Materials modelling with CASTEP

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History and Prehistory

- Complete re-engineering of a new plane-wave code from scratch beginning 1999. (Original CASTEP code by Mike Payne/Accelrys reached end of life in 1990s.)
- Core “Developer Group” of P. Hasnip, S. Clark, M. Probert, C. Pickard, M. Segall, P. Lindan, (Payne) and in 2002, K. Refson and 2007, Jonathan Yates
- Commercialised by Accelrys and integrated into Materials Studio – flexible, easy to use GUI.
- Aim: build a flexible, well-engineered development platform for new physics using modular software practices and documented API specification.
- Parallel and HPC use built in from start.
- Release 1 in late 2001. Now at release 7.0.
- Comprehensive “Core” functionality with broad suite of capabilities for Structure, dynamics and spectroscopy.

Availability and Licenses

- Free of charge UK academic license through UK Car-Parrinello Consortium agreement. Forms and instructions at

  `http://ccpforge.cse.rl.ac.uk/projects/castep`

  N.B. Your research group must be licensed before access is granted to Archer version.
- European academic source code license €1800. Available
- from Accelrys inc. `http://www.accelrys.com`
- Commercial version available worldwide through Materials Studio

  prroduct, also from Accelrys inc. `http://www.accelrys.com`

Support and Resources

- Website: http://www.castep.org
- Mailing list CASTEP@jiscmail.ac.uk. sign up at http://www.jiscmail.org/CASTEP
- UK developer/support/download site http://ccpforge.cse.rl.ac.uk/projects/castep

CASTEP Training Workshop

- August 18-23, Oxford
- Focus on NMR, Vibrational spectroscopy and AIRSS
- Sponsored by CCP-NC. Fee £100
- Application deadline 31 May 2014
- http://www.castep.org/CASTEP/Workshop2014

Huge range of science

- Nanotechnology (CNT, QD)
- Minerals and materials
- High-pressure physics
- Catalysis
- Optical spectroscopy
- Liquids and solutions
- Molecular crystals
- Battery and fuel cell materials
- Surface physics/chemistry
- Defects/colour centres
- NMR Crystallography
- Ex-nihilo crystal structure prediction
- INS, IXS, spectroscopy
- Optical spectroscopy
- EELS
- XAS
- Dielectric materials

CASTEP core capabilities

- DFT – LDA, GGA (PW91, PBE, rPBE, BLYP, WC,..)
- LSDA and spin-polarized GGAs
- Hartree-Fock (expensive)
- Hybrid DFT (PBE0, B3LPY, sX-LDA)
- LDA+U, GGA+U
- Vanderbilt ultrasoft and norm-conserving pseudopotentials
- Built in “on-the-fly” pseudopotentials.
- Self-consistent pseudopotentials (no frozen-core approximation).
- PAW for (core-level) properties

Structure and Dynamics in CASTEP

- Geometry optimization with Cartesian BFGS or internal co-ordinates.
- Standard (BFGS) or loe-memory (L-BFGS) variants.
- Variable cell geometry optimization under pressure.
- Molecular dynamics in NVE, NVT, NPH ensembles,

  damped and langevin MD
- Path integral MD (PIMD) for nuclear quantum dynamics.
- Genetic algorithm structure searching
- LST/QST transition-state searching
- (L-BFGS, NEB and more under development)

Spectroscopy in CASTEP

CASTEP can perform wide variety of spectroscopic calculations

- *IR and raman spectroscopy (vibrational/phonon)*
- *INS and IXS spectroscopy (vibrational phonon)*
- *Conduction-band optical dielectric spectra (EELS etc)*
- *Core level spectroscopy (ELNES, XANES)*
- *NMR chemical shifts*

CASTEP has a variety of Hamiltonians and XC functionals

- *Pure local DFT (LDA,LSDA, PBE, RPBE, WC,...)*
- *Hybrid HF exchange methods (HF, Screened HF, PBE0, B3LYP*
- *Model methods (LDA+U)*
- *More under development.*

Recent developments

- DFT+D for dispersion forces (Tkatchenko/Scheffler and Grimme schemes)
- Finite-displacement phonons with hybrid functionals and LDA+U.
- L_BFGS for geometry optimisation of very large systems.
- Better adaptive parallelism.
- Band parallelism
- Optimised disk I/O for massively parallel case
- Optimised FFT parallelism for multicore clusters using system V shared memory
- Phonons for metallic systems using DFPT
- Electron localisation functions (ELF) and Hirshfeld charges
- Non-collinear magnetism
- Time-dependent DFT

Running CASTEP

Input and Output files

CASTEP I/O based on root name <seed> with suffixes

Input files

<seed>.cell	Input structure and structure-related quantities
<seed>.param	Parameters and options to control the calculation

Output files

<seed>.castep	Main human-readable output file
<seed>.bands	Electronic eigenvalues from SCF, Bandstructure, DOS
<seed>.orbitals	Electronic eigenvectors from DOS/Bandstructure
<seed>.den_fmt	Formatted electron density for analysis or visualization
<seed>.geom	Formatted optimization trajectory
<seed>.phonon	Phonon eigenvectors and eigenvalues
...	

Input & Output files

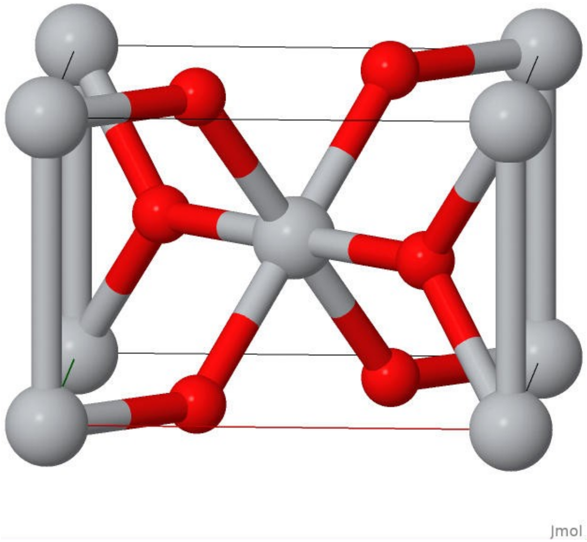
<seed>.check	Binary checkpoint file, containing all orbitals
<seed>.castep_bin	Binary checkpoint file, without orbitals

The .cell file (1)

```
%BLOCK lattice_cart
    4.5286520000    0.0000000000    0.0000000000
    0.0000000000    4.5286520000    0.0000000000
    0.0000000000    0.0000000000    3.0303690000
%ENDBLOCK lattice_cart

%BLOCK positions_frac
O           0.303615    0.303615    0.000000
O           0.696385    0.696385    0.000000
O           0.803615    0.196385    0.500000
O           0.196385    0.803615    0.500000
Ti          0.000000    0.000000    0.000000
Ti          0.500000    0.500000    0.500000
%ENDBLOCK positions_frac

symmetry_generate

kpoint_mp_grid 4 4 4
```

The .cell file

```
%BLOCK lattice_abc
    4.528652     4.528652     3.030369
    90.0         90.0         90.0
%ENDBLOCK lattice_abc

%BLOCK positions_abs
   ang
   O              1.3749666       1.3749666     -0.0000000
   O              3.1536853       3.1536853      0.0000000
   O              3.6392926       0.8893593      1.5151845
   O              0.8893593       3.6392926      1.5151845
   Ti            -0.0000000      -0.0000000     -0.0000000
   Ti             2.2643260       2.2643260      1.5151845
%ENDBLOCK positions_abs

kpoint_mp_spacing 0.05 1/bohr
```



Jmol can visualise .cell file directly: $ `jmol tio2.cell`
Use to check your input!

The .param file

```
task                   : geometryoptimisation
fix_occupancy          : true
opt_strategy_bias      : 3
xc_functional          : PBE
cut_off_energy         : 400 eV
grid_scale             : 1.75
fine_grid_scale        : 3.0
elec_method            : dm
mixing_scheme          : Pulay
mix_charge_amp         : 0.6
elec_energy_tol        : 1.0e-8 eV
energy_unit            : hartree
calculate_stress       : true
backup_interval        : 1800
```

Some useful options

On Archer, after “`module load castep.serial`”

```
castep.serial --version
```

```
castep.serial -dryrun quartz
```

Read input files, check syntax generate pseudopotentials and exit

```
castep.serial -help search kpoint
```

Print list of cell and param keywords matching “`kpoint`”

```
castep.serial -help xc_functional
```

Print brief description of “`xc_functional`” keyword

Preparing Input Structures

- Crystal structures – eg from ICSD cif2cell (http://sourceforge.net/projects/cif2cell/)
  - Supports many codes in addition to CASTEP
  - Advanced options for supercell generation/alloys
- GUI (Commercial) Accelrys – Materials Studio (http://www.accelrys.com/)
- GUI (Free) aten (http://www.projectaten.org/)
- GUI (Free) Avogadro (http://avogadro.cc/)

The .castep output file

Aims to be definitive record of run:

