Removing pseudo-linear dependence in Gaussian basis set calculations on crystalline systems with the CRYSTAL code

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Abstract

We have implemented a full projector method in the CRYSTAL code. We demonstrate the new method's ability to converge calculations for a metal (Li), insulator (LiF), molecular crystal (NH_3) and a low band gap semiconductor (Ge) with the `DEF2-TZVP` basis for a range of lattice parameters and projector cutoff values.

1 Introduction

In Hartree-Fock theory [1] the electronic ground state is found by minimising the total energy of the system with respect to a set of N normalised spin orbitals ψ_i,

$$E =< \psi_i H \psi_i >$$

The Hamiltonian, H, is composed of one-electron terms and two-electron (Coulomb and Fock-exchange) terms,

$$H = \sum_i h_i + \frac{1}{2}\sum_{i \neq j} g_{ij}$$

where

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha}^{N} \frac{Z_\alpha}{|\vec{r_i} - \vec{R_i}|}$$

and

$$g_{ij} = \sum_{i \neq j} \frac{1}{|\vec{r_i} - \vec{r_j}|}$$

in which $\vec{r_i}$ and $\vec{R_\alpha}$ represent electronic and nuclear coordinates respectively (atomic units are used throughout). This generates a set of N equations, one for each orbital, which are solved using a self consistent field (SCF) procedure to find the ground state orbitals, eigenvalues (one-particle energies) and the total energy. The same approach can be extended to density functional theory (DFT). In this case, the Fock-exchange component originating in the electron-electron repulsion terms g_{ij} from the antisymmetry condition imposed by the Hartree-Fock wave-function is replaced by a local exchange-correlation (xc) term.

In the Gaussian basis set formalism implemented in CRYSTAL [2] [3], all one- and two-electron terms are computed analytically, with the exception of the xc term, which is estimated by quadrature on a grid. The xc is, in general, unknown, and needs to be approximated. Several xc approximations are available in CRYSTAL, and the code is particularly well optimised to treat hybrid xc terms (e.g. B3LYP, PBE0, double and range separated hybrids) with extremely high efficiency in periodic systems. This unique capability is virtually unparalleled by any other currently available first-principles software for solid state calculations.

For a periodic system, the one-particle orbitals (crystalline orbitals) are labelled by a crystal quasi-momentum index $\vec{k}$ representing the reciprocal-space dispersion of the orbital and, in the formalism implemented in CRYSTAL, they are expressed as linear combinations of atom centred atomic orbitals (AOs) $\phi(\vec{r})$,

$$\psi_i(\vec{r};\vec{k}) = \sum_{\mu} a_{\mu,i}(\vec{k}) \sum_{g} \phi_\mu(\vec{r} - \vec{A_\mu} - \vec{g}) e^{i\vec{k}.\vec{g}}$$

where $\vec{A_\mu}$ denotes the coordinate of a nucleus in a reference cell in the periodic lattice on which the orbital ϕ_μ is centred, $\vec{g}$ are direct space lattice vectors and $a_{\mu,i}(\vec{k})$ are the expansion coefficients of the crystalline orbitals in the AO basis, which are determined by solving the SCF equations. Each AO is expressed as a linear combination of individually normalised Gaussian type functions (GTFs) $G(\alpha_j; \vec{r} - \vec{A_\mu} - \vec{g})$ of particular angular symmetry (s, p, d, f, etc), with fixed coefficients d_j and exponents α_j defining their radial dependence:

$$\phi(\vec{r} - \vec{A_\mu} - \vec{g}) = \sum_{j}^{n_G} d_j G(\alpha_j; \vec{r} - \vec{A_\mu} - \vec{g})$$

The collection of all atomic orbitals is referred to as the basis set.

For a particular Hamiltonian (Hartree-Fock, DFT, etc.) the coefficients $a_{\mu,i}(\vec{k})$ are determined by solving a k-dependent Roothan-Hall like equation (RHLE)

$$H(\vec{k})A(\vec{k}) = S(\vec{k})A(\vec{k})E(\vec{k})$$

in which $S(\vec{k})$ is an overlap matrix (in a basis of linear combinations of AOs satisfying Bloch's theorem), $E(\vec{k})$ is a (diagonal) matrix of eigenvalues, corresponding to band energies, and

$$H(\vec{k}) = \sum_{\vec{g}} H^{\vec{g}} e^{i\vec{k}.\vec{g}}$$

is the Fourier transform of the Hamiltonian matrix in direct space. At the solution of the RHLE, the total energy is given by

$$E_{tot} = \frac{1}{2} \sum_{ij} \sum_{\vec{g}} P_{ij}^{\vec{g}} H_{ij}^{\vec{g}}$$

