a Nosé-Hoover chain is used. The Liouvillian is constructed, and the integrator constructed using the splitting of Shinoda et al [120],

\[
iL = iL_r + iL_h + iL_v + iL_{\text{bath}}, \tag{A17}
\]

which can be further decomposed,

\[
iL_{\text{bath}} = iL_{\text{box}} + iL_{\text{particles}} \tag{A18}
\]

\[
iL_{\text{box}} = iL_{v\text{box}} + iL_\xi + iL_{v_\xi}, + iL_{v_\xi k} + iL_{v_\xi M} \tag{A19}
\]

\[
iL_{\text{particles}} = iL_{v\text{part}} + iL_\xi + iL_{v_\xi}, + iL_{v_\xi k} + iL_{v_\xi M} \tag{A20}
\]

Then, using Liouville’s theorem, we have,
\[ iL_r = \sum_{i=1}^{N} [v_i + v_gr_i] \cdot \nabla r_i \quad \text{(A21)} \]
\[ iL_h = \sum_{\alpha,\beta} v_{g,\alpha\beta} h_{\alpha\beta} \frac{\partial}{\partial h_{\alpha\beta}} \quad \text{(A22)} \]
\[ iL_v = \sum_{i=1}^{N} \left( \frac{\mathbf{F}_i}{m_i} \right) \cdot \nabla v_i \quad \text{(A23)} \]
\[ iL_{\text{bath}} = iL_{v_{\text{part}}} + iL_{v_{\text{box}}} + iL_{v_{\xi}} + iL_{v_{\xi_k}} + iL_{v_{\xi_M}} \quad \text{(A24)} \]

In this instance, we use \( M \) Nosé-Hoover heat baths. The equations of motion can then be expanded via the Trotter-Suzuki identity, and directly translated into an algorithm.

\[ e^{iL \Delta t} = e^{iL_{\text{bath}} \Delta t} e^{iL_r \Delta t} e^{iL_h \Delta t} e^{iL_v \Delta t} e^{iL_{\text{bath}} \Delta t}. \quad \text{(A25)} \]

This integrator is tested on a bulk crystalline silicon system, as explained in Sec. III C.

c. Weak-coupling thermostat and barostat

The Berendsen weak coupling method [122] involves global coupling to a pressure and/or heat bath via a Langevin-type equation of motion with a global friction constant. In the case of the thermostat, the ionic velocities are rescaled by a factor \( \lambda \), which is scaled towards the target temperature \( T_0 \) by the coupling frequency \( 1/\tau_T \).

\[ \lambda = \left[ 1 + \frac{\Delta t}{\tau_T} \left( \frac{T_0}{T} - 1 \right) \right]^{\frac{1}{2}}. \quad \text{(A26)} \]

Similarly, for the barostat, the cell is rescaled by the matrix \( \mu \), which is scaled towards a target pressure tensor \( \mathbf{P}_0 \) by the pressure coupling frequency \( 1/\tau_P \) and the estimated bulk modulus \( \beta \).

\[ \mu = \mathbf{I} - \frac{\beta \Delta t}{3 \tau_P} (\mathbf{P}_0 - \mathbf{P}). \quad \text{(A27)} \]

While trivial to implement, weak coupling will not generate the correct canonical or isobaric-isothermal velocity distribution, and the thermostat has the pathological effect of systematically transferring energy to the most slowly changing degrees of freedom (the “flying ice cube” effect). However, it may be useful for equilibration.
d. Stochastic velocity rescaling

Stochastic velocity rescaling \cite{121} is essentially a modification of the weak coupling method that does not suffer from the flying ice cube effect. A correctly constructed random force is added to enforce the correct NVT (or NPT) phase space distribution. The kinetic energy is rescaled such that the change in kinetic energy between ionic steps is,

\[
dK = (\bar{K} - K) \frac{dt}{\tau} + 2 \sqrt{\frac{\bar{K} \bar{K}}{N_f} dW},
\]  

(A28)

where \(\bar{K}\) is the target kinetic energy (i.e. heat bath temperature), \(dt\) is the time step, \(\tau\) is the time scale of the thermostat, \(N_f\) is the number of degrees of freedom and \(dW\) is a Wiener process. In practice, the particle velocities are resecaled by a factor \(\alpha\), defined as,

\[
\alpha^2 = e^{-\Delta t / \tau} + \frac{\bar{K}}{N_f K} \left( 1 - e^{-\Delta t / \tau} \right) \left( R_1^2 + \sum_{i=2}^{N_f} R_i^2 \right) + 2e^{-\Delta t / 2\tau} \sqrt{\frac{\bar{K}}{N_f K} \left( 1 - e^{-\Delta t / \tau} \right) R_1},
\]  

(A29)

where \(R_i\) is a set of \(N_f\) normally distributed random numbers with unitary variance. This thermostat can be used in NPT dynamics \cite{89} by barostating the system via the Parrinello-Rahman method, but with additional \(R_i\)'s for the cell degrees of freedom, thermostating the cell velocities as well as the ionic velocities.