- Output optimised for human readability
- Version of CASTEP used
- Values of user-specified and default input parameters
  - everything necessary to re-create at later date.
- Progressive log of run details
- SCF and geometry convergence progress
- Final geometry
- Phonon frequencies, spectroscopic information
- Timing and memory information
- Can be directly read by Jmol for visualisation

```
+-------------------------------------------------+
 |                                                 |
 |      CCC   AA    SSS  TTTTT  EEEEE  PPPP        |
 |     C     A  A  S       T    E      P   P       |
 |     C     AAAA   SS     T    EEE    PPPP        |
 |     C     A  A     S    T    E      P           |
 |      CCC  A  A  SSS     T    EEEEE  P           |
 |                                                 |
 +-------------------------------------------------+
 |                                                 |
 | Welcome to Academic Release CASTEP version 7.02 |
 | Ab Initio Total Energy Program                  |
 |                                                 |
 | Authors:                                        |
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 |                                                 |
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 |     Agreement between the United Kingdom        |
 |     Car-Parrinello (UKCP) Consortium,           |
 |     Daresbury Laboratory and Accelrys, Inc.     |
 |                                                 |
 | Please cite                                     |
 |                                                 |
 |     "First principles methods using CASTEP"     |
 |                                                 |
 |         Zeitschrift fuer Kristallographie       |
 |           220(5-6) pp. 567-570 (2005)           |
 |                                                 |
 | S. J. Clark, M. D. Segall, C. J. Pickard,       |
 | P. J. Hasnip, M. J. Probert, K. Refson,         |
 | M. C. Payne                                     |
 |                                                 |
 |       in all publications arising from          |
 |              your use of CASTEP                 |
 |                                                 |
 +-------------------------------------------------+
```

```
 ***************************** General Parameters ******************************

 output verbosity                               : normal  (1)
 write checkpoint data to                       : Si2-geom.check
 type of calculation                            : geometry optimization
 stress calculation                             : off
 density difference calculation                 : off
...
 *********************** Exchange-Correlation Parameters ***********************

 using functional                               : Local Density Approximation
 Divergence correction                          : off
 DFT+D: Semi-empirical dispersion correction    : off
...
 ***************************** Basis Set Parameters *****************************

 basis set accuracy                             : FINE
 plane wave basis set cut-off                   :   108.8455   eV
 size of standard grid                          :     1.7500
 size of   fine   grid                          :     3.0000
 size of   fine   gmax                          :    16.0349   1/A
...
 **************************** Electronic Parameters ****************************

 number of  electrons                           :  8.000
 net charge of system                           :  0.000
 net spin   of system                           :  0.000
...
 ********************* Electronic Minimization Parameters **********************

 Method: Treating system as metallic with density mixing treatment of electrons,
         and number of  SD  steps               :          1
         and number of  CG  steps               :          4

 total energy / atom convergence tol.           : 0.1000E-04   eV
 eigen-energy convergence tolerance             : 0.1000E-05   eV
```

```
+---------------- MEMORY AND SCRATCH DISK ESTIMATES PER PROCESS --------------+
|                                                     Memory          Disk    |
| Model and support data                               15.5 MB         2.3 MB |
| Electronic energy minimisation requirements           0.7 MB         0.1 MB |
|                                               ----------------------------- |
| Approx. total storage required per process           16.2 MB         2.4 MB |
|                                                                             |
| Requirements will fluctuate during execution and may exceed these estimates |
+-----------------------------------------------------------------------------+
Calculating finite basis set correction with  3 cut-off energies.
Calculating total energy with cut-off of   98.846eV.
------------------------------------------------------------------------ <-- SCF
SCF loop      Energy           Fermi           Energy gain       Timer   <-- SCF
                               energy          per atom          (sec)   <-- SCF
------------------------------------------------------------------------ <-- SCF
Initial  -9.55691424E+000  0.00000000E+000                        10.98  <-- SCF
      1  -2.98642516E+002  8.50306978E+000   1.44542801E+002      11.13  <-- SCF
      2  -3.22530892E+002  5.98069026E+000   1.19441881E+001      11.23  <-- SCF
      3  -3.23350195E+002  5.58050764E+000   4.09651079E-001      11.31  <-- SCF
      4  -3.23130108E+002  5.80496213E+000  -1.10043094E-001      11.47  <-- SCF
      5  -3.23113582E+002  5.90225188E+000  -8.26313227E-003      11.64  <-- SCF
      6  -3.23113840E+002  5.90677071E+000   1.28878855E-004      11.80  <-- SCF
      7  -3.23113881E+002  5.91037067E+000   2.03552610E-005      11.95  <-- SCF
      8  -3.23113881E+002  5.91039673E+000   5.85819903E-008      12.10  <-- SCF
      9  -3.23113881E+002  5.91039217E+000   5.15119118E-009      12.25  <-- SCF
------------------------------------------------------------------------ <-- SCF

Final energy, E             =  -323.1138724516     eV
Final free energy (E-TS)    =  -323.1138806912     eV
(energies not corrected for finite basis set)

NB est. 0K energy (E-0.5TS)      =  -323.1138765714     eV
```

Checkpoint and Restart

In-run checkpointing enabled by parameter

```
    backup_interval 2600
```

Or

```
    num_backup_iter 5
```

Which will periodically write `<seed>.check`

Run can be continued by setting

```
   continuation : default
```

Or

```
  continuation : <seed>.check
```

In param file.

Allows continuations of geometry, MD, phonon calculations.

Bandstructure restart uses temporary mechanism and is
Under revision.

Pseudopotentials

General remarks on pseudopotentials

Pseudopotentials have acquired some mystique – even seen as a “black art”

Not so – they are theoretically well-founded and rigorous, BUT

- No easy physical picture as with atomistic potentials.
- Ab initio nature hidden away
- Too many different recipies for generating them
- Transferrability and accuracy can be systematically improved, but are not guaranteed by any procedure.
- Known pitfalls such as “ghost states” can occur unpredictably.
- Only trial-and-error generation testing can give accurate PSPs

Pseudopotential generation and testing requires expertise and patience – not for beginners.

On-the-fly (OTF) generation

Unique to CASTEP – built-in pseudopotential generation

1. Explicit specification

```
%BLOCK species_pot
Si   3|1.8|2|4|6|30:31:32
O    2|1.0|1.3|0.7|13|16|18|20:21(qc=7)
%ENDBLOCK species_pot
```

2. Built-in library

```
%BLOCK species_pot
%ENDBLOCK species_pot
```

Cutoff defaults embedded in string. Select by param keyword

```
    basis_precision : coarse/medium/fine
```

as alternative to

```
    cut_off_energy : 500 eV
```

Also need to choose size of second (fine) FFT grid for augmentation density in case of ultrasoft PPs.

Easiest way to choose is parameter

```
    fine_grid_scale : s
```

with scale-factor s usually in range 2-4. Unfortunately no automatic default (yet).

Pseudopotential files and libraries

Can also specify pseudopotentials saved in files

```
%BLOCK species_pot
Si   Si_00.usp
%ENDBLOCK species_pot
```

Recognised formats are

<name>.usp - CASTEP's own format. Used for legacy USPP library and for saving OTF potentials. Can contain USPP or NC.

<name>.recpot - Older format for norm-conserving (NC) only. Used for 1990S NC library and Opium-generated NC PSPs.

<name>.upf - The Quantum Espresso universal format. (Not available until CASTEP 8.0)

Set environment variable PSPOT_DIR to search directory file PSP files – no need to copy these around.

```
$ export PSPOT_DIR=/usr/local/share/pseudopotentials
```

Available Pseudopotential Libraries

OTF USP library (built in default).
All XC functionals. Comprehensive coverage of elements at
High accuracy. Includes PAW - suitable for NMR and EELS.

Vanderbilt USP library (1995-) `xx_00.usp`
LDA and PBE-GGA. Comprehensive coverage of periodic table. Mostly
reasonable accuracy with occasional exceptions (`Fe_00.usp`). Supplied along
with CASTEP (commercial and academic).

Accelrys OTF USP library (*otfg.cell*)
All XC functionals. Comprehensive coverage of elements at
Near all-electron accuracy. Suitable for NMR and EELS.

Rappe and Bennett library http://opium.sourceforge.net
Norm-conserving with DNL. Good accuracy. partial converage of elements.
LDA and PBE-GGA versions available.
.recpot version downloadable from http://ccpforge.cse.rl.ac.uk/gf/project/castep/

New norm-conserving library (2010-) `xx_OP_00PBE.recpot`
LDA and PBE-GGA. Sporadic converage of elements. Higher accuracy and
Transferrability. Supplied along with commercial and academic CASTEP.

Old Norm-conserving library (1990s) `xx_00.recpot`
LDA-only. Comprehensive coverage of periodic table (except lanthanides/actinides).
Moderate accuracy, with some poor, but well documented.
Supplied along with commercial and academic CASTEP.

Accuracy Benchmarks

Crystal structure of rutile TiO_2

	a/A	c/A	u
PW-LDA (OTF1)	4.550 (-0.18%)	2.919 (-0.03%)	0.3039
PW-LDA (OTF2)(SC)	4.549 (-0.20%)	2.919 (-0.03%)	0.3039
PW-LDA (00.usp)	4.551 (-0.15%)	2.921 (+0.03%)	0.3039
PW-LDA (VASP-PAW)	4.557 (-0.22%)	2.928 (+0.27%)	0.304
PW-LDA (Rappe-Bennett)	4.563 (+0.11%)	2.932 (+0.41%)	0.3040
PW-LDA (Old recpot)	4.596 (+0.84%)	2.984 (+2.19%)	0.3041
PW-LDA (New recpot)	4.526 (-0.70%)	2.908 (-0.41%)	0.3041
PW-LDA (TM)	4.536 (-0.48%)	2.915 (-0.17%)	0.304
FP-LAPW-LDA	4.558	2.920	0.3039
Expt	4.582 (+0.53%)	2.953 (+1.13%)	0.305

Electronic SCF

Electronic solvers in CASTEP

CASTEP has three SCF solvers

- Density-Mixing
  - all purpose for metals and insulators
  - Fastest but least robust
  - Prone to “charge sloshing” in long narrow simulation cells.
  - Non-variational – forces can be noisy
  - Default if `fix_occupancy = false`
- Allbands
  - Insulators only
  - Default if `fix_occupancy = true`
  - Usually robust unless system is really metallic.
  - Variational scheme so forces more accurate.
- Ensemble DFT (EDFT)
  - Use only for metals
  - Self-consistently updates occupancies as well as orbitals
  - Robust – rarely fails to converge
  - Very slow.