where the direct-space Hamiltonian matrix elements represent the basis set representation of the one- and two-electron terms h_i and g_{ij} and the direct-space density matrix $P^{\vec{g}}$ is given by

$$P_{kl}^{\vec{g}} = 2 \int_{BZ} d\vec{k} e^{i\vec{k}.\vec{g}} \sum_{m} a_{k,m}^{\dagger}(\vec{k}) a_{l,m}(\vec{k}) \theta[\epsilon_F - \epsilon_m(\vec{k})]$$

where $a_{k,m}(\vec{k})$ are elements of the eigenvector matrix $A(\vec{k})$, θ is a step function, ϵ_F is the Fermi energy and ϵ_m is the m-th eigenvalue of the RHLE. The integral is restricted to the first Brillouin Zone (BZ).

The RHLE defines a generalised eigenvalue problem, which can be solved by diagonalising the associated eigenvalue equation (AEE)

$$H'(\vec{k})A'(\vec{k}) = A'(\vec{k})E(\vec{k})$$

with $H'(\vec{k}) = S^{-\frac{1}{2}}(\vec{k})H(\vec{k})S^{-\frac{1}{2}}(\vec{k})$ and $A'(\vec{k}) = S^{\frac{1}{2}}(\vec{k})A(\vec{k})$. The algorithm used in CRYSTAL to compute the ground state energy, along with a number of related properties, can then be summarised as follows.

1. Calculate analytically the one- and two-electron (Coulomb and exchange) terms in AO basis, to determine the Hamiltonian matrix elements $H_{ij}^{\vec{g}}$. If necessary, add the xc components obtained from quadrature.

2. Fourier transform the Hamiltonian to its reciprocal-pace representation $H(\vec{k})$.

3. Compute $S^{-\frac{1}{2}}(\vec{k})$ and solve the AEE by direct diagonalisation at each k-point in the BZ.

4. Calculate the Fermi energy, the new density matrix $P^{\vec{g}}$ and the new total energy.

5. Repeat steps 2-4. until convergence in the total energy.

One method to form $S^{-\frac{1}{2}}(\vec{k})$ is to diagonalise $S(\vec{k})$, take the inverse square root of each eigenvalue to form a diagonal matrix and to then *un-diagonale* by transforming back to the initial representation. $S(\vec{k})$ is Hermitian and positive definite and its square root is therefore well defined. However, there are cases in which some of the eigenvalues are almost vanishing. In this situation the calculation of $H'(\vec{k})$ involves scaling $H(\vec{k})$ with small eigenvalues of the order of 10^{-n}, with the consequent loss of $2n$ significant digits. The resulting numerical noise is amplified at each cycle of the SCF procedure, which leads to slow convergence or spurious energy oscillations. In practice, when some of the eigenvalues of S are of the order of 1×10^4, a double precision calculation is likely to suffer from numerical instability. This situation is referred to as basis set linear dependence, and it occurs when GTFs with very diffuse exponents α_j contribute to one or more AOs. The linear dependence problem is usually considered one of the main limitations of non-orthogonal (localised) basis set functions in electronic structure theory.

The problem of linear dependence can however be circumvented. After diagonalising the overlap matrix the N positive eigenvalues can be reordered in decreasing size. A cutoff can then be introduced (denoted by STOL in what follows) and the m lowest eigenvalues classified as too small and therefore to be associated with linear combinations of atomic orbitals that will cause numerical instabilities. The transformation matrix $S^{-\frac{1}{2}}(\vec{k})$ can then be truncated by eliminating the last m elements to obtain an N by $(N-m)$ rectangular matrix that can be used in Step 3 to obtain a Hamiltonian matrix defined in a space of $N-m$ transformed orthonormal basis functions. If the eliminated eigenvalues were exactly zero, this $N-m$ function set would span exactly the same space as the original basis set and no loss of accuracy is incurred. In general, however, eliminating finite eigenvalues will introduce an error in the total energy, density and ground state orbitals, and this error will need to be quantified empirically.

The work proposed is devoted to implementing a general method for eliminating linear dependence in calculations on extended crystalline systems, replicated parallel and data distributed parallel (MPP) versions of the CRYSTAL code. The aim of the work is to code a projector method that eliminates the numerical noise caused by linear dependence during the SCF. This will be done in two stages. First, we will implement a simple projector approach in which: (a) the matrix $S(\vec{k})$ is diagonalised; (b) columns of $S(\vec{k})$ corresponding to eigenvalues lower than a predefined threshold are set to zero; (c) $S^{-\frac{1}{2}}(\vec{k})$ is computed from the derived matrix at all cycles of the SCF. The size of all matrices will be left unchanged. This approach is guaranteed to remove linear dependence, but it suffers from a significant drop in performance caused but the loss of pre-conditioning.