Can be explicitly chosen with param keyword `elec_method=dm/allbands/edft`

Metals and Insulators

Param file keyword to allow/forbid metallic behaviour is

```
fix_occupancy : true/false
```

Convergence failure or even false convergence possible if metallic system Treated as fixed occupancy.

N.B. `fix_occupancy : true` changes default solver from DM to allbands.

Use eigenvalue smearing scheme to accelerate k-point convergence in a metal

```
smearing_scheme : Gaussian/coldsmearing/...
```

Additional parameter controls degree of broadening applied

```
smearing_width : 0.2 eV
```

This is analogous to setting a high temperature for the electrons, and 0K results are only recovered in the w->0 limit.

Nonzero TS term in .castep output is sure sign of metallic occupancy.

```
Final energy, E               =  -3158.505634320     eV
Final free energy (E-TS)      =  -3158.663886719     eV
(energies not corrected for finite basis set)

NB est. 0K energy (E-0.5TS)       =  -3158.584760519     eV
```

Magnetism

Spin-polarisation activated by param keywords `spin=s` or `spin_polarised : true`

Use SPIN= modifier in .cell file to specify initial spin state (DM solver only)

```
%BLOCK POSITIONS_FRAC
  O  -0.25  -0.25  -0.25
  O   0.25   0.25   0.25
 Mn   0.00   0.00   0.00 SPIN=  2.0
 Mn   0.50   0.50   0.50 SPIN= -2.0
%ENDBLOCK POSITIONS_FRAC
```

N.B. Sum of SPIN= .cell file must be consistent with spin= in .param.

After SCF converged the final spin state is reported in .castep (antiferromagnetic)

```
  2*Integrated Spin Density    =    0.150754E-07
  2*Integrated |Spin Density| =     9.18570

Final energy, E              =  -6430.818475862     eV
```

Ferromagnetic

```
  2*Integrated Spin Density    =     4.89553
  2*Integrated |Spin Density| =     4.89568

Final energy, E              =  -3215.241900426     eV
```

SCF convergence failures

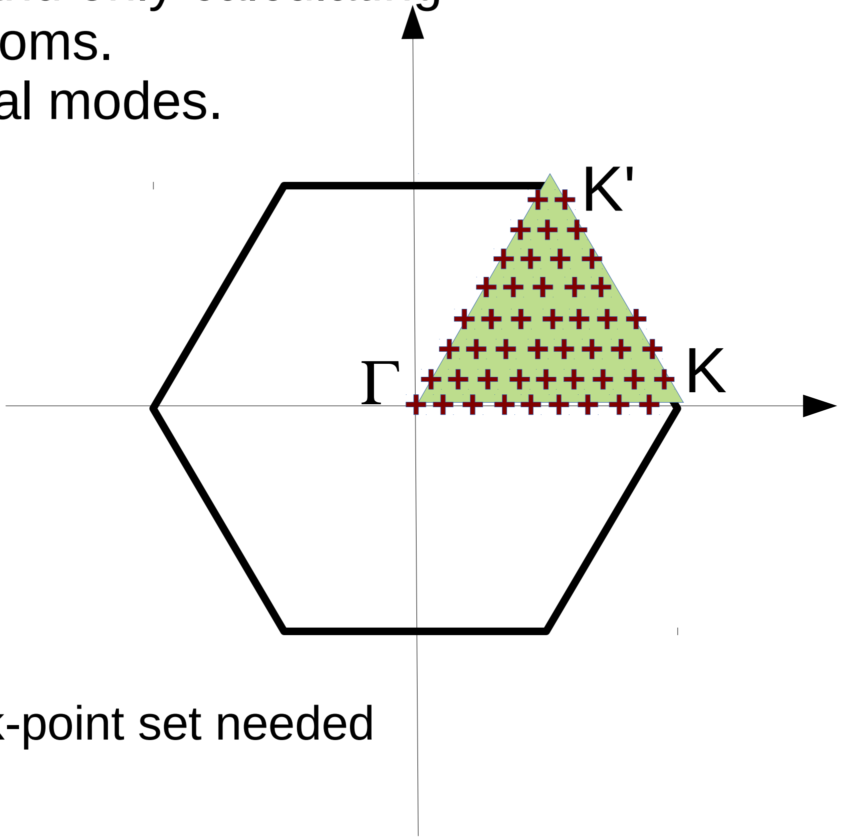
- Is there a mistake in the geometry violating the rules of chemical bonding?
- Are you treating as an insulator a system which is trying to be metallic.
- Are you treating a system trying to be magnetic as unpolarised?
- Have you broken the spin symmetry for a magnet?

- If using Broyden density mixing, try switching to Pulay and vice versa
- Try increasing mix_cut_off_energy, decreasing mixing parameters
- If all else fails, switch to EDFT

Symmetry

CASTEP uses crystallographic symmetry for

- SCF: Reduce memory and calculation by treating only part of k-point set within irreducible Brillouin zone (IBZ)
- Geometry: Constrain optimisation not to break symmetry
- Phonons: Reducing q-point grids to IBZ and only calculating Perturbations of inequivalent atoms.
- Phonons: Symmetry analysis of vibrational modes.



Example: graphite – 6-fold reduction in size of k-point set needed

Using Symmetry in CASTEP

Straightforward way is to use .cell file keywords

```
  SYMMETRY_GENERATE
 KPOINT_MP_GRID  : p  q  r
```

which automatically detects symmetry and generates reduced k-point mesh.

Alternatively,
cif2cell and Materials Studio generate explicit symmetry operations in .cell:

```
%BLOCK symmetry_ops
# Symm. op. 1       E
       1.000000000000000       0.000000000000000       0.000000000000000
       0.000000000000000       1.000000000000000       0.000000000000000
       0.000000000000000       0.000000000000000       1.000000000000000
       0.000000000000000       0.000000000000000       0.000000000000000
# Symm. op. 2       I
      -1.000000000000000       0.000000000000000       0.000000000000000
       0.000000000000000      -1.000000000000000       0.000000000000000
       0.000000000000000       0.000000000000000      -1.000000000000000
       0.000000000000000       0.000000000000000       0.000000000000000
# Symm. op. 3       c
       1.000000000000000       0.000000000000000       0.000000000000000
       0.000000000000000      -1.000000000000000       0.000000000000000
       0.000000000000000       0.000000000000000       1.000000000000000
       0.000000000000000       0.500000000000000       0.500000000000000
# Symm. op. 4     2_1
      -1.000000000000000       0.000000000000000       0.000000000000000
       0.000000000000000       1.000000000000000       0.000000000000000
       0.000000000000000       0.000000000000000      -1.000000000000000
       0.000000000000000       0.500000000000000       0.500000000000000
%ENDBLOCK symmetry_ops
```

Using symmetry in CASTEP (2)

- Symmetry analyser requires that crystal is oriented correctly w.r.t Cartesian axes.

- Good precision of atomic co-ordinates and cell vectors is vital for successful detection of symmetry. Otherwise CASTEP may abort with:

```
Error - symmetry operations do not form a group:
```

- Co-ordinate and cell vector precision can be sharpened up with cell keyword

```
SNAP_TO_SYMMETRY
```

- Precision used for symmetry detection may be specified using

```
SYMMETRY_TOL : 0.001 ang
```

  (But only in CASTEP 8.0 and later).

- Initial magnetic structure with `SPIN=` will lower detected symmetry.

Bandstructure and DOS

Bandstructure calculation

```
%BLOCK LATTICE_ABC
       3.24826       3.24826       5.2033
       90.0          90.0        120.0
%ENDBLOCK LATTICE_ABC

%BLOCK positions_frac
O           0.333333333333333       0.666666666666667       0.381840368591548
O          -0.333333333333333      -0.666666666666667       0.881840368591548
Zn          0.333333333333333       0.666666666666667       0.000759631408452
Zn         -0.333333333333333      -0.666666666666667       0.500759631408452
%ENDBLOCK positions_frac

kpoint_mp_grid 3 3 2

symmetry_generate

%BLOCK bs_kpoint_path
0.0 0.0 0.0
0.5 0.0 0.0
0.33333333333 0.33333333333  0.0
0.0 0.0 0.0
0.0 0.0 0.5
0.5 0.0 0.5
0.33333333333 0.33333333333  0.5
0.0 0.0 0.5
%ENDBLOCK bs_kpoint_path

bs_kpoint_path_spacing 0.05 1/ang
```

Plus `task: bandstructure` in .param

Easy visualisation

```
$ dispersion.pl -symmetry hexagonal -xg <seed>.bands
```

DOS calculation

```
%BLOCK LATTICE_ABC
       3.24826       3.24826       5.2033
       90.0          90.0        120.0
%ENDBLOCK LATTICE_ABC

%BLOCK positions_frac
O           0.333333333333333       0.666666666666667       0.381840368591548
O          -0.333333333333333      -0.666666666666667       0.881840368591548
Zn          0.333333333333333       0.666666666666667       0.000759631408452
Zn         -0.333333333333333      -0.666666666666667       0.500759631408452
%ENDBLOCK positions_frac

kpoint_mp_grid 3 3 2

symmetry_generate

bs_kpoint_mp_spacing 0.05 1/ang
```

Plus `task: bandstructure` in .param

Second set of k-points distinct from SCF
Only difference between bandstructure and DOS is choice of k-points

In both cases additional `<seed>.orbitals` file written containing orbitals at new set.

Easy visualisation $ `dos.pl -xg <seed>.bands`

Better DOS calculation

```
%BLOCK LATTICE_ABC
       3.24826       3.24826       5.2033
       90.0          90.0        120.0
%ENDBLOCK LATTICE_ABC

%BLOCK positions_frac
O           0.333333333333333       0.666666666666667       0.381840368591548
O          -0.333333333333333      -0.666666666666667       0.881840368591548
Zn          0.333333333333333       0.666666666666667       0.000759631408452
Zn         -0.333333333333333      -0.666666666666667       0.500759631408452
%ENDBLOCK positions_frac

kpoint_mp_grid 3 3 2

symmetry_generate

optics_kpoint_mp_spacing 0.05 1/ang
```

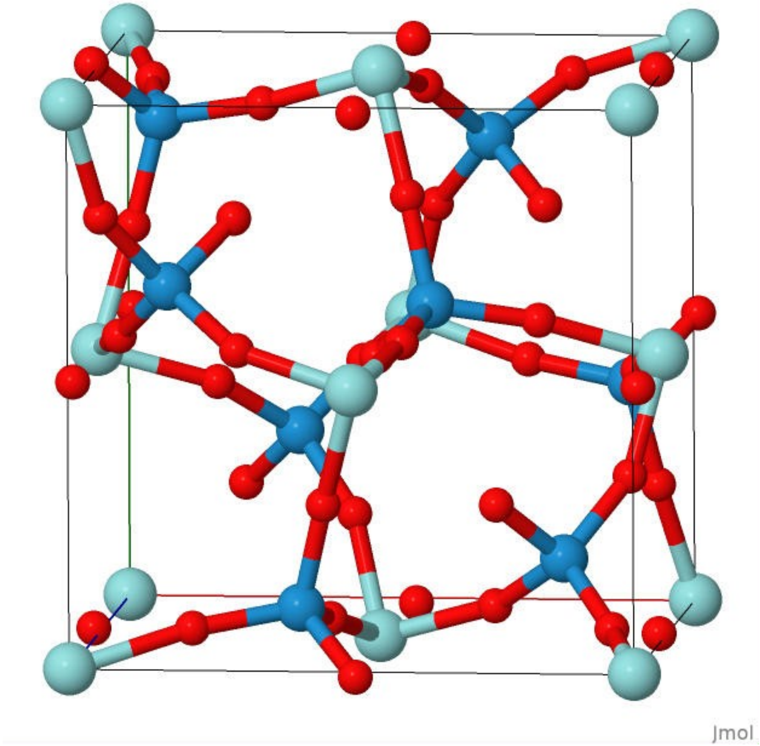
Plus `task: optics`
`pdos_calculate_weights: true`

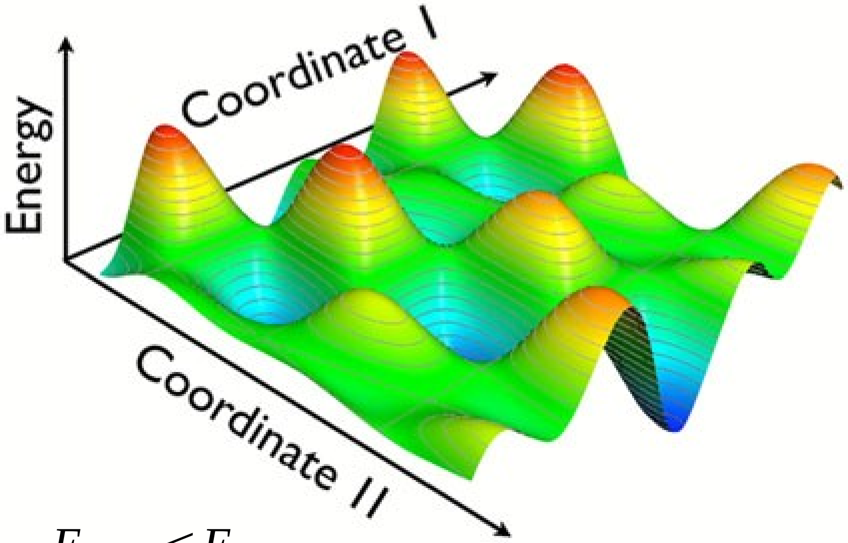
in .param. This also writes <seed>.cse_ome and <seed>.pdos_weights.
Only difference between bandstructure and DOS is choice of k-points

More sophisticated visualisation including partial DOS and more accurate Broadening using OPTADOS: http://www.optados.org.

Structure Optimzation

The Optimization Problem





$E_{global} \leq E_{local}$

$E(x1, y1, z1, \ldots) \leq E_0$

iterative downhill optimization methods can find local minima

Calculating Forces

Downhill optimizers require *gradients* $\nabla_i E\left(=-F_i\right)$

$$\frac{\partial\langle E\rangle}{\partial\lambda}=\langle\frac{\partial\Psi}{\partial\lambda}|\hat{H}|\Psi\rangle+\langle\Psi|\frac{\partial\hat{H}}{\partial\lambda}|\Psi\rangle+\langle\Psi|\hat{H}|\frac{\partial\Psi}{\partial\lambda}\rangle$$

$$=E\left\{\langle\frac{\partial\Psi}{\partial\lambda}|\Psi\rangle+\langle\Psi|\frac{\partial\Psi}{\partial\lambda}\rangle\right\}+\langle\Psi|\frac{\partial\hat{H}}{\partial\lambda}|\Psi\rangle$$

$$=E\frac{\partial\Psi}{\partial\lambda}\langle\Psi|\Psi\rangle+\langle\Psi|\frac{\partial\hat{H}}{\partial\lambda}|\Psi\rangle$$

$$=\langle\Psi|\frac{\partial\hat{H}}{\partial\lambda}|\Psi\rangle$$

- This result is the Hellman-Feynmann theorem
- N.B. Only correct for a complete, orthonormal basis set, *ie* plane-wave basis.
- For incomplete basis must retain all three terms
- If basis set moves with atoms – as in Gaussian basis - then additional terms appear in derivatives. These are known as Pulay forces.

Algorithms - BFGS

Based on Taylor expansion of energy about local minimum.

$$E(\boldsymbol{X}-\boldsymbol{X}_{\boldsymbol{min}})=E_0+\frac{1}{2}(\boldsymbol{X}-\boldsymbol{X}_{\boldsymbol{min}})\cdot\boldsymbol{A}\cdot(\boldsymbol{X}-\boldsymbol{X}_{\boldsymbol{min}})+O(\geq 3)$$

$$A_{\alpha\beta}=\frac{\partial^2 E}{\partial X_\alpha \partial X_\beta}$$

Hessian matrix $\boldsymbol{A}$ is unknown *a priori.*

BFGS algorithm iteratively steps $\boldsymbol{X}$ in downhill direction building approximation to $\boldsymbol{A}^{-1}$ as it goes.

$$\boldsymbol{X}_{\boldsymbol{i+1}}=\boldsymbol{X}_{\boldsymbol{i}}+\lambda\Delta\boldsymbol{X}_{\boldsymbol{i}} \quad \text{with} \quad \Delta\boldsymbol{X}_{\boldsymbol{i}}=\boldsymbol{A}^{\boldsymbol{-1}}\cdot\boldsymbol{F}_{\boldsymbol{i}}$$

Positions $\boldsymbol{X}$ and inverse Hessian $\boldsymbol{A}^{-1}$ are updated at each step.
Suitable step size λ is determined by a line search along fixed direction.

Underlying assumption is that energy hypersurface is *parabolic* near minimum.
BFGS is default geometry optimiser in CASTEP.

Algorithms (2) – L-BFGS

BFGS algorithm is currently default in CASTEP.

Requires storage of 3N x 3N inverse Hessian matrix.

For a 1000 atom system this requires 69MB memory just to store. As this is not distributed, this is 69MB per MPI process!

Newly implemented algorithm “low-memory” or L-BFGS.

Instead of storing entire $\boldsymbol{A}^{-1}$, only keep record of previous m updates. ($m << N$) .

May become default in CASTEP but until then, select it using

```
geom_method : LBFGS
```

BFGS Convergence

Geometry convergence is tested against multiple criteria

```
geom_force_tol  : δF (default 0.05 eV/ang)
geom energy_tol : δE (default 0.00002 eV)
geom_disp_tol   : δR (default 0.001 ang)
```

```
 BFGS: finished iteration     6 with enthalpy= -4.31982518E+003 eV

 +-----------+-----------------+-----------------+------------+-----+ <-- BFGS
 | Parameter |      value      |    tolerance    |    units   | OK? | <-- BFGS
 +-----------+-----------------+-----------------+------------+-----+ <-- BFGS
 |  dE/ion   |   1.128044E-006 |   2.000000E-005 |         eV | Yes | <-- BFGS
 |  |F|max   |   1.828172E-002 |   1.000000E-003 |       eV/A | No  | <-- BFGS
 |  |dR|max  |   7.819760E-004 |   1.000000E-003 |          A | Yes | <-- BFGS
 +-----------+-----------------+-----------------+------------+-----+ <-- BFGS

================================================================================
 Starting BFGS iteration          7 ...
================================================================================
```

And continues for at most `geom_max_iter` (default 30) cycles.

```
 BFGS: finished iteration    40 with enthalpy= -4.31981431E+003 eV

 +-----------+-----------------+-----------------+------------+-----+ <-- BFGS
 | Parameter |      value      |    tolerance    |    units   | OK? | <-- BFGS
 +-----------+-----------------+-----------------+------------+-----+ <-- BFGS
 |  dE/ion   |   2.833764E-009 |   2.000000E-005 |         eV | Yes | <-- BFGS
 |  |F|max   |   9.419588E-004 |   1.000000E-003 |       eV/A | Yes | <-- BFGS
 |  |dR|max  |   1.962071E-005 |   1.000000E-003 |          A | Yes | <-- BFGS
 +-----------+-----------------+-----------------+------------+-----+ <-- BFGS

 BFGS: Geometry optimization completed successfully.
```