In the second part of the work, we will implement a full projector approach, in which a new $N \times (N-m)$ matrix $S^{-\frac{1}{2}}(\vec{k})$ is built by reordering $S(\vec{k})$ and removing eigenvectors with eigenvalues below STOL. This approach will be extended from the sequential to the data-replicated and massively parallel version of the code.

2 Implementation

CRYSTAL assumes that the Hamiltonian and eigenvector matrices are the same size at every k point, where the size is the number of basis functions N. The main change in the code is to relax this asssumption, which requires an array to store the new size $N-m$ for each k point (`sdik_dims`). When a cutoff is specified in the user input, the overlap matrix created in the routine `SDIK` is diagonalised, truncated and the size is stored for each k. This size is then used in the routine `ADIK` which transforms the $N \times N$ Hamiltonian matrix in the basis function space to the $N-m \times N-m$ orthogonal space and then diagonalises the matrix. For the serial and data replicated codes the bloch functions are symmetry adapted so there are multiple matrices of different sizes at each k related to the irreducible representations of the space group each of which may be reduced in size. The m missing values in the N eigenvalues are filled with a large value which effectively excludes them from the Fermi energy search without needed to modify the `FERMI` subroutine. The routine `PDIG` which constructs the real space density from the eigenvectors only needs to be changed to read the correct size of matrix, as the truncated vectors are in the unoccupied space and don't contribute to the density.

The equivalent routines in the MPP code are init_k_space_evecs `adik` `mpp_pdig`. The original code also allocated ScaLapack descriptors in the `init_k_space`. The code to generate descriptors has been separated into a subroutine `gen_descriptors` and new routines to diagonalise the overlap matrix `sdik_diag` and map the truncated result into the new descriptor `map_sdik` have been added. The original k independent $N \times N$ descriptor has been replaced by descriptors for the initially constructed $N \times N$ Hamiltonian matrix, the $N \times (N-m)$ transformation/eigenvector matrix and the $(N-m) \times (N-m)$ transformed Hamiltonian which is diagonalised. These descriptors are all initialised to the $N \times N$ default and are unchanged unless a cutoff is specified in the user input. In the original code allocation of the eigenvector matrices was in `init_k_space`, this is now postponed until after the overlap matrix has been formed and its size identified.

For Coupled-Perturbed Hartree-Fock(CPHF) calculations there are changes to `SACOTOAO` which expands the symmetry adapted eigenvectors (in the non-MPP versions) into a single matrix at each k which is no longer symmetry adapted. This requires summing the sub-matrix sizes into a single value in `sdik_dims`. These values are then further mapped into sizes for the different k point grids due to different symmetries in each cartesian direction in the CPHF initialisation. Unlike the SCF code, CPHF also does matrix operations on the number of unoccupied states, requiring extra changes to `CP_PDIG` compared to `PDIG`

3 Using the Full projector method

The changes to CRYSTAL are controlled by a keyword, `OVERLAPTOL` which takes 2 parameters on the following input line. The first is a floating point number specifying the value of the eigenvalue below which states are removed and the second is an integer parameter from 1 to 3 controlling the verbosity of information on the eigenvalues and truncation at each k point (3 is most verbose).

When using the high quality quantum chemistry basis sets which contain diffuse guassians with the projector method it is important to make sure that the integral tolerances are high enough to remove negative eigenvalues from the overlap matrix, which should be positive definite. The program will generate warnings for any negative eigenvalues. Increasing the integral tolerances with the `TOLINTEG` keyword may also require increasing the size of real space lattice vector array with the `LATVEC` keyword. Tolerances > 15 attempt to sum values of the size of the machine double precision limit into elements of the overlap matrix that are of order 1.0 which is numerically unreliable.

At high integral tolerances it is also likely that the k point sampling will need to be increased for stable convergence (keyword `SHRINK`). If the sampling is too small then the integration over k to reconstruct the density may fail to sample to full region of real space over which the Hamiltonian is constructed.

Calculations with high quality basis sets are expensive. The main cost is in the two-electron integrals due to increased tolerances and the larger set of real space lattice vectors required by the diffuse Gaussian functions.

4 Full projector method tests

The inital bulk test cases specified in the work plan were a metal (Li), insulator (LiF), molecular crystal (NH_3), and a small gap semiconductor (Ge). The bulk results are compared using the Birch-Murnaghan equation of state fitting used in the deltacodes [6] project. These are extended to a 2D system (graphene).