Force Convergence

At incomplete SCF convergence
Error residual in orbitals is $\delta\psi$

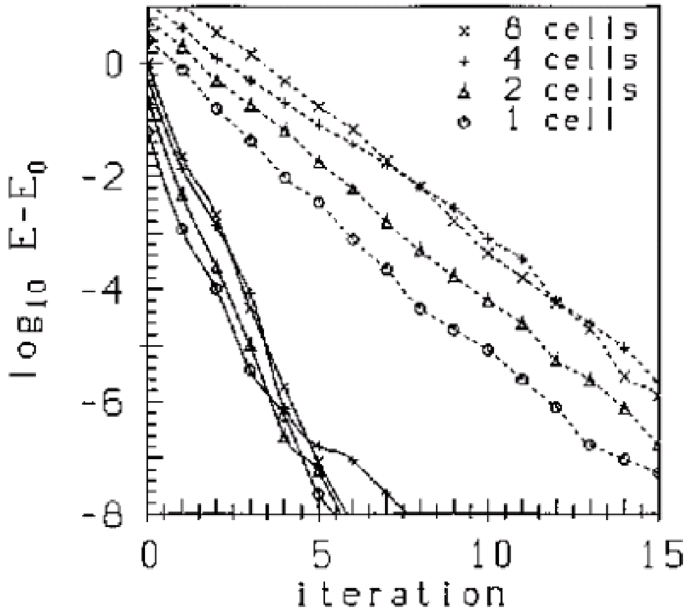
Error in energy $\delta E \propto \delta\psi^2$

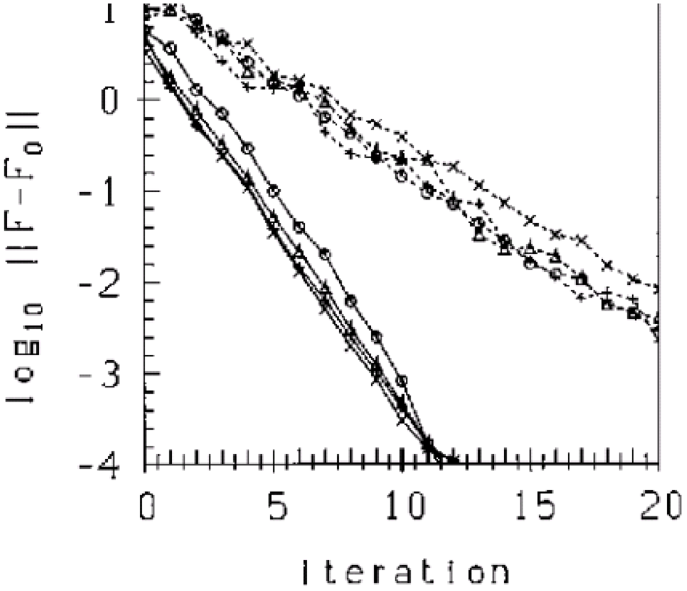
Error in forces $\delta F \propto \delta\psi$

For a given error in orbitals $\delta\psi$ energy may be well converged but forces are not.

BFGS algorithm performance depends on consistent definition of energy surface and gradient.

BFGS convergence can fail as a result of numerical “noise” from residual error $\delta\psi$.





Common causes of failure

BFGS convergence can fail as a result of numerical “noise” from residual error δψ.

```
BFGS: Warning - looks like this system is as converged as possible.
      Maybe your geometry convergence tolerances are too tight?

BFGS: finished iteration    11 with enthalpy= -5.14190600E+003 eV

+-----------+-----------------+-----------------+------------+-----+ <-- BFGS
| Parameter |      value      |    tolerance    |    units   | OK? | <-- BFGS
+-----------+-----------------+-----------------+------------+-----+ <-- BFGS
|  dE/ion   |   6.473966E-008 |   2.000000E-005 |         eV | Yes | <-- BFGS
|  |F|max   |   3.188140E-003 |   5.000000E-004 |       eV/A | No  | <-- BFGS
|  |dR|max  |   1.203050E-004 |   1.000000E-003 |          A | Yes | <-- BFGS
+-----------+-----------------+-----------------+------------+-----+ <-- BFGS

BFGS: Geometry optimization completed successfully.
```

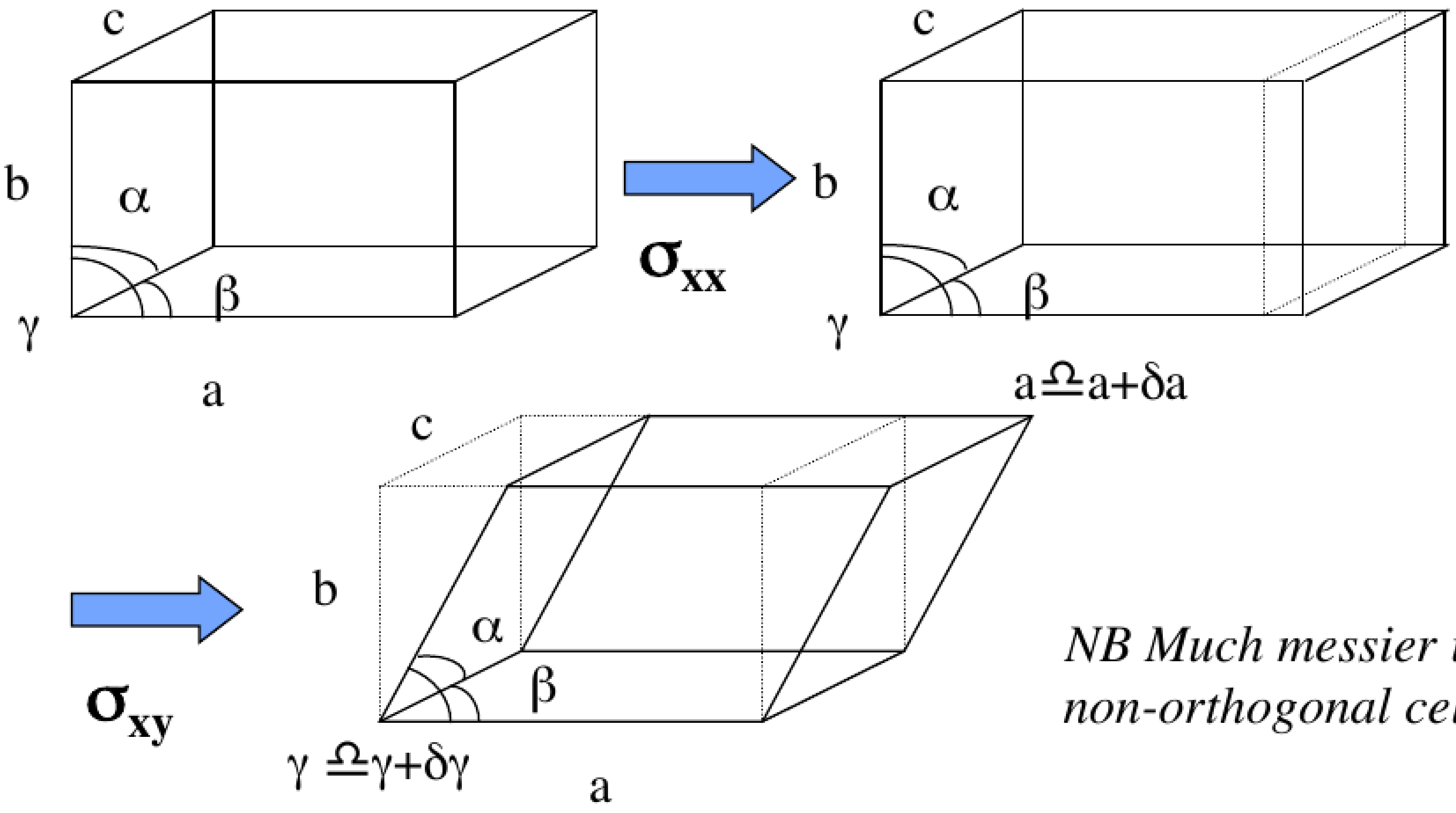
Cure is usually to reduce residual error δψ.

Decrease parameter `elec_energy_tol` – 10^{-8} eV or lower can work.

Alternatively set force tolerance for SCF loop via `elec_force_tol`.

Hydrogen-bonded or other “mixed-strength” systems can require many BFGS cycles to converge because PE surface is far from parabolic. May need to increase `geom_max_iter` and decrease `geom_force_tol`.

Variable-Cell optimization



NB Much messier if non-orthogonal cell

Variable-Cell optimization

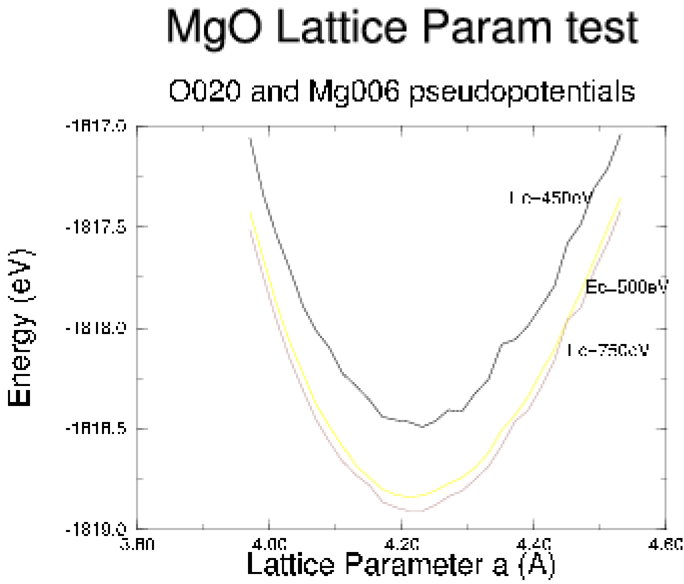
```
%BLOCK external_pressure
GPa
10.0 0.0 0.0
     10.0 0.0
          10.0
%ENDBLOCK external_pressure
```

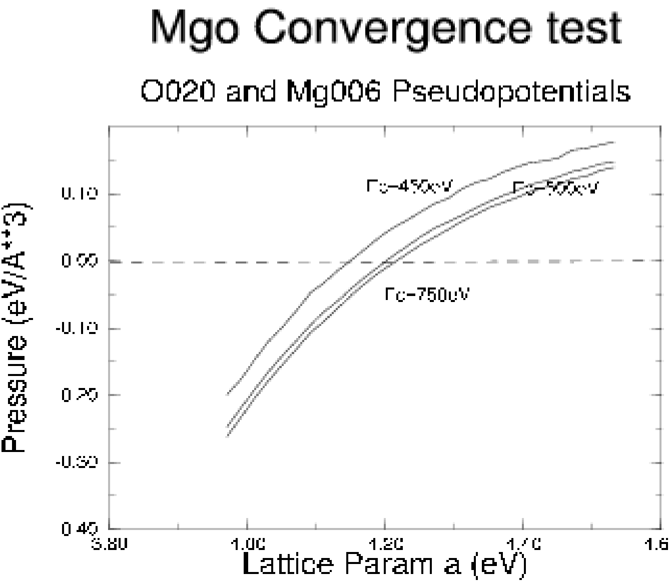
```
BFGS: finished iteration     9 with enthalpy= -1.66415046E+004 eV

 +-----------+-----------------+-----------------+------------+-----+ <-- BFGS
 | Parameter |      value      |    tolerance    |   units    | OK? | <-- BFGS
 +-----------+-----------------+-----------------+------------+-----+ <-- BFGS
 |  dE/ion   |   1.007678E-007 |   2.000000E-005 |         eV | Yes | <-- BFGS
 |  |F|max   |   4.005459E-003 |   5.000000E-003 |       eV/A | Yes | <-- BFGS
 |  |dR|max  |   7.662148E-005 |   1.000000E-003 |          A | Yes | <-- BFGS
 |   Smax    |   7.805532E-003 |   2.500000E-002 |        GPa | Yes | <-- BFGS
 +-----------+-----------------+-----------------+------------+-----+ <-- BFGS

 BFGS: Geometry optimization completed successfully.
================================================================================
 BFGS: Final Configuration:
================================================================================

 *********** Symmetrised Stress Tensor ***********
 *                                               *
 *          Cartesian components (GPa)           *
 * --------------------------------------------- *
 *             x             y             z     *
 *                                               *
 *  x     -9.999806      0.000000      0.000000  *
 *  y      0.000000    -10.001444      0.000000  *
 *  z      0.000000      0.000000     -9.999316  *
 *                                               *
 *  Pressure:   10.0002                          *
 *                                               *
 *************************************************
```

```
%BLOCK cell_constraints
    1    2    3
    0    0    0
%ENDBLOCK cell_constraints
```

```
fix_all_cell : true
```

Finite-basis correction





“Jagged" E vs V curve due to discreteness of N_{PW}.
Plane-wave basis size depends on *volume* of cell => Pulay Stresses

$$\sigma_{\text{pulay}} = \frac{2}{3V}\frac{dE_{\text{tot}}}{d\ln E_{\text{cut}}}$$

Corrected using Francis-Payne method [J. Phys. Conden. Matt **2**, 4395 (1990)]

CASTEP performs (usually) 3 SCF calculations with changed cutoff to compute derivative.

Keywords for geometry optimisation

```
task                    : geometryoptimisation
geom_method             : LBFGS/BFGS/dampedmd/delocalized/fire/tpsd
geom_max_iter           : n  (default 30)
geom_force_tol          : δF (default 0.05 eV/ang)
geom energy_tol         : δE (default 0.00002 eV)
geom_disp_tol           : δR (default 0.001 ang)
geom_stress_tol         : δσ (default 0.1 Gpa)
geom_convergence_win: 2  (default 30)

geom_frequency_est      : 50 THz
geom_modulus_est        : 500 GPa


elec_energy_tol         : 1e-5 eV
elec_force_tol          : Not set by default
```

Remember that

```
castep.serial --help search geom
```

Will generate a reminder of these.

Parallelism in CASTEP

Largest memory objects in CASTEP are *wavefunctions* (orbitals really) $\Psi_{m\mathbf{k}}(\mathbf{G})$

Stored as 4-d array coeffs(N_{pw},N_k,N_b,N_s) with

- N_{pw} plane-waves (G-vectors) (typically 10000-100000)
- N_k k-points (typically 1-1000)
- N_b bands (typically 100-5000)
- N_s spins (1 or 2)

Parallel scheme best considered as distribution of coeffs array over MPI processes.

Plane-wave and k-point parallelism controlled by param keyword

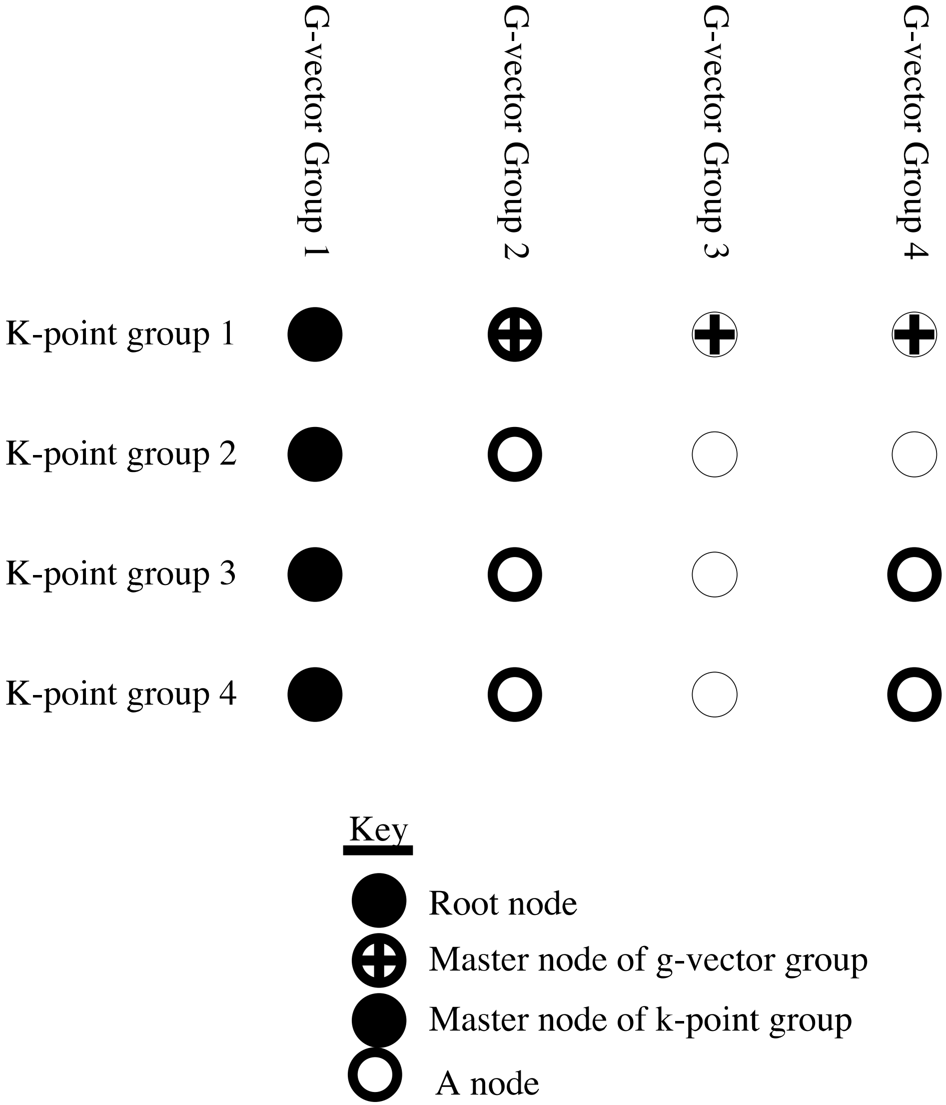
```
data_distribution : mixed (default)/kpoint/gvector
```

Mixed GV-kpoint parallelism automatically chosen to be fairly optimal.

Band parallelism new: provisionally invocation is controlled by param

```
devel_code : PARALLEL:bands=4;kpoint=10:ENDPARALLEL
```

Parallel distribution



	G-vector Group 1	G-vector Group 2	G-vector Group 3	G-vector Group 4
K-point group 1	●	⊕	⊕	⊕
K-point group 2	●	○	○	○
K-point group 3	●	○	○	○
K-point group 4	●	○	○	○

Key

●	Root node
⊕	Master node of g-vector group
●	Master node of k-point group
○	A node