In order to compare total energy calculations CRYSTAL requires the use of the `FIXINDEX` keyword. Combined with a common inital geometry this ensures the integral screening tables used are the same for each calculation, which avoids discontinuities in the total energy due to screening changes. The following calculations have

Table 1: Walltime (s) of 1 SCF cycle at the tolerances specified in the text on 1 core

Basis set	Li	LiF	NH_3	Ge	Graphene
POB-TZVP	84	190	246	204	40
DEF2-TZVP	591	19237	1320	1327	717
DEF2-QZVP	-	-	14167	-	-

Table 2: Smallest eigenvalue in overlap matrix

Basis set	Li	LiF	NH_3	Ge	Graphene
POB-TZVP	1.71×10^{-2}	4.10×10^{-4}	5.72×10^{-4}	1.74×10^{-3}	1.57×10^{-4}
DEF2-TZVP	2.90×10^{-11}	2.76×10^{-12}	2.05×10^{-4}	7.51×10^{-7}	8.99×10^{-11}
DEF2-QZVP	-	-	6.72×10^{-7}	-	-

been run with a reduced volume of 10% in the initial geometry to allow for an adequate sampling of the energy-volume relationship about the original lattice parameter. Once the geometry with the minimum volume has been found it is normal practice to run a new calculation at this optimal geometry. Since this geometry will be different to the one used with `FIXINDEX`, with different screening tables it may not converge. In order to test this we also run some of the test cases with different lattice parameters and without `FIXINDEX`.

Results using the projector cutoff are for the `DEF2-TZVP` [4] basis sets unless stated otherwise, with comparisons to the `POB-TZVP` [5] basis set. For each of the test cases we plot energy-volume curves using an energy relative to the minimum of the curve. This creates a common energy scale for the different basis sets and emphasizes the relative shape of the curves. The energy difference between each curve and the `DEF2-TZVP` calculation with a 1×10^{-4} cutoff are listed in tables for each test case. We also tabulate the states that remain after applying the projector cutoff and the results of the Birch-Murnaghan equation of state fitting.

4.1 Li

Using an initial lattice parameter of 3.509Å for the body-centred cubic structure, `TOLINTEG 12 12 12 18 60`, `SHRINK 48 192`, `PBE` xc functional, and `TOLDEE 7` produces the energy-volume results in figure 1. The reciprocal space sampling is converged to approximately $1\mu H$. The equation of state fit used the calculated values from -10% to -1% in 1% steps about the approximate minimum of -6% (-8% to +1% for POB-TZVP).

Figure 1: Li total energy vs Lattice Volume for various eigenvalue cutoffs

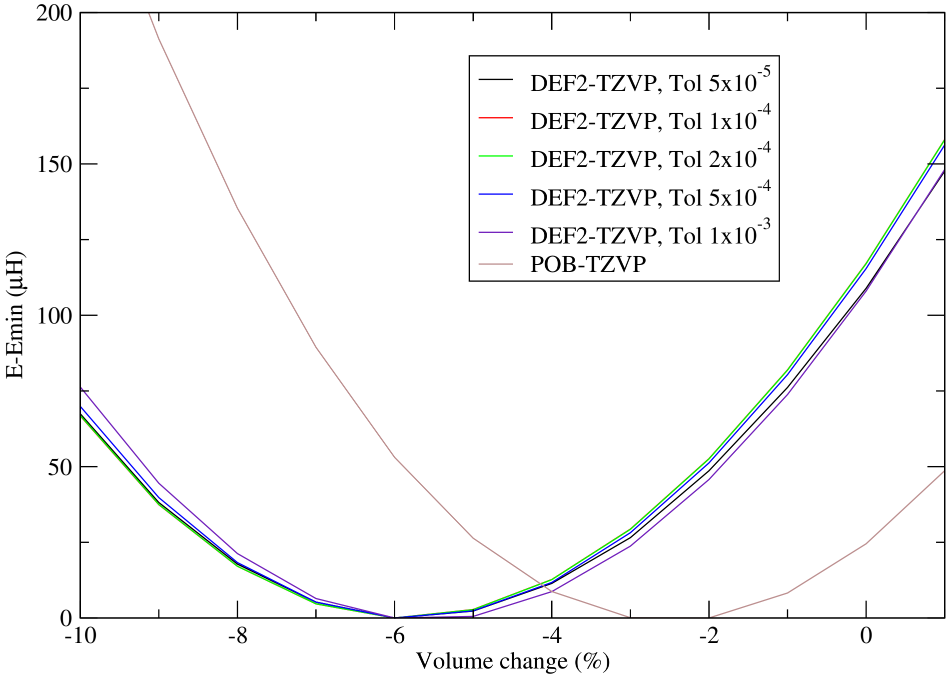


Table 3: Li total energy differences

Overlap Tol	$\delta E(\mu H)$	States per k point (basis size)
POB-TZVP	3644	7 (7)
1×10^{-3}	14	10-13 (14)
5×10^{-4}	2	10-13 (14)
2×10^{-4}	0	10-13 (14)
1×10^{-4}	0	10-13 (14)
5×10^{-5}	-1	10-13 (14)