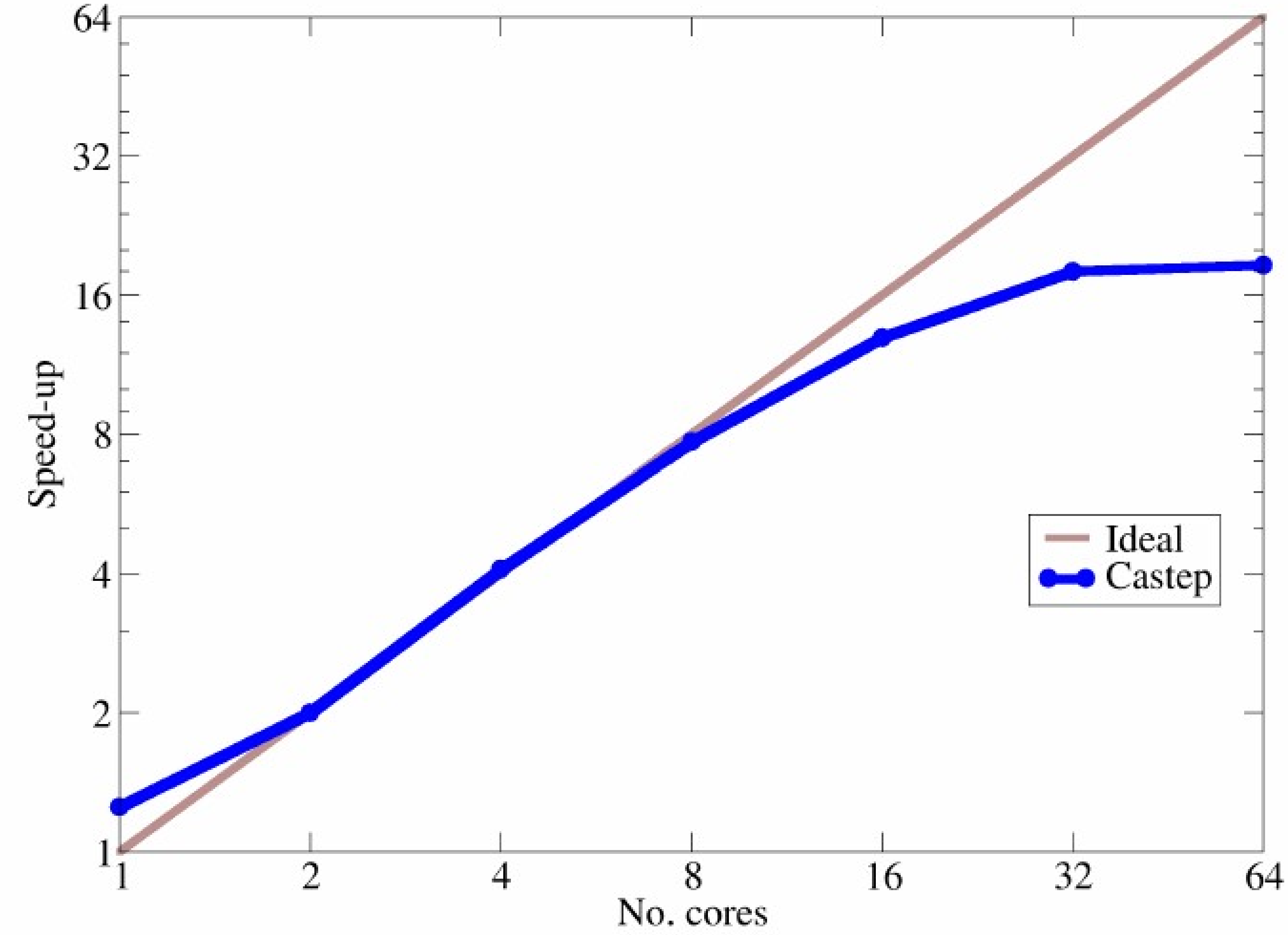
Three data distribution strategies

1. k-points
2. g-vectors
3. bands

G-vector parallelism

- 3-D FFT is distributed over G-vector group.
- Implementation as 3x 1-D FFTs with parallel transpose
- Parallel transpose must exchange data between all processors.
- Implementation using MPI_Alltoallv means comms time scales as N^2_{proc}.
- As N_{proc} increases comms time comes to dominate.
- Typical useful limit of 256-512-way GV parallelism

G-vector parallel scaling



TiN benchmark: 33 atoms, 8 k-points, 164 bands, 10972 G-vectors

Shared-Memory GV parallel

- Parallel FFT performance can be improved using shared memory on node.
- Only one MPI processor on each Archer core participates in MPI_alltoallv, instead of 24.
- Processors within a core communicate using shared memory segment - much lower latency
- Can usually double size of GV group for same efficiency.
- Activated by param keyword

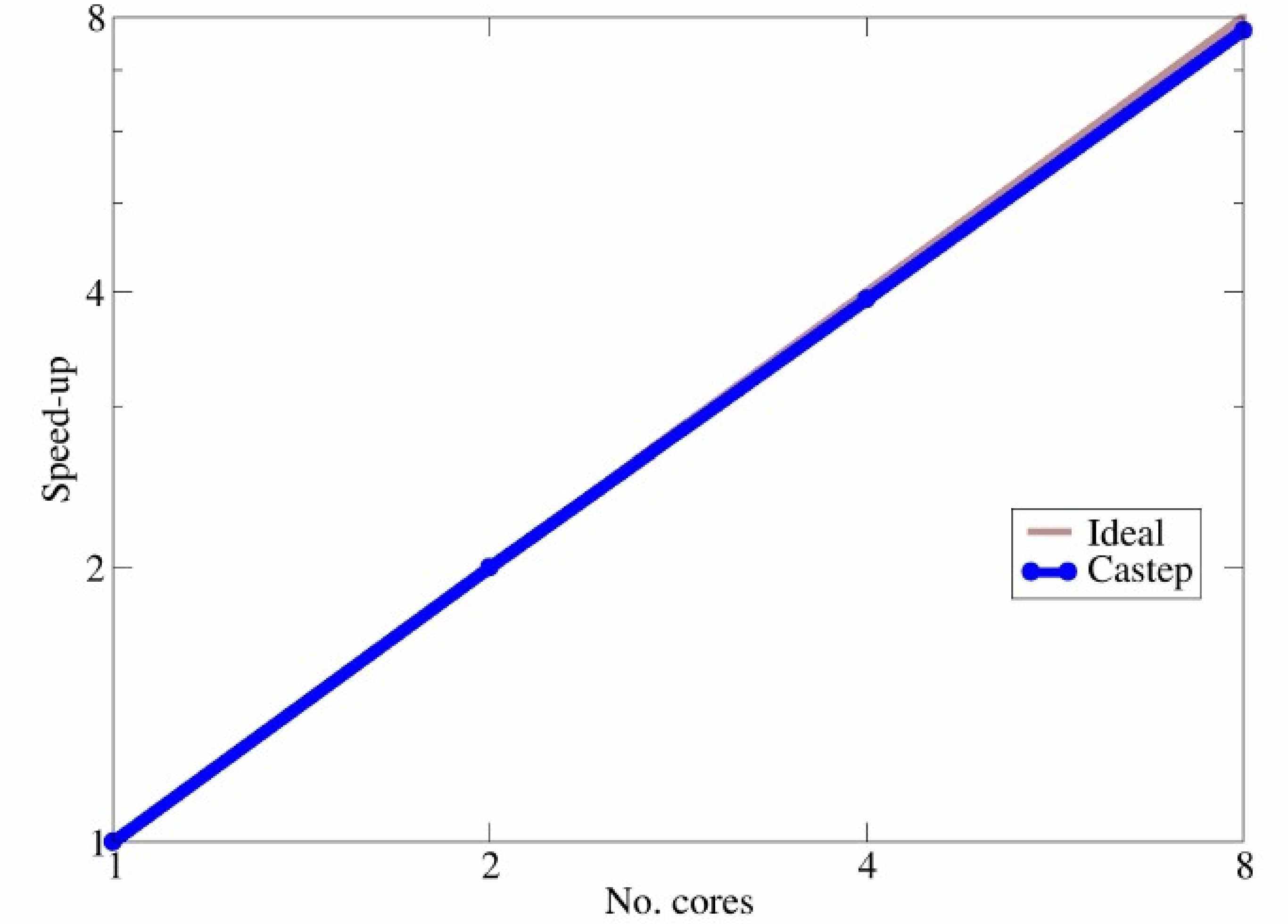
  `num_proc_in_smp :12`
- Because of NUMA architecture on Archer, 24 is usually slower than 12.

K-point parallelism

- Hamiltonian diagonalization at each k-point is nearly independent.
- Very low comms cost when k-points distributed

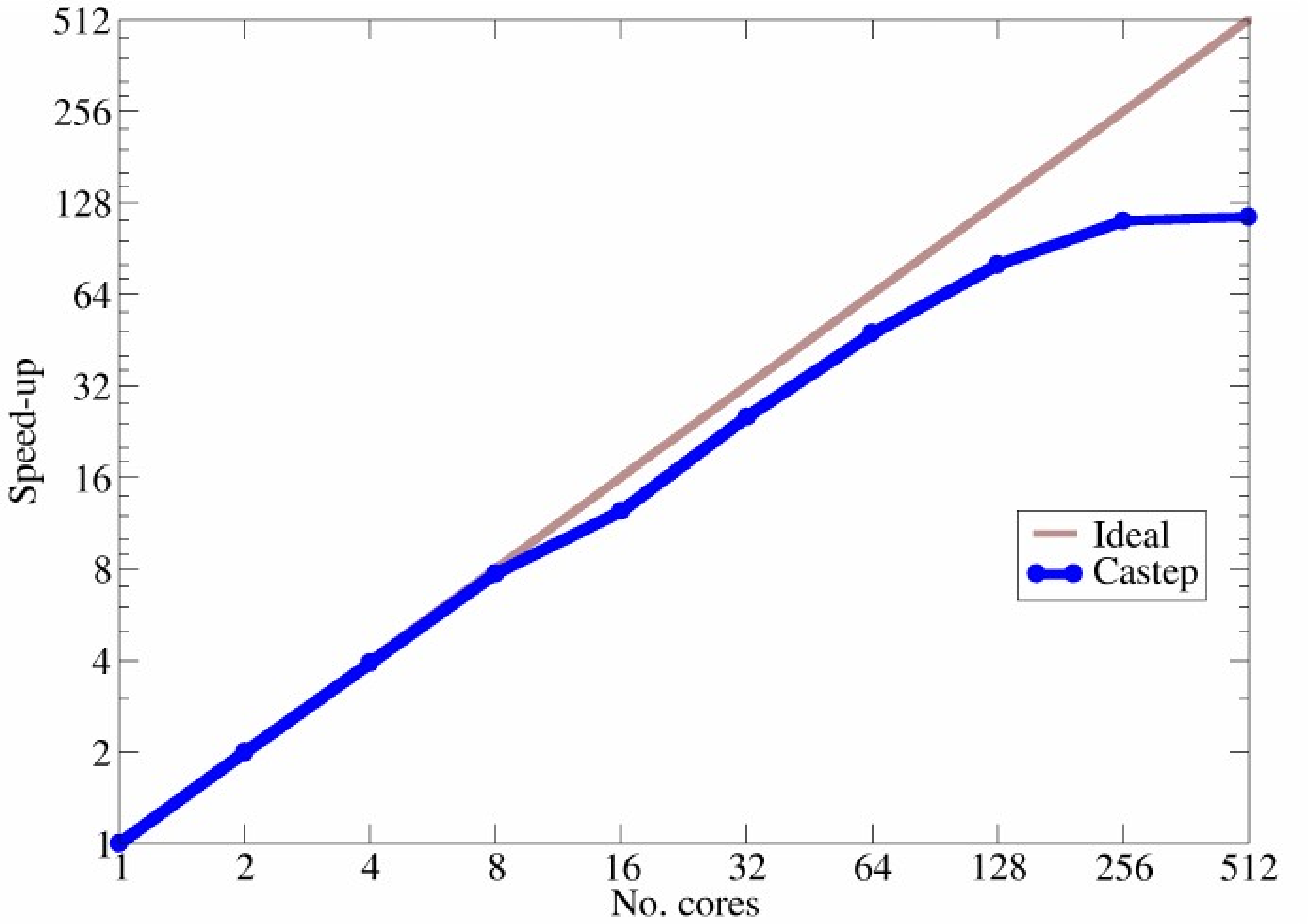
  \- parallelism is near perfect.
- Problem: $N_{\boldsymbol{k}}\ \mu\ 1/V\ \mu\ 1/N_{atoms}$
- For large insulating systems k-points parallelism limited by small $N_{\boldsymbol{k}}$.
- Not a problem for metals though.