Table 4: Li Equation of state

Overlap Tol	Min Volume (Å^3/atom)	Bulk Modulus	δ (meV/atom)	δ (%)
POB-TZVP	21.06525	16.65791	2.458	133.2
1×10^{-3}	20.39057	14.28276	0.184	12.6
5×10^{-4}	20.34735	14.21196	0.055	3.8
2×10^{-4}	20.33239	14.04692	0.003	0.2
1×10^{-4}	20.33172	14.03891	0	0
5×10^{-5}	20.34839	13.56175	0.071	5.0

Figure 2: LiF total energy vs Lattice Volume for various eigenvalue cutoffs

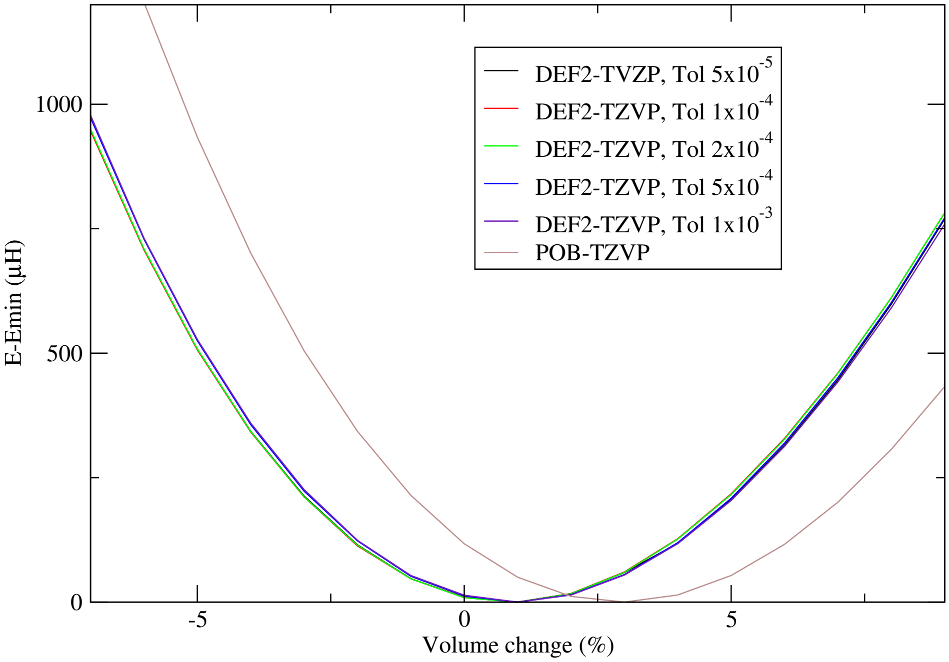


Table 5: LiF total energy differences

Overlap Tol	$\delta E(\mu H)$	States per k point (basis size)
POB-TZVP	5020	25 (25)
1×10^{-3}	93	40-43 (45)
5×10^{-4}	47	41-43 (45)
2×10^{-4}	16	41-43 (45)
1×10^{-4}	0	41-44 (45)
5×10^{-5}	-1	41-44 (45)

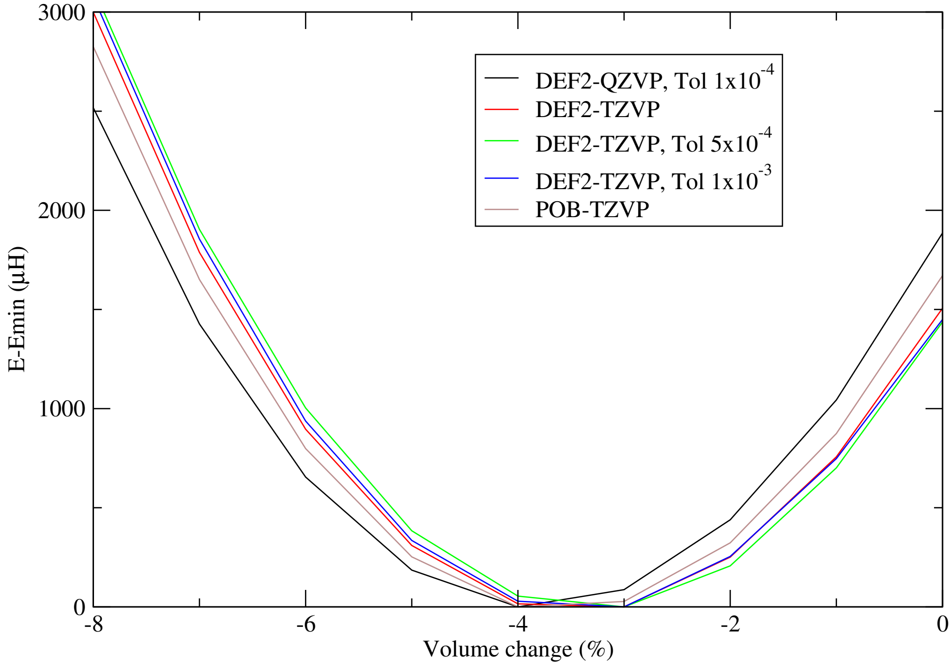
4.2 LiF

Using an initial lattice parmeter of 4.027Å, `TOLSHORT 10`, `SHRINK 32 64`, `B3LYP`, and `TOLDEE 7` produces figure 2. All the results except for the lowest cutoff also converge with `SHRINK 24 48`. All but the lowest cutoff also converge when run with lattice changes between -9% and +9% without `FIXINDEX`. 5. The equation of state results in table 6 are fitted to lattice changes from -7% to +9% about the apparent minimum of +1%.

Table 6: Delta code values for LiF

Overlap Tol	Min Volume (Å^3/atom)	Bulk Modulus	δ (meV/atom)	δ (%)
POB-TZVP	16.80577	71.30894	5.348	84.2
1×10^{-3}	16.48330	72.17029	0.318	5.3
5×10^{-4}	16.47900	72.71818	0.247	4.1
2×10^{-4}	16.46421	72.41129	0.024	0.4
1×10^{-4}	16.46280	72.27275	0	0
5×10^{-5}	16.47239	71.66546	0.133	2.2

Figure 3: NH_3 total energy vs Lattice Volume for various eigenvalue cutoffs



4.3 NH_3

Using the ICSD 638341 structure with lattice parameter 4.77Å based on a 10% lattice shrink there is no linear dependence with `DEF2-TZVP` at 2×10^{-4} and below, so a calculation is also run with `DEF2-QZVP` to properly test the new code (figure 3) The calculations use `TOLSHORT 8`, `SHRINK 8 16`, `B3LYP`, and `TOLDEE 7`. The equation of state is fitted from -7% to 0%, an equal number of 1% steps about the apparent minimum at -3%.

Table 7: NH_3 total energy differences

Overlap Tol	$\delta E(\mu H)$	States per k point (basis size)
POB-TZVP	17250	144 (144)
1×10^{-3}	583	188-190 (196)
5×10^{-4}	271	191-194 (196)
DEF2-TZVP	0	196 (196)
DEF2-QZVP 1×10^{-4}	-22550	530-532 (552)

Table 8: Delta code values for NH_3

Overlap Tol	Min Volume (Å^3/NH_3)	Bulk Modulus	δ (meV/NH_3)	δ (%)
POB-TZVP	26.15537	106.54191	0.977	7.0
1×10^{-3}	26.20284	104.74043	0.623	4.5
5×10^{-4}	26.23824	106.20512	0.457	3.3
DEF2-TZVP	26.19818	105.45877	0	0
DEF2-QZVP 1×10^{-4}	26.09333	105.10752	2.448	17.5

4.4 Ge

Using an initial lattice paramter of 5.762Å, `TOLSHORT 10`, `SHRINK 32 64`, `B3LYP`, and `TOLDEE 7` we get the results in figure 4. The higher cutoff values will also converge at reduced tolerances and k point sampling. The calculations also converge with lattice changes from -9% to +9% without `FIXINDEX`. The equation of state curve is fitted from -6% to +8% for `DEF2-TZVP` and from -9% to +6% for `POB-TZVP`.