K-point parallelism



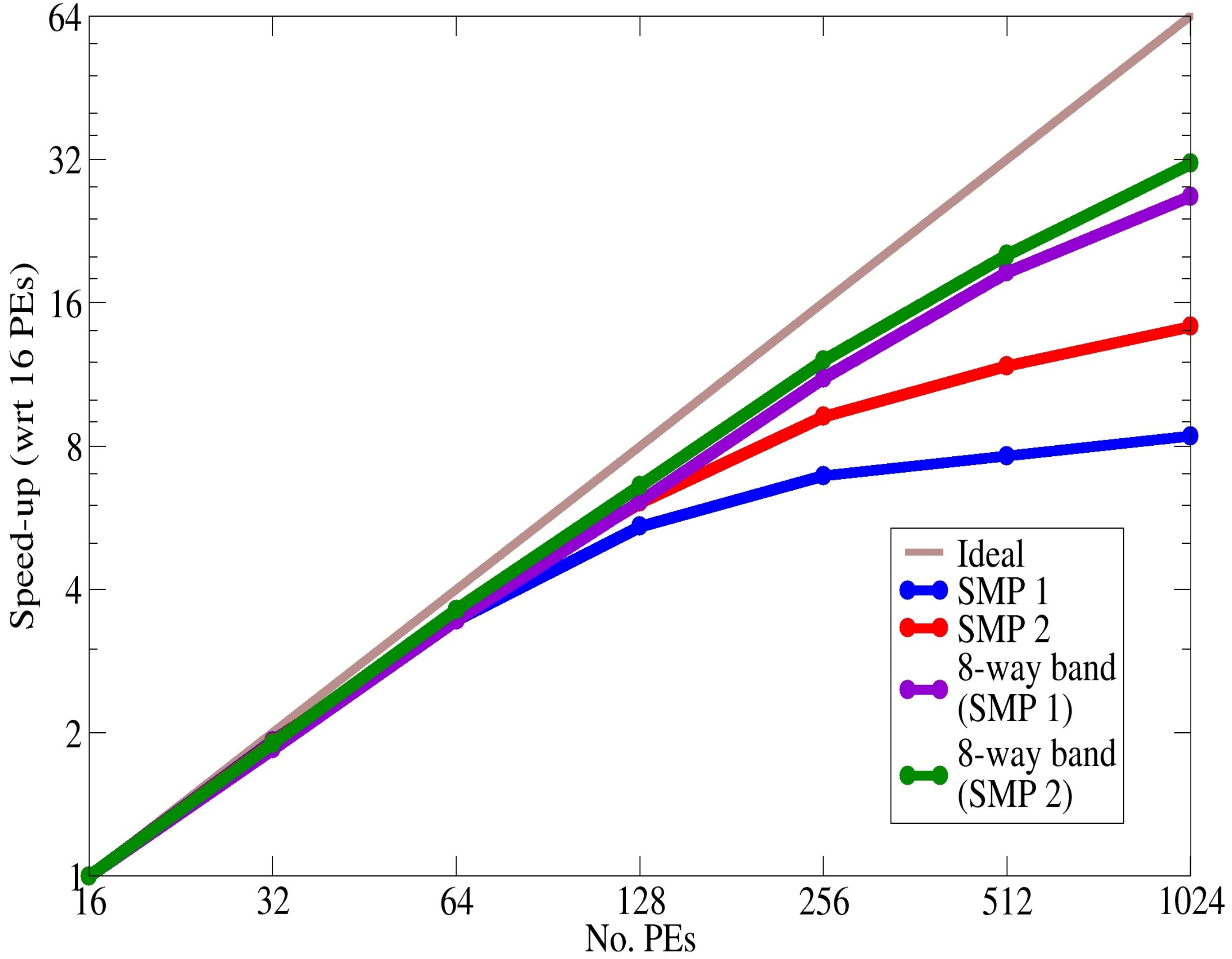
TiN benchmark: 33 atoms, 8 k-points, 164 bands, 10972 G-vectors

Combined G+k distribution



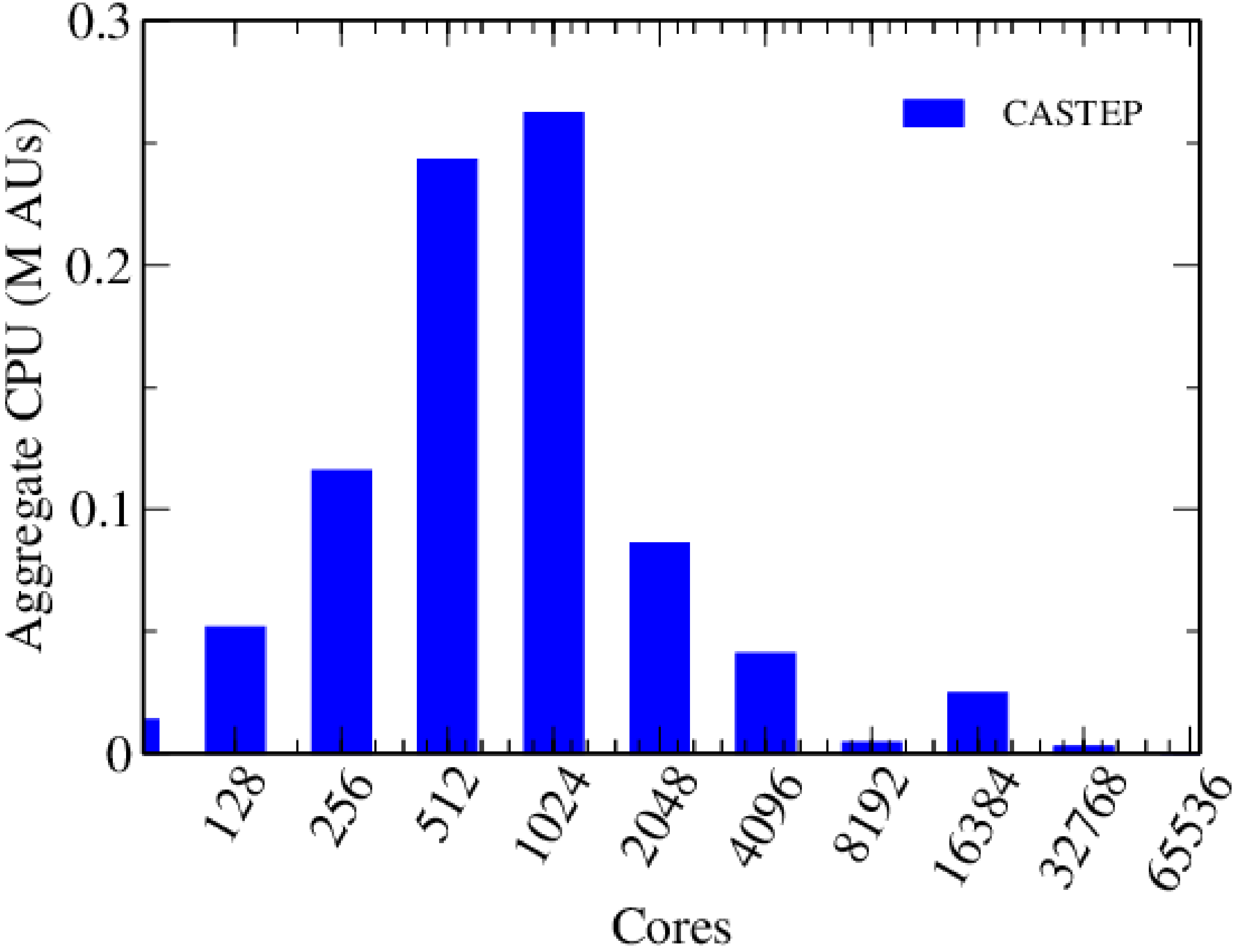
TiN benchmark: 33 atoms, 8 k-points, 164 bands, 10972 G-vectors

Band parallelism



Al2O3 3x3 slab benchmark

Overall HeCToR usage



Parallel efficiency Report

At end of successful run, final block in .castep file reads

```
Initialisation time =      7.74 s
Calculation time    =  36895.35 s
Finalisation time   =     17.74 s
Total time          =  36920.83 s
Peak Memory Use     = 1343184 kB

Overall parallel efficiency rating: Good (79%)

Data was distributed by:-
G-vector (14-way); efficiency rating: Very good (83%)
k-point (45-way); efficiency rating: Excellent (94%)
```