Table 9: Ge total energy differences

Overlap Tol	$\delta E(\mu H)$	States per k point (basis size)
POB-TZVP	-1960	82 (82)
1×10^{-3}	362	90-93 (96)
5×10^{-4}	336	92-93 (96)
2×10^{-4}	189	92-93 (96)
1×10^{-4}	0	92-94 (96)
5×10^{-5}	-38	92-95 (96)

Figure 4: Ge total energy vs Lattice Volume for various eigenvalue cutoffs

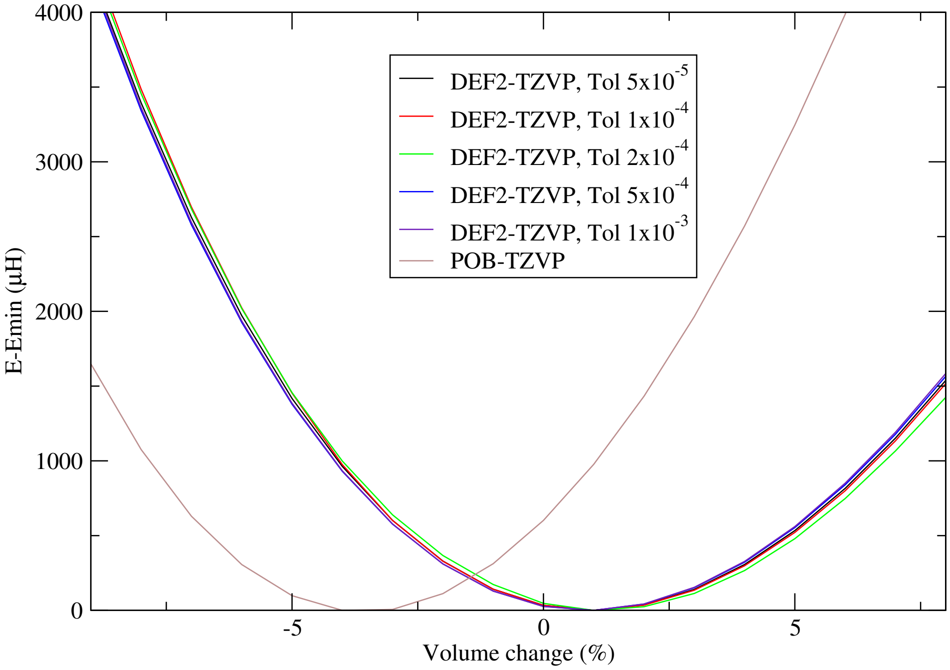


Table 10: Delta code values for Ge

Overlap Tol	Min Volume (Å^3/atom)	Bulk Modulus	δ (meV/atom)	δ (%)
POB-TZVP	23.06024	89.77262	18.477	157.0
1×10^{-3}	24.12175	65.64929	0.428	5.3
5×10^{-4}	24.12434	65.06626	0.410	5.1
2×10^{-4}	24.18526	63.34386	0.485	6.1
1×10^{-4}	24.14511	65.59355	0	0
5×10^{-5}	24.14425	65.15311	0.150	1.9

Figure 5: Graphene total energy vs Lattice Volume for various eigenvalue cutoffs

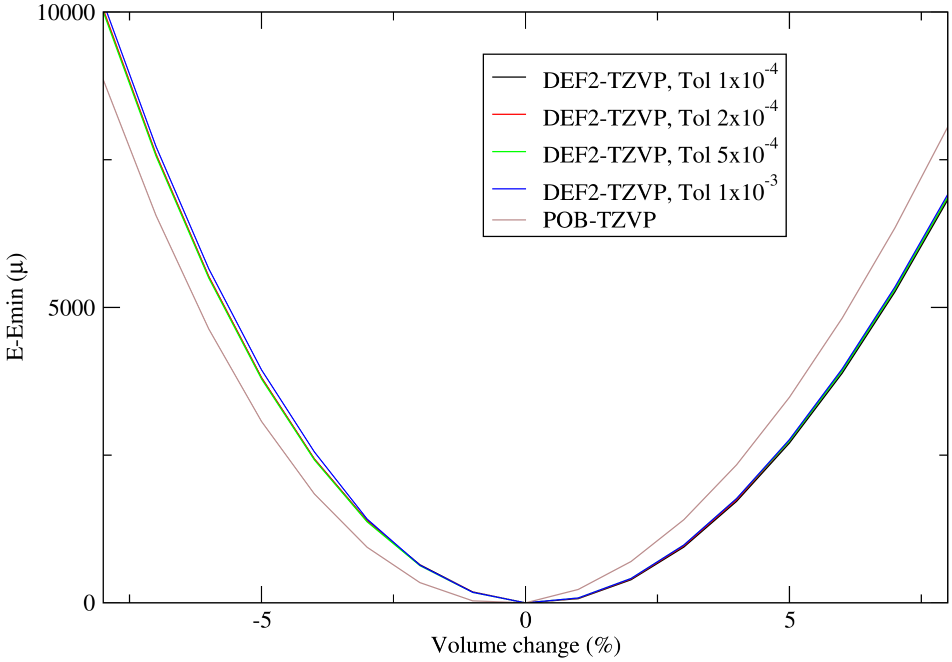


Table 11: Graphene total energy differences and minimum area

Overlap Tol	$\delta E(\mu H)$	States per k point (basis size)	Min Area (Å^2)
POB-TZVP	15360	36 (36)	5.220
1×10^{-3}	119	51-55 (62)	5.250
5×10^{-4}	115	51-56 (62)	5.249
2×10^{-4}	35	53-57 (62)	5.249
1×10^{-4}	-	55-57 (62)	5.250
5×10^{-5}	-48	56-58 (62)	-

4.5 Graphene

With `TOLSHORT 10`, `B3LYP`, `SHRINK 48 96` and `TOLDEE 7` we get the results in figure 5. The are problems with and without `FIXINDEX` at a -8% lattice change and a cutoff of 5×10^{-5}. All other cutoff values converge with and without `FIXINDEX`.

Table 12: `FMIXING` for covergence with `TOLSHORT` 8 vs overlap tolerance for Full projector

Lattice Volume (%)	1×10^{-4}	4×10^{-5}	2×10^{-5}	1.5×10^{-5}	1×10^{-5}
-10	50	50	50	50	50
-9	50	50	50	50	50
-8	50	50	50	50	50
-7	50	50	50	50	-
-6	50	50	50	50	-
-5	50	50	50	95	-
-4	50	50	50	50	-
-3	50	50	50	90	-
-2	50	50	50	70	50
-1	50	50	50	50	50
0	50	50	50	50	90
1	50	50	70	90	90
2	50	50	70	70	70
3	50	50	50	50	50
4	50	50	50	50	50
5	50	50	50	50	50

5 Simple vs Full projection - BCC Li

Running exactly the same inputs with the simple projector we find fewer converged results for a tolerance $<= 2 \times 10^{-5}$.

Table 13: `FMIXING` for covergence with `TOLSHORT` 8 vs overlap tolerance for simple projector

Lattice Volume (%)	1×10^{-4}	4×10^{-5}	2×10^{-5}	1.5×10^{-5}	1×10^{-5}
-10	50	50	50	50	50
-9	50	50	50	50	50
-8	50	50	50	50	50
-7	50	50	50	50	-
-6	50	50	50	-	-
-5	50	50	-	-	-
-4	50	50	50	-	-
-3	50	50	50	-	-
-2	50	50	50	-	-
-1	50	50	50	-	50
0	50	50	50	-	-
1	50	50	-	-	-
2	50	50	-	-	70
3	50	50	50	50	50
4	50	50	50	50	50
5	50	50	50	50	50

6 Conclusions and Further development

We have implemented the full projector method in CRYSTAL. This makes calculations with high quality Gaussian basis sets, which suffer from linear dependence problems in the original code, practical. Calculations can be reliably converged with a cutoff of 1×10^{-4} with minimal effect on the geometry.

These developments were begun in CRYSTAL14 v1.0.3. The current development version is a beta for CRYSTAL17 which is being tested and the new functionality is already frozen. It is unlikely therefore that these developments will be included in the first general release of CRYSTAL17 and Archer users requiring earlier access than this should contact us. The developments will need further testing with the new version, especially the CPHF which has added 'dynamic polarizabilty' options which will need to be modified to work with the eigenvector cutoff.

Other issues which should be investigated are

- A truncated SCF calculation needs to be tested with a properties calculation, which wasn't part of the work plan.
- The memory allocation for large k point grids in the Fermi energy calculation can become an issue and needs further investigation.
- The performance of the routines that reconstruct the density matrix can also become significant with large k point grids.

7 Acknowledgements

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References

[1] A. Szabo and N. S. Ostlund,Modern Quantum Chemistry, Dover Publications Inc., New York, 1989.

[2] R. Dovesi et al., CRYSTAL14: A Program for the Ab Initio Investigation of Crystalline Solids, Int. J. Quantum Chem. 114, 1287 (2014)

[3] http://www.crystal.unito.it

[4] F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design an assessment of accuracy. Phys. Chem. Chem. Phys. 7, 3297 (2005).

[5] Peintinger, M. F., Oliveira, D. V. and Bredow, T. (2013), Consistent Gaussian basis sets of triple-zeta valence with polarization quality for solid-state calculations. J. Comput. Chem., 34: 451459. doi: 10.1002/jcc.23153

[6] K. Lejaeghere et al, Reproducibility in density functional theory calculations of solids, Science 351 (6280), aad3000 (2